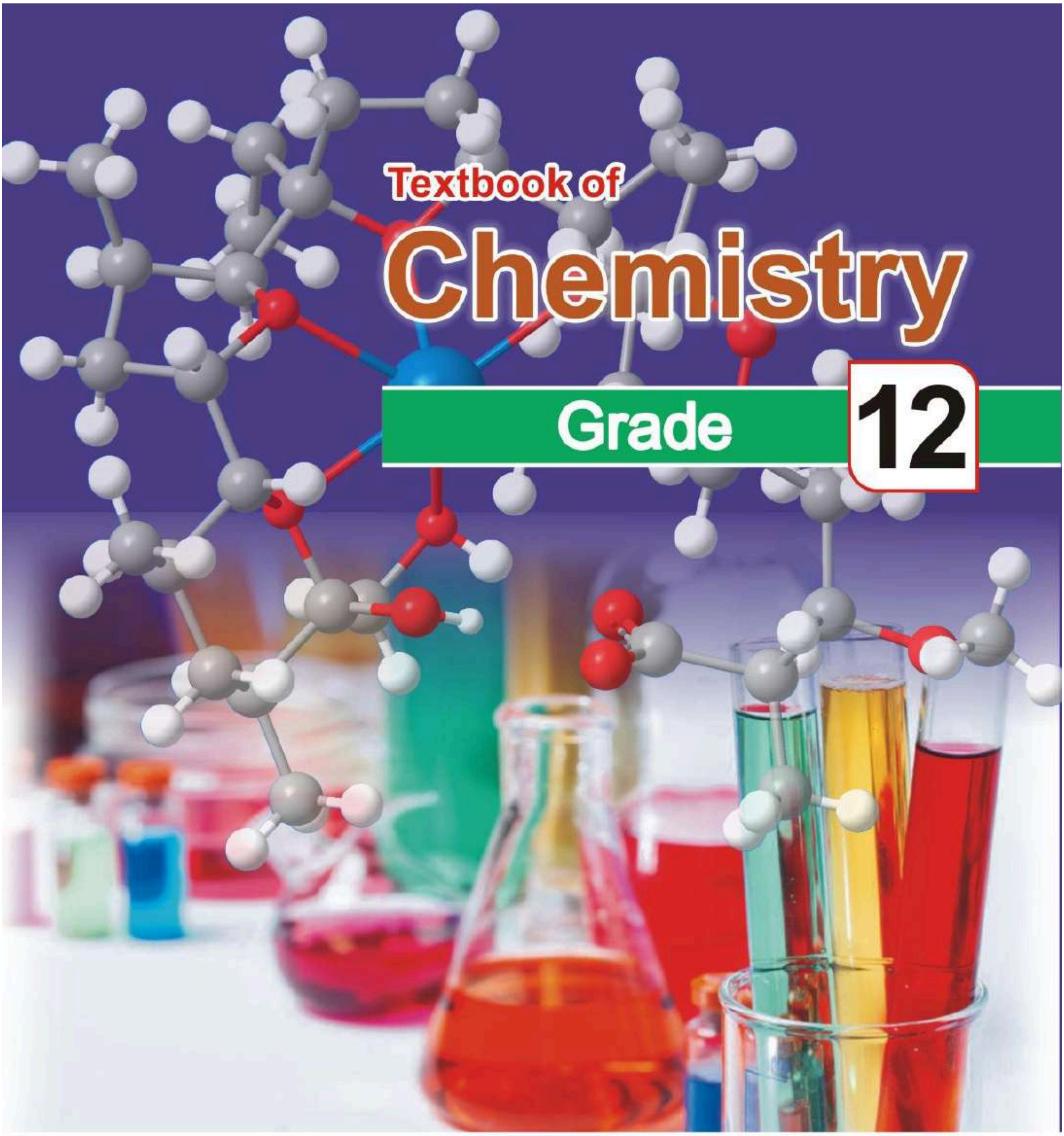

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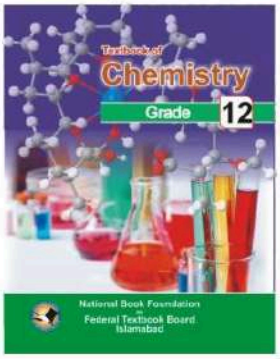

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PREFACE

CHEMISTRY for GRADE - 12 is developed according to the National Curriculum 2006 and National Style Guide. It is presented under the management and supervision of textbook development principles and guidelines, design and layout.

This textbook provides several ways to develop this approach. Wherever an important new skill or concept is introduced, you will find a worked-out example. A special feature of the book is that the text has been illustrated with a large number of diagrams and the data presented in the form of numberous tables and comparison.

There has accordingly been a distinct change in approach and content with the result that a shortage of suitable text written on these lines was being keenly felt. The authors seek justification in presenting the present volume in the sincere attempts that they have made to fill up the requisition.

Considerable thought has been given to the topics for discussion. The great care has been taken to elucidate the fundamentals and the approach to discussion in modern throughout. Particular mention may be made in this connection of the chapter on Transition Elements, Analytical Chemistry, Biochemistry, Environmental Chemistry and the most important in Organic portion.

There is a possibility of finding the errors, mistakes, omissions and lack of continuity of ideas somewhere in the book. So any suggestion to make the book better will be appreciated. It will make you to hep us and will cause the uplifting of the standard of the book and ultimately nation. Actually we need cooperation in the form of liberal criticism and valuable suggestions from the fellow teachers and students. It will be gratefully received and acknowledged.

Our efforts are to make textbooks teachable with quality, i.e. maintaining of standards. It is a continuous effort and we will get feedback of the yearly feasibility reports and redesign the textbook every year.

Quality of Standards, Pedagogical Outcomes, Taxonomy Access and Actualization of Style is our motto.

With these elaborations, this series of new development is presented for use.

Prof. Dr. Inam ul Haq Javeid
(Pride of Performance)
Managing Director
National Book Foundation

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِيْمِ

شروع اللہ کے نام سے جو بڑا مہربان، نہایت رحم والا ہے۔

CONTENTS

13

s AND p - BLOCK ELEMENTS

After completing this lesson, you will be able to:

This is 28 days lesson (period including homework)

- Recognize the demarcation of Periodic Table into s block, p block d block, and f block.
- Describe how physical properties like atomic radius, ionization energy, electro negativity, electrical conductivity and melting and boiling points of element change within a group and within a period and the Periodic Table.
- Describe reactions of period 3 elements with water, oxygen and chlorine.
- Describe reaction of oxides and chlorides of period 3 elements with water.
- Describe reaction of group I elements with water, oxygen and chlorine.
- Describe reaction of group I elements with water, oxygen and chlorine.
- Discuss the trend in solubility f the hydroxides, sulphates and carbonates of group II elements.
- Discuss the trends in thermal stability of the nitrates and carbonates of group II elements.
- Explain the trends in physical properties and oxidation states in group I, II IV and VII of the periodic table.
- Explain effects of heat on nitrates, carbonates and hydrogen carbonated of Group I elements.
- Differentiate beryllium from other members of its group.

Reading

13.1 PERIOD 3 (Na TO Ar)

13.1.1 Atomic and Physical Properties of the Period 3 Elements

(This period contains Na, Mg, Al, Si, P, S, Cl and Ar)

This topic describes and explains the trends in atomic and physical properties of the Period 3 elements from sodium to argon. It covers ionization energy, atomic radius, electronegativity, electrical conductivity, melting point and boiling point.

(a) Atomic Properties

Electronic Structures

In Period 3 of the Periodic Table, the 3s and 3p orbitals are filling with electrons. Just as a reminder, the shortened versions of the electronic structures for the eight elements are:

Na $[Ne]\ 3s^1$
Mg $[Ne]\ 3s^2$
Al $[Ne]\ 3s^2\ 3p_x^1$
Si $[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1$

P $[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
S $[Ne]\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
Cl $[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
Ar $[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

In each case, [Ne] represents the complete electronic structure of a neon atom.

Quick Quiz

1. The electron structure of Mg is $1s^2$, $2s^2$, $2p^6$, $3s^2$. Write down electron structure of Al in the same notation.
2. Which of the two elements Mg or Al has the more stable structure?

Trends in Atomic Radius

We know that the number of shells in all the elements of a given periods remains the same but the value of effective nuclear charge, increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right. Thus in going from left to right in a period of s-and p-block elements atomic and ionic radi decrease with the increase of atomic number. This fact can be illustrated by considering the atomic (covalent) and ionic radii of the elements as shown below.

Table 13.1: Ionic radii (in A^0) of representative elements (s-and p- block elements). In parentheses are given the oxidation states of the elements.

Group → Period ↓	s-block elements		p-block elements				
1	IA	IIA	IIIA	IVA	VA	VIA	VIIA
2	H 2.08 (-1) 2.09 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3)	C 2.60 (-4) 0.15 (+4)	N 1.71 (-3) 0.11 (+5)	O 1.40 (-2) 0.09 (+6)	F 1.36 (-1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (-1) 0.41 (+4)	P 2.12 (-3) 0.34 (+5)	S 1.84 (-2) 0.29 (+6)	Cl 1.81 (-1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (-3) 0.47 (+5)	Se 1.98 (-2) 0.42 (+6)	Br 1.95 (-1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 0.45 (-3) 0.62 (+5)	Te 2.21 (-2) 0.56 (+6)	I 2.16 (-1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Ti 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po - -	At - -
7	Fr 1.76 (+1)	Rs 1.40 (+2)					

Trends in Electronegativity

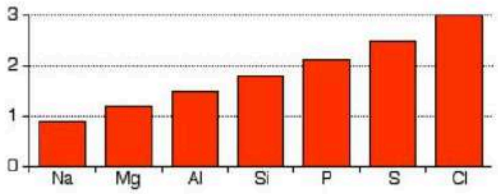


Fig. 13.1 Electronegativities

Electro negativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.

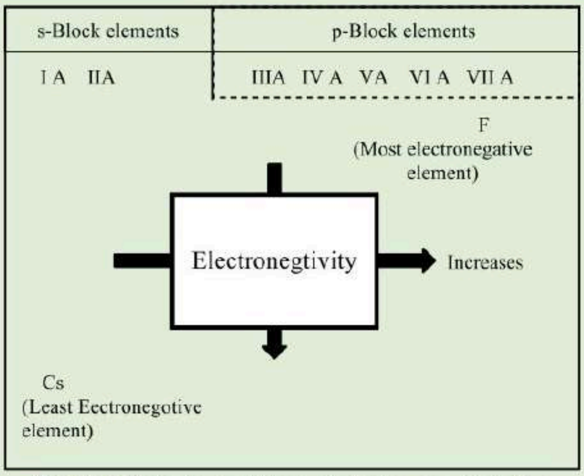


Fig 13.2 Periodic variations of electro negativity in s and p block elements are mentioned.

The Trend

The trend across Period 3 looks like this:

In going from left to right in a period of s- and p-block elements, the electronegativity values increase. This increase can be explained on the basis of any of the following facts.

(i) On moving from left to right in a period, there is a decrease in the size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves i.e. smaller atoms have higher electronegativity values.

(ii) On moving from left to right in a period there is an increase of ionization energy and electron affinity of the elements. The atoms of the elements, which have higher value of ionization energies and electron affinities also have higher electro negativities.

The variation of electro negativity in a period and a group of representative elements (s- and p-block elements) is show in Fig. 13.2

Notice that argon is not included. Electronegativity is about the tendency of an atom to attract a *bonding* pair of electrons. Since argon does not form covalent bonds, you obviously can't assign it electronegativity.

Explaining the Trend

The trend is explained in exactly the same way as the trend in atomic radii.

As you go across the period, the bonding electrons are always in the same level - the 3-level. They are always being screened by the same inner electrons.

All that differs is the number of protons in the nucleus. As you go from sodium to chlorine, the number of protons steadily increases and so attracts the bonding pair more closely.

(b) Physical Properties

This section is going to look at the electrical conductivity and the melting and boiling points of the elements. To understand these, you first have to understand the structure of each of the elements.

Structures of the Elements

The structures of the elements change as you go across the period. The first three (i.e. Na, Mg, Al) are metallic, silicon is giant covalent, and the rest (i.e. P, S, Cl, Ar) are simple molecules.

Three Metallic Structures

Sodium, magnesium and aluminium all have metallic structures.

In sodium, only one electron per atom is involved in the metallic bond - the single 3s electron. In magnesium, both of its outer electrons are involved, and in aluminium all three.

The coordination number of atoms in the metal crystal is also different in these metals.

Sodium is 8-co-ordinated - each sodium atom is touched by only 8 other atoms.Both magnesium and aluminium are 12-co-ordinated (although in slightly different ways). This is a more efficient way to pack atoms, leading to less wasted space in the metal structures and to stronger bonding in the metal.

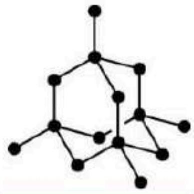


Fig 13.3

A Giant Covalent Structure

Silicon has a giant covalent structure just like diamond. A tiny part of the structure looks like this: The structure is shown in figure 13.3.

Four Simple Molecular Structures

The structures of phosphorus (i.e. white etc) and sulphur (i.e. rhombic or monoclinic etc) vary depending on the type of phosphorus or sulphur you are talking about.

The atoms in each of these molecules are held together by covalent bonds and argan is a monoatomic molecule.

In the liquid or solid state, the molecules are held close to each other by Van der Waals dispersion forces.

Electrical Conductivity

- Sodium, magnesium and aluminium are all good conductors of electricity. Conductivity increases as you go from sodium to magnesium to aluminium as they have free electrons
- Silicon is a semiconductor.
- None of the rest conduct electricity.

The three metals (Na, Mg and Al) conduct electricity because the delocalised electrons (the "sea of electrons") are free to move throughout the solid or the liquid metal.

In the silicon case, explaining how semiconductors conduct electricity is beyond the scope of this level. With a diamond structure, you mightn't expect it to conduct electricity, but it does!

The rest do not conduct electricity because they are simple molecular substances. There are no electrons free to move around.

Trends in Melting and Boiling Points

The chart shows how the melting and boiling points of the elements change as you go across the period. The figures are plotted in Kelvin rather than °C to avoid having negative values.

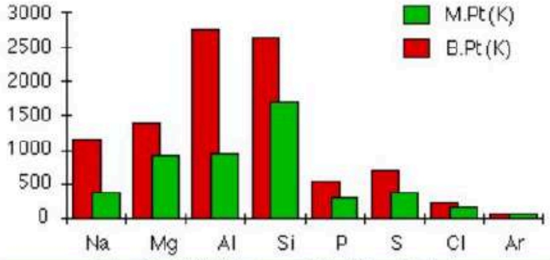


Fig 13.4 Melting and Boiling Point

Silicon

Silicon has high melting and boiling points because it is a giant covalent structure. You have to break strong covalent bonds before it will melt or boil.

Because you are talking about a different type of bond, it is not profitable to try to directly compare silicon's melting and boiling points with aluminium's.

The Four Molecular Elements

Phosphorus, sulphur, chlorine and argon are simple molecular substances with only van der Waals attractions between the molecules. Their melting or boiling points will be lower than those of the first four members of the period, which have giant structures.

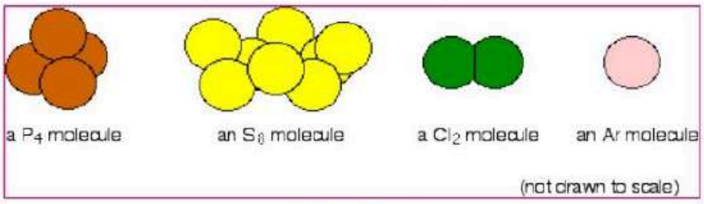


Fig. 13.5

The melting and boiling points are governed entirely by the sizes of the molecules. Remember the structures of the molecules:

Phosphorus

Phosphorus contains P_4 molecules. To melt phosphorus you do not have to break any covalent bonds - just the much weaker van der Waals forces between the molecules.

Sulphur

Sulphur consists of S_8 rings of atoms. The S_8 smolecules are bigger than phosphorus molecules, and so the Van der Waals attractions will be stronger, leading to a higher melting and boiling point.

Chlorine

Chlorine, Cl_2, is a much smaller molecule with comparatively weak Van der Waals attractions, and so chlorine will have a lower melting and boiling point than sulphur or phosphorus.

Argon

Argon molecules are just single argon atoms, Ar. The scope for Van der Waals attractions between these is very limited and so the melting and boiling points of argon are lower again.

Quick Quiz

(a) List the symbols of elements present in the third period of the periodic table, in order of increasing atomic number.
(b) Which of the above elements are:
  (i) s-block elements
  (ii) d-block elements
(c) (i) Write the empirical formula of the chloride formed by the element with atomic number 13.
  (ii) Describe briefly how can you prepare a sample of this chloride?

13.1.2 Chemical Reactions of the Period 3 Elements

This section describes the reactions of the period 3 elements from sodium to argon with water, oxygen and chlorine.

(a) Reactions with Water

Sodium

Sodium has a very exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide.

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

Magnesium

Magnesium has a very slight reaction with cold water, but burns in steam.

A very clean coil of magnesium dropped into cold water eventually gets covered in small bubbles of hydrogen which float it to the surface. Magnesium hydroxide is formed as a very thin layer on the magnesium and this tends to stop the reaction.

$$\underset{\text{Cold}}{Mg + 2H_2O} \longrightarrow Mg(OH)_2 + H_2$$

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

$$\underset{\text{Steam}}{Mg + H_2O} \longrightarrow MgO + H_2$$

Aluminium

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

$$\underset{\text{Steam}}{2Al + 3H_2O} \longrightarrow Al_2O_3 + 3H_2$$

Phosphorus and Sulphur

These have no reaction with water.

Chlorine

Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chlorous (I) acid (hypochlorous acid).

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

In the presence of sunlight, the chloric(I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas, and you may come across an equation showing the overall change:

$$2Cl_2 + 2H_2O \xrightarrow{\text{Sunlight}} 4HCl + O_2$$

Argon

There is no reaction between argon and water.

(b) Reactions with Oxygen

Sodium

Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.

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

For the simple oxide:

For the peroxide:

$$4Na + O_2 \longrightarrow 2Na_2O_2$$

Magnesium

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

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

Silicon

Silicon will burn in oxygen if heated strongly. Silicon dioxide is produced.

$$Si + O_2 \longrightarrow SiO_2$$

Phosphorus

White phosphorus catches fire spontaneously in air, burning with a white flame and producing clouds of white smoke - a mixture of phosphorus (III) oxide and phosphorus (V) oxide. The proportions of these depend on the amount of oxygen available. In an excess of oxygen, the product will be almost entirely phosphorus (V) oxide.

For the phosphorus (III) oxide:

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

For the phosphorus (V) oxide:

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

Sulphur

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

$$S + O_2 \longrightarrow SO_2$$

Chlorine and Argon

Despite having several oxides, chlorine would not react directly with oxygen. Argon does not react either.

Table 13.2: Properties of the oxides of elements in period 3

Formula of Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
					(P_4O_6)	(SO_2)	(Cl_2O)
State of Oxide	solid	solid	solid	solid	solid	gas	liquid
Conduction of Electricity by Molten or liquid Oxide	good	good	good	Very poor	Nil.	Nil.	Nil.
Structure of oxide	Giant Structures				Simple molecular structure		
Enthalpy change of Formation of oxide at 298K/kJ mol-1	-416	-602	-1676	-910	-2984	-395	80
Enthalpy change of Formation of oxide at 298K/kJ mol-1 O/kJ	-416	-602	-559	-455	-298	-132	80
Effect of adding oxide to water	reacts to form NaOH (aq) alkaline solution	reacts to form $Mg(OH)_2$	does not react with water but it is amphoteric	does not react with water but it is acidic	P_4O_{10} reacts to form H_3PO_4 acid solution	SO_3 reacts to form H_2SO_4 acid solution	Cl_2O_7 reacts to form $HClO_4$ acid solution
Nature of Oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

(c) Reactions with Chlorine

Sodium

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

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

Magnesium

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

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Aluminium

Aluminium is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube. The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride. This sublimes (turns straight from solid to vapour and back again) and collects further down the tube where it is cooler.

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

Silicon

When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride. This is a colourless liquid which vaporises and can be condensed further along the apparatus.

Phosphorus

White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus(III) chloride and phosphorus(V) chloride (phosphorus trichloride and phosphorus pentachloride).

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

Phosphorus(III) chloride is a colourless fuming liquid.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Phosphorus(V) chloride is an off-white (going towards yellow) solid.

Sulphur

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

When a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, evil-smelling liquid, disulphur dichloride, S_2Cl_2.

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

Chlorine and Argon

It obviously doesn't make sense to talk about chlorine reacting with itself, and argon doesn't react with chlorine.

13.1.3 Physical Properties of the Oxides

This section explains the relationship between the physical properties of the oxides of Period 3 elements (sodium to chlorine) and their structures. Argon is obviously omitted because it doesn't form an oxide.

A quick Summary of the Trends

The Oxides

The oxides we'll be looking at are:

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

Those oxides in the top row are known as the ***highest oxides*** of the various elements. These are the oxides where the Period 3 elements are in their highest oxidation states. In these oxides, all the outer electrons in the Period 3 element are being involved in the bonding formation just as one with sodium, to all seven of chlorine's outer electrons.

I. Structures

The trend in structure is from the metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

II. Melting and Boiling Points

The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions. The oxides of phosphorus, sulphur and chlorine consist of individual molecules - some small and simples; others polymeric.

The attractive forces between these molecules will be Van der Waals dispersion and dipole-dipole interactions. These vary depending on the size, shape and polarity of the various molecules - but will always be much weaker than the ionic or covalent bonds you need to break in a giant structure. These oxides tend to be gases, liquids or low melting point solids.

III. Electrical Conductivity

None of these oxides has any free or mobile electrons. That means that none of them will conduct electricity when they are solid. The ionic oxides can, however, undergo ***electrolysis*** when they are molten. They can conduct electricity because of the movement of the ions towards the electrodes and the discharge of the ions when they get there.

i) The Metallic Oxides (e.g Sodium, Magnesium, Aluminium etc.)

Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride.

ii) Giant Covalent Oxides (e.g Silicon dioxide (Silicon (IV) oxide))

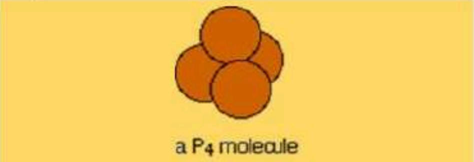
Structure

Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide. Each silicon atom is bridged to its neighbours by an oxygen atom.

iii) The molecular oxides (e.g. Phosphorus, sulphur and chlorine oxides)

(a) The Phosphorus oxides

Phosphorus has two common oxides, phosphorus(III) oxide, P_4O_6, and phosphorus(V) oxide, P_4O_{10}.


a P_4 molecule
Fig. 13.6

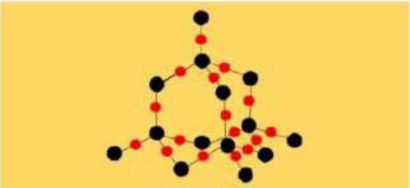


Fig. 13.7

(i) Phosphorus (III) oxide

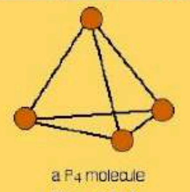


Fig. 13.8

Phosphorus (III) oxide is a white solid, melting at 24°C and boiling at 173°C. The structure of its molecule is best worked out starting from a P_4 molecule, which is a little tetrahedron.

Pull this apart so that you can see the bonds . . . . . . and then replace the bonds by new bonds linking the phosphorus atoms via oxygen atoms. These will be in a V-shape (rather like in water). The phosphorus is using only three of its outer electrons (the 3 unpaired p electrons) to form bonds with the oxygens.

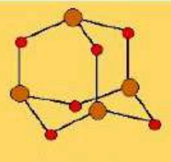


Fig. 13.9

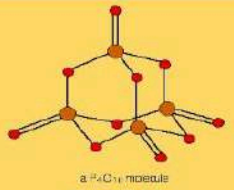


Fig 13.10

(ii) Phosphorus(V) oxide

Phosphorus (V) oxide is also a white solid, subliming (turning straight from solid to vapour) at 300°C. In this case, the phosphorus uses all five of its outer electrons in the bonding.

Solid phosphorus(V) oxide exists in several different forms - some of them polymeric. We are going to concentrate on a simple molecular form, and this is also present in the vapour.

This is most easily drawn starting from P_4O_6. The other four oxygens are attached to the four phosphorus atoms via double bonds.

(b) The Sulphur Oxides

Sulphur has two common oxides, sulphur dioxide (sulphur(IV) oxide), SO_2, and sulphur trioxide (sulphur(VI) oxide), SO_3.

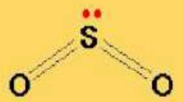


Fig 13.11

(i) Sulphur dioxide

Sulphur dioxide is a colourless gas at room temperature with an easily recognised choking smell. It consists of simple SO_2 molecules. The sulphur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the sulphur. The bent shape of SO_2 is due to this lone pair.

(ii) Sulphur trioxide

Pure sulphur trioxide is a white solid with a low melting and boiling point.

Gaseous sulphur trioxide consists of simple SO_3 molecules in which all six of the sulphur's outer electrons are involved in the bonding.

There are various forms of solid sulphur trioxide. The simplest one is a trimer, S_3O_9, where three SO_3 molecules are joined up and arranged in a ring.

There are also other polymeric forms in which the SO_3 molecules join together in long chains. For example:

The fact that the simple molecules join up in this way to make bigger structures is what makes the sulphur trioxide a solid rather than a gas.

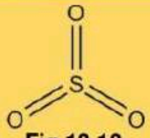


Fig 13.12

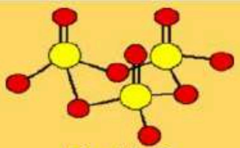


Fig. 13.13

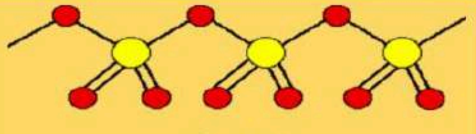


Fig. 13.14

(c) The Chlorine oxides

Chlorine forms several oxides. Here we discuss only two which are – chlorine (I) oxide, Cl_2O, and chlorine (VII) oxide, Cl_2O_7.

Fig. 13.15

Chlorine (I) oxide

Chlorine (I) oxide is a yellowish-red gas at room temperature. It consists of simple small molecules. In this structure chlorine uses its one outer electron and bonds with oxygen.

Chlorine (VII) oxide

Chlorine (VII) oxide is a colourless oily liquid at room temperature.

In chlorine (VII) oxide, the chlorine uses all of its seven outer electrons and bonds with oxygen. This produces a much bigger molecule.

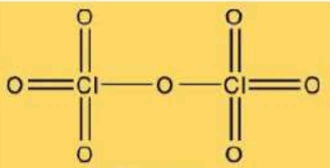


Fig. 13.16

13.1.4. Acid-Base Behaviour of the Oxides

This topic looks at the reactions of the oxides of Period 3 elements (sodium to chlorine) with water and with acids or bases where relevant.(Take quick review from table 13.2)

I. Trend in Acid-Base Behaviour

The trend in acid-base behaviour is shown in various reactions, but as a simple summary:

The trend is from strongly basic oxides on the left-hand side to strongly acidic ones on the right, via an amphoteric oxide (aluminium oxide) in the middle. An amphoteric oxide is one which shows both acidic and basic properties.

II. Reactions of Oxides with Water, Acids and Bases

Chemistry of the individual oxides

Sodium oxide (Na_2O)

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion, O^{2-}, which is a very strong base with a high tendency to combine with hydrogen ions.

Reaction with Water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Reaction with Acids

As a strong base, sodium oxide also reacts with acids. For example, it would react with dilute hydrochloric acid to produce sodium chloride solution.

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

Magnesium oxide (MgO)

Magnesium oxide is again a simple basic oxide, because it also contains oxide ions. However, it isn't as strongly basic as sodium oxide because the oxide ions aren't so free. In the sodium oxide case, the solid is held together by attractions between 1^+ and 2^- ions. In the magnesium oxide case, the attractions are between 2^+ and 2^-. It takes more energy to break these.

Reaction with Water

If you shake some white magnesium oxide powder with water, nothing seems to happen (it doesn't look as if it reacts). However, if you test the pH of the liquid, you find that it is somewhere around pH 9 (showing that it is slightly alkaline). There must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction, but this is almost insoluble and so not many hydroxide ions actually get into solution.

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

Reaction with Acids

Magnesium oxide reacts with acids as you would expect any simple metal oxide to react. For example, it reacts with warm dilute hydrochloric acid to give magnesium chloride solution.

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

Aluminium oxide (Al_2O_3)

As it is amphoteric oxide, it has reactions as both a base and an acid.

Reaction with Water

Aluminium oxide doesn't react in a simple way with water and doesn't dissolve in it. Although it still contains oxide ions, they are held too strongly in the solid lattice to react with the water.

Reaction with Acids

Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution.

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

Reaction with Bases

Aluminium oxide has also got an acidic side to its nature, and it shows this by reacting with bases such as sodium hydroxide solution.

Various aluminates are formed, compounds where the aluminium is found in the negative ion. This is possible because aluminium has the ability to form covalent bonds with oxygen.

With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

Phosphorus (V) oxide (P_4O_{10})

Reaction with Water

Phosphorus (V) oxide reacts violently with water to give a solution containing a mixture of acids, the nature of which depends on the conditions. We usually just consider one of these, phosphoric(V) acid, H_3PO_4 (also known just as phosphoric acid or as orthophosphoric acid).

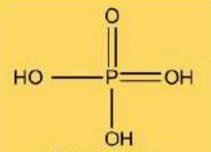


Fig: 13.17

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Reaction with Base:

As it is acidic so it reacts with NaOH as follows:

$$NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$$
$$2NaOH + H_3PO_4 \longrightarrow Na_2HPO_4 + 2H_2O$$
$$3NaOH + H_3PO_4 \longrightarrow Na_3HPO_4 + 3H_2O$$

Again, if you were to react phosphorus (V) oxide directly with sodium hydroxide solution rather than making the acid first, you would end up with the same possible salts.

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

The Sulphur oxides (SO_x)

We are going to be looking at sulphur dioxide, SO_2, and sulphur trioxide, SO_3.

Sulphur dioxide

Reaction with Water:

Sulphur dioxide is fairly soluble in water, reacting with it to give a solution of sulphurous acid, H_2SO_3.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Reaction with Base:

As it is acidic so it reacts with NaOH and CaO as follows:

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$
$$CaO + SO_2 \longrightarrow CaSO_3$$

Sulphur trioxide

Sulphur trioxide reacts violently with water to produce a fog of concentrated sulphuric acid droplets.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Reaction with Base:

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

In principle, you can also get sodium hydrogensulphate solution by using half as much sodium hydroxide and just reacting with one of the two acidic hydrogens in the acid.

Sulphur trioxide itself will also react directly with bases to form sulphates. For example, it will react with calcium oxide to form calcium sulphate. This is just like the reaction with sulphur dioxide described above.

$$CaO + SO_3 \longrightarrow CaSO_4$$

The Chlorine oxides (Cl_2O_x)

Chlorine forms several oxides, but the only two are chlorine (VII) oxide, Cl_2O_7, and chlorine (I)oxide, Cl_2O. Chlorine (VII) oxide is also known as dichlorine heptoxide, and chlorine (I) oxide as dichlorine monoxide.

Chlorine (VII) oxide

Chlorine (VII) oxide is the highest oxide of chlorine - the chlorine is in its maximum oxidation state of +7. It continues the trend of the highest oxides of the Period 3 elements towards being stronger acids.

Reaction with Water:

Chlorine (VII) oxide reacts with water to give the very strong acid, chloric(VII) acid - also known as perchloric acid. The pH of typical solutions will, like sulphuric acid, be around 0.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

Reaction with Base:

Chloric (VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate(VII).

$$NaOH + HClO_4 \longrightarrow NaClO_4 + H_2O$$

Chlorine (VII) oxide itself also reacts with sodium hydroxide solution to give the same product.

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

Chlorine (I) oxide

Reaction with Base:

Chlorine (I) oxide is far less acidic than chlorine(VII) oxide. It reacts with water to some extent to give chloric(I) acid, HOCl - also known as hypochlorous acid.

$$Cl_2O + H_2O \rightleftharpoons 2HOCl$$

Reaction with Base:

Chloric (I) acid reacts with sodium hydroxide solution to give a solution of sodium chlorate(I) (sodium hypochlorite).

$$NaOH + HOCl \longrightarrow NaOCl + H_2O$$

Chlorine (I) oxide also reacts directly with sodium hydroxide to give the same product.

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

Quick Quiz

(a) What is the nature of bonds in the oxides formed when Na, Mg, Al and S react with excess oxygen?

(b) How do these oxides react with (i) Water (ii) dilute acids, (iii) alkali

(c) Magnesium chloride is a high melting point solid, aluminium chloride is a solid which sublimes readily at about 180^0 C and silicon tetrachloride is a volatile liquid. Explain the nature of the chemical bonding in these chlorides and show how this accounts for the above differences in volatility.

13.1.5 Chlorides of the Period 3 Elements

This topic looks at the structures of the chlorides of the Period 3 elements (sodium to sulphur), their physical properties and their reactions with water.

The Structures

Sodium chloride and magnesium chloride are ionic and consist of giant ionic lattices at room temperature. Aluminium chloride and phosphorus (V) chloride are tricky! They change their structure from ionic to covalent when the solid turns to a liquid or vapour. The others are simple covalent molecules.

Melting and Boiling Points

Sodium and magnesium chlorides are solids with high melting and boiling points because of the large amount of heat which is needed to break the strong ionic attractions.

The rest are liquids or low melting point solids. Leaving aside the aluminium chloride and phosphorus (V) chloride cases where the situation is quite complicated, the attractions in the others will be much weaker intermolecular forces such as Van der Waals dispersion forces. These vary depending on the size and shape of the molecule, but will always be far weaker than ionic bonds.

Electrical Conductivity

Sodium and magnesium chlorides are ionic and so will undergo electrolysis when they are molten. Electricity is carried by the movement of the ions and their discharge at the electrodes.

In the aluminium chloride and phosphorus (V) chloride cases, the solid doesn't conduct electricity because the ions aren't free to move. In the liquid (where it exists - both of these sublime at ordinary pressures), they have converted into a covalent form, and so do not conduct either. The rest of the chlorides do not conduct electricity either solid or molten because they do not have any ions or any mobile electrons.

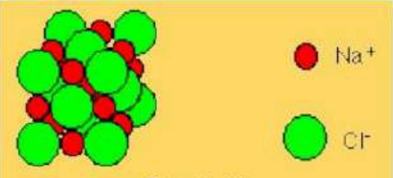


Fig: 13.18

Reactions with Water

Sodium and magnesium chloride just dissolve in water. The other chlorides all react with water in a variety of ways described below for each individual chloride. The reaction with water is known as hydrolysis.

The Individual Chlorides

Sodium Chloride, NaCl

Sodium chloride is a simple ionic compound consisting of a giant array of sodium and chloride ions. A small representative bit of a sodium chloride lattice looks like this:

This is normally drawn in an exploded form as:

The strong attractions between the positive and negative ions need a lot of heat energy to break, and so sodium chloride has high melting and boiling points.

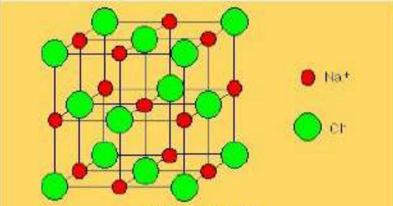


Fig: 13.19

It doesn't conduct electricity in the solid state because it hasn't any mobile electrons and the ions aren't free to move. However, when it melts it undergoes electrolysis.

Sodium chloride simply dissolves in water to give a neutral solution.

Magnesium Chloride, $MgCl_2$

Magnesium chloride is also ionic, but with a more complicated arrangement of the ions to allow for having twice as many chloride ions as magnesium ions. Again, lots of heat energy is needed to overcome the attractions between the ions, and so the melting and boiling points are again high.

Solid magnesium chloride is a non-conductor of electricity because the ions aren't free to move. However, it undergoes electrolysis when the ions become free on melting. Magnesium chloride dissolves in water to give a faintly acidic solution (pH = approximately 6).

When magnesium ions are broken off the solid lattice and go into solution, there is enough attraction between the Mg^{2+} ions and the water molecules to get co-ordinate bonds formed between the magnesium ions and lone pairs on surrounding water molecules.

Hexaaquamagnesium ions are formed, $[Mg(H_2O)_6]^{2+}$.

$$MgCl_{2(s)} + 6H_2O_{(l)} \longrightarrow [Mg(H_2O)_6]^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Ions of this sort are acidic.

Aluminium Chloride, $AlCl_3$

Solid aluminium chloride doesn't conduct electricity at room temperature because the ions aren't free to move. Molten aluminium chloride (only possible at increased pressures) doesn't conduct electricity because there aren't any ions any more.

The reaction of aluminium chloride with water is surprising. If you drop water onto solid aluminium chloride, you get a violent reaction producing clouds of steamy fumes of hydrogen chloride gas.

The aluminium chloride reacts with the water rather than just dissolving in it. In the first instance, hexaaquaaluminium ions are formed together with chloride ions.

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

You will see that this is very similar to the magnesium chloride equation given above - the only real difference is the charge on the ion.

Summary

- At room temperature, solid aluminium chloride has an ionic lattice with a lot of covalent character.
- At temperatures around 180 - 190°C (depending on the pressure), aluminium chloride converts to a molecular form, Al_2Cl_6. This causes it to melt or vaporise because there are now only comparatively weak intermolecular attractions.
- As the temperature increases a bit more, it increasingly breaks up into simple $AlCl_3$ molecules.

Silicon Tetrachloride, $SiCl_4$

Silicon tetrachloride is a simple covalent chloride. There isn't enough electronegativity difference between the silicon and the chlorine for the two to form ionic bonds.

It fumes in moist air because it reacts with water in the air to produce hydrogen chloride. If you add water to silicon tetrachloride, there is a violent reaction to produce silicon dioxide and fumes of hydrogen chloride. In a large excess of water, the hydrogen chloride will, of course, dissolve to give a strongly acidic solution containing hydrochloric acid.

Do you know?
Silicon tetrachloride is a colourless liquid at room temperature, which fumes in moist air. The only attractions between the molecules are van der Waals dispersion forces.
It does not conduct electricity because of the lack of ions or mobile electrons.

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

The Phosphorus Chlorides

There are two phosphorus chlorides - phosphorus(III) chloride, (PCl_3), and phosphorus(V) chloride, (PCl_5).

Phosphorus (III) Chloride (phosphorus Trichloride), (PCl_3).

This is another simple covalent chloride - again a fuming liquid at room temperature.

Phosphorus(III) chloride reacts violently with water. You get phosphorous acid, H_3PO_3, and fumes of hydrogen chloride (or a solution containing hydrochloric acid if lots of water is used).

Do you know?
Phosphorus trichloride is a liquid because there are only van der Waals dispersion forces and dipole-dipole attractions between the molecules. It does not conduct electricity because of the lack of ions or mobile electrons.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Phosphorus (V) Chloride (Phosphorus pentachloride), ((PCl_5).

Unfortunately, phosphorus (V) chloride is structurally more complicated.

Phosphorus (V) chloride has a violent reaction with water producing fumes of hydrogen chloride. As with the other covalent chlorides, if there is enough water present, these will dissolve to give a solution containing hydrochloric acid.

The reaction happens in two stages. In the first, with cold water, phosphorus oxychloride, $POCl_3$, is produced along with HCl.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

Do you know?
Phosphorus (V) chloride is a white solid which sublimes at 163°C. The higher the temperature goes above that, the more the phosphorus (V) chloride dissociates (splits up reversibly) to give phosphorus (III) chloride and chlorine.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Solid phosphorus (V) chloride contains ions - which is why it is a solid at room temperature. The formation of the ions involves two molecules of PCl_5.

If the water is boiling, the phosphorus(V) chloride reacts further to give phosphoric(V) acid and more HCl. Phosphoric(V) acid is also known just as phosphoric acid or as orthophosphoric acid.

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

The overall equation in boiling water is just a combination of these:

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Disulphur dichloride, S_2Cl_2

Disulphur dichloride is formed when chlorine reacts with hot sulphur.

Disulphur dichloride is a simple covalent liquid (orange and smelly).

The shape is difficult to draw convincingly. The atoms are all joined up in a line but twisted:

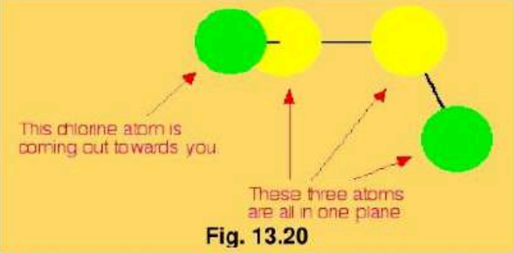


Fig. 13.20

The reason for drawing the shape is to give a hint about what sort of intermolecular attractions are possible. There is no plane of symmetry in the molecule and that means that it will have an overall permanent dipole.

Do you know?
Disulphur Dichloride has van der Waals dispersion forces and dipole-dipole attractions. There are no ions in disulphur dichloride and no mobile electrons - so it never conducts electricity.

Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various sulphurcontaining acids and anions (negative ions).

Quick Quiz

1. Which of the following give acidic solution water $MgCl_2$, $AlCl_3$, $SiCl_4$, NaCl?
2. Why NaCl has high melting and boiling point?
3. Write equations for reactions of PCl_5 with hot and cold water.
4. What products are obtained on reaction of disulphide dichloride with water?
5. Why $AlCl_3$ is non-conductor in solid as well as in liquid state but NaCl and $MgCl_2$ are conductor in liquid state and non-conductor in solid state?

13.1.6 Hydroxides of the Period 3 Elements

This topic looks briefly at how the chemistry of the "hydroxides" of the Period 3 elements from sodium to chlorine varies as you cross the period.

Sodium and magnesium hydroxides are ionic compounds and are simple basic hydroxides. Both react with acids to form salts. For example, with dilute hydrcloric acid, colourless solution of sodium chloride or magnesium chloride are formed.

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

Aluminium hydroxide, like aluminium oxide, is amphoteric - it has both basic and acidic properties. With dilute hydrochloric acid, a colourless solution of aluminium chloride is formed.

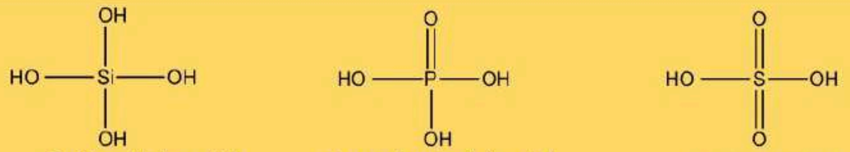
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

But aluminium hydroxide also has an acidic side to its nature. It will react with sodium hydroxide solution to give a colourless solution of sodium tetrahydroxoaluminate.

$$Al(OH)_3 + NaOH \longrightarrow NaAl(OH)_4$$

Hydroxide of Si, P and S have hydroxides -OH groups covalently bounded to the atoms. These compounds are all acidic-ranging from the very weakly acidic silicic acids (one of which is shown below) to the very strong sulphuric or chloric acids.

There are other acids (also containing -OH groups) formed by these elements, but these are the ones where the Period 3 element is in its highest oxidation state.



Orthosilicic acid   phosphoric (v) acid   Sulphuric acid

Fig. 13.21

Aluminium hydroxide is amphoteric.

Like sodium or magnesium hydroxides, it will react with acids. This is showing the basic side of its nature.

- Orthosilicic acid is very weak.
- Phosphoric(V) acid is a weak acid - although somewhat stronger than simple organic acids like ethanoic acid.
- Sulphuric acid and chloric (VII) acids are both very strong acids.

Quick Quiz

1. Justify that NaOH and Mg $(OH)_2$ are basic in nature.
2. Justify that Al $(OH)_3$ is amphoteric compound.

13.2 GROUP 1 ELEMENTS

13.2.1 Atomic and Physical Properties of the Group 1 Elements (Alkali Metals)

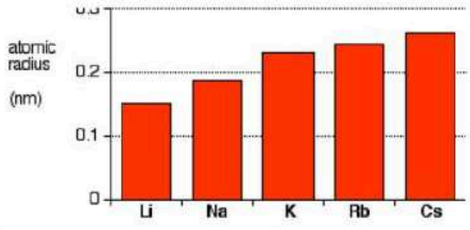


Fig. 13.22 Atomic Radii of the Group 1 Elements

This section explores the trends in some atomic and physical properties of the Group 1 elements - lithium, sodium, potassium, rubidium and caesium. You will find separate sections below covering the trends in atomic radius, first ionization energy, electronegativity, melting and boiling points, and density.

Trends in Atomic Radius

As we move from lithium to caesium, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic volume. We find therefore, that there is an increase of atomic and ionic radii (of M^+ ions) as we move from lithium to caesium.

Table 13.3 Some Physical Properties of Alkali Metals

Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.1	25.47	132.91
Atomic volume	12.97	23.63	45.36	55.8	69.95
Atomic (i.e. metallic radius for coordination number 12	1.55	1.9	2.35	2.46	2.6
covalent radius	1.23	1.54	2.03	2.16	2.36
Ionic radius of M+ ions	0.6	0.95	1.33	1.48	1.69
Melting point	180.5	97.8	63.7	38.9	28.7
Boiling point	1330	892	760	688	670
Ionisation energies (kJ/mol) (I_1)	520.3	495.8	418.9	403.0	375.7
I_2	7298.1	4562.4	3051.4	2633.0	2230.0
Standard oxidation potential	3.04	2.71	2.99	2.99	2.99
Sublimation energy (eV/ion)	1.7472	1.2432	1.032	0.984	0.9024
Hydration energy (eV/ion)	5.904	3.792	3.6955	3.36	0.624
Electronegativity	1	0.9	0.8	0.8	0.7
Colour of the flame	Crimson red	Golden yellow	Violet	Violet	Violet
Heat of atomisation at 25C (eV/atm)	1.7472	1.2432	1.032	0.984	0.9024
Ionic conduction of M+ ion	33.5	43.5	64.6	67.5	63

Trends in First Ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions - in other words, for 1 mole of this process:

$$X_{(g)} \longrightarrow X^{+}_{(g)} + e^{-}$$

Notice that first ionization energy falls as you go down the group. We know that alkali metal have only one electron in their outermost shell (ns^1 electron). This ns^1 electron is so weakly held with the nucleus that it can be removed very easily. Alkali metals therefore have low ionisation energies.

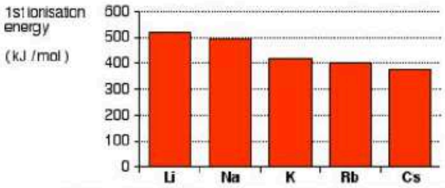


Fig. 13.23 First Ionization Energy of the Group 1 elements

As the distance of ns^1 electron from the nucleus increases on moving from Li to Cs its removal becomes more and more easy as we proceed from Li to Cs i.e. the amount of energy (ionization energy) used in the removal of ns^1 electron is maximum in case of energies of alkali metals go on decreasing from Li to Cs as shown in table 13.3.

The second ionisation energies are fairly high, since the loss of the second electron from M+ cation which has a noble gas configuration is quite difficult.

Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

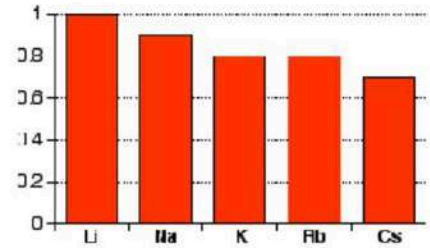


Fig 13.24 Electronegativties of the Group 1 elements

We have seen that the outer electron (i.e. ns^1 electron) of the atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy. During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic. Since the amount of energy absorbed during the excitation process is different in different atoms, different colours are imparted by the atoms to the flame. The property of alkali metals to give colouration in the burner flame has been used to detect their presence in salts by a test, known as flame test.

Trends in Melting and Boiling Points

You will see that both the melting points and boiling points fall as you go down the Group.

The melting and boiling points are very low because of the presence of weak inner atomic bonds in the solid state of the alkali metals. These bonds are due to their atomic radii and mainly due to the their electronic configuration having a single valence electrons as

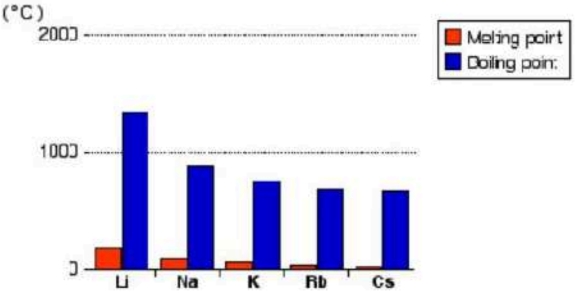


Fig 13.25: Melting and Boiling Points of the Group 1 elements

compared to large number of available vacant orbital. As the size of the metal atoms increases, the repulsion of the non-bonding electrons also increases. This increase in the repulsion of non-bonding electron decreases the melting and boiling points of alkali metals when we move from Li to Cs (as shown in table 13.3).

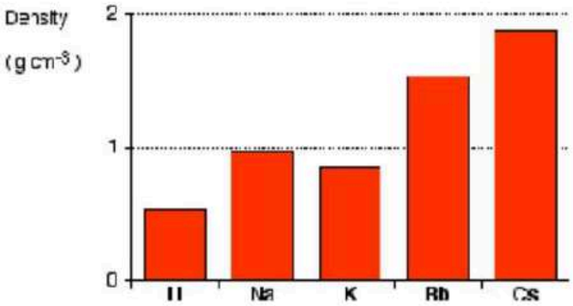


Fig. 13.26: Densities of the Group 1 elements

Trends in Density

The densities of alkali metals are quite low due to the large atomic volumes. Li, Na and K are lighter than water. The densities increase with the increase in atomic from Li to Cs indicating that greater atomic with more than compensates for the bigger size of the atoms. K is however, lighter than Na which is due to an unusual increase in atomic size of K.

Elements	Li	Na	K	Rb	Cs
Densities at 0^0C (g/c.c)	0.534	0.972	0.859	1.525	1.903

Quick Quiz

1. Different element imparts different colours in flame?
2. Explain that 2^{nd} ionization energy is greater than 1^{st} ionization energy
3. Why melting point of alkali metals are low as compared to alkaline earth metals?

13.2.2 Trends in Reactivity with Water

In this topic, we discuss the reactions of the Group 1 elements; lithium, sodium, potassium, rubidium and caesium with water. It uses these reactions to explore the trend in reactivity in Group 1.

With the exception of Li, the alkali metals are extremely soft and readily fused. They are highly malleable (i.e. can be pressed out into sheets) and ductile (i.e. can be drawn into wires). When freshly cut, they have a bright lustre which quickly tarnished as soon as metal comes in contact with atmosphere.

Summary of the trend in reactivity

The Group 1 metals become more reactive towards water as you go down the Group.

Explaining the trend in Reactivity

Looking at the enthalpy changes for the reactions

The overall enthalpy changes

As you go down the Group, the amount of heat given off increases as you go from lithium to caesium. Not so!

The table gives estimates of the enthalpy change for each of the elements undergoing the reaction:

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

	enthalpy change (kJ / mol)
Li	-222
Na	-184
K	-196
Rb	-195
Cs	-203

You will see that there is no pattern at all in these values. They are all fairly similar and, surprisingly, lithium is the metal which releases the most heat during the reaction!

When these reactions happen, the differences between them lie entirely in what is happening to the metal atoms present. In each case, you start with metal atoms in a solid and end up with metal ions in solution.

Overall, what happens to the metal is this:

$$X(s) \longrightarrow X^{+}_{(aq)} + e^{-}$$

13.2.3 Reactions with Oxygen

This topic mainly looks at the reactions of the Group 1 elements (lithium, sodium, potassium, rubidium and caesium) with oxygen - including the simple reactions of the various kinds of oxides formed.

The Reactions with Air or Oxygen

Alkali metals react with O_2 or air rapidly and thus get tarnished due to the formation of their oxide on the surface of the metals. It is for this reason that alkali metals are stored in kerosene or paraffin oil.

Li when burnt in O_2 gives mainly lithium monoxide, (normal oxide) Li_2O.

$$4Li + O_2 \longrightarrow 2Li_2O$$

Na when burnt in O_2 forms sodium peroxide, Na_2O_2

$$2Na + O_2 \longrightarrow Na_2O_2$$

Other alkali metals react with O_2 to form super oxide of MO_2 type.

$$M + O_2 \longrightarrow MO_2$$

Since the normal oxides of alkali metals other than that of Li (Li_2O) are not formed by the direct reaction between the metals and O_2 they are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metals itself.

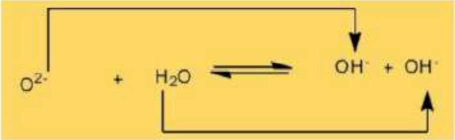
$$2Na_2O_2 + 4Na \longrightarrow 4Na_2O$$

$$2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$$

$$2NaNO_2 + 10Na \longrightarrow 6Na_2O + N_2$$

Properties: Normal oxides (O^{2-}) react with H_2O to form hydroxides by proton exchange.

Gains proton
Loses proton

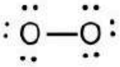


The peroxides (O_2^{2-}) and superoxides (O^{2-}) are strong oxidising agents and react with H_2O to give H_2O_2 and O_2.

$$2O_2^{2-} + 2H_2O \longrightarrow 2H_2O_2 + O_2$$

Normal oxides have anti-fluorite structure and are ionic in nature since they contain monoxide in, O^{2-} Peroxides contain peroxide ion, O_2^{2-} or $[\text{-O-O}]^{2-}$.

The super oxide ion has a three electron bond as shown below:



The presence of one unpaired electron in it makes this in paramagnetic and coloured.

Reactions of the Oxides with Water and Dilute Acids

I. The simple oxides, X_2O

Reaction with Water

These are simple basic oxides, reacting with water to give the metal hydroxide. For example, lithium oxide reacts with water to give a colourless solution of lithium hydroxide.

$$X_2O + H_2O \longrightarrow 2XOH$$

Reaction with dilute Acids

These simple oxides all react with an acid to give a salt and water. For example, sodium oxide will react with dilute hydrochloric acid to give colourless sodium chloride solution and water.

$$X_2O + 2HCl \longrightarrow 2XCl + H_2O$$

II. The peroxides, X_2O_2

Reaction with Water

If the reaction is done in ice cold (and the temperature controlled so that it doesn't rise even though these reactions are strongly exothermic), a solution of the metal hydroxide and hydrogen peroxide is formed.

$$X_2O_2 + 2H_2O \longrightarrow 2XOH + H_2O_2$$

If the temperature increases (as it inevitably will unless the peroxide is added to water very slowly), the hydrogen peroxide produced decomposes into water and oxygen. The reaction can be very violent overall.

Reaction with dilute Acids

These reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed. The hydrogen peroxide will decompose to give water and oxygen if the temperature rises again, it is almost impossible to avoid this. Another potentially violent reaction!

$$X_2O_2 + 2HCl \longrightarrow 2XCl + H_2O_2$$

III. The Superoxides, XO_2

Reaction with Water

This time, a solution of the metal hydroxide and hydrogen peroxide is formed, but oxygen gas is given off as well. Once again, these are strongly exothermic reactions and the heat produced will inevitably decompose the hydrogen peroxide to water and more oxygen. Again violent!

$$2XO_2 + 2H_2O \longrightarrow 2XOH + H_2O_2 + O_2$$

Reaction with dilute Acids

Again, these reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed together with oxygen gas. The hydrogen peroxide will again decompose to give water and oxygen as the temperature rises. Violent!

$$2XO_2 + 2HCl \longrightarrow 2XCl + H_2O_2 + O_2$$

13.2.4 Reactions of the Elements with Chlorine

Sodium burns with an intense orange flame in chlorine is exactly the same way that it does in pure oxygen. The rest also behave the same in both gases.

In each case, there is a white solid residue which is the simple chloride, XCl. There is nothing in any way complicated about these reactions!

$$2X + Cl_2 \longrightarrow 2XCl$$

13.2.5. Effect of heat on Nitrates, Carbonates and Hydrogen-Carbonates

I. The Facts

Group 1 compounds are more stable to heat than the corresponding compounds in Group 2 You will often find that the lithium compounds behave similarly to Group 2 compounds, but the rest of Group 1 are in some way different.

Nature of Carbonates, Bicarbonates and Nitrates

The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) are highly stable to heat. With increase of electropositive character from Li to Cs, the stability of these salts increases.

Their nitrates decompose on strong heating to the corresponding nitrite and O_2, (Exception is $LiNO_3$).

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

II. Explaining the trend in terms of the polarising ability of the positive ion

When alkali metal cations approach near an anion, attracts the outer most electrons of the anion and repels the nucleus. Thus the distortion or polarisation of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions, i.e. the bond between the cation and anion becomes partly covalent in character. In general the smaller cations polarise the anions more effectively than bigger one. Therefore, the lithium salts are slightly covalent while other alkali metal salts are ionic.

Quick Quiz

1. Why lithium salts are more covalent in nature while salts of other alkali metals are ionic.
2. Give trend of stability of carbonales of alkali and alkaline earth metals along group.
3. Show bonding in superoxide ion.
4. Why alkali metals stores in kerosene paraffin oil.

13.2.6 Flame Tests

Flame tests are used to identify the presence of a relatively small number of metal ions in a compound. Not all metal ions give flame colours.

For Group 1 compounds, flame tests are usually by far the easiest way of identifying which metal you have got. For other metals, there are usually other easy methods which are more reliable - but the flame test can give a useful hint as to where to look.

Carrying out a Flame Test

Practical details

Clean a platinum or nichrome (a nickel-chromium alloy) wire by dipping it into concentrated hydrochloric acid and then holding it in a hot Bunsen flame. Repeat this until the wire doesn't produce any colour in the flame.

When the wire is clean, moisten it again with some of the acid and then dip it into a small amount of the solid you are testing so that some sticks to the wire. Place the wire back in the flame again. If the flame colour is weak, it is often worthwhile to dip the wire back in the acid again and put it back into the flame as if you were cleaning it. You often get a very short but intense flash of colour by doing that.

The Colours

Different colours shown by different elements are given below.

Elements	flame colour	Elements	flame colour
Li	red	Ca	orange-red
Na	golden yellow	Sr	red
K	lilac (pink)	Ba	pale green

Rb	red (reddish-violet)	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	greyish-white

Note: What do you do if you have a red flame colour for an unknown compound and do not know which of the various reds it is?
Get samples of known lithium, strontium (etc) compounds and repeat the flame test, comparing the colours produced by one of the known compounds and the unknown compound side by side until you have a good match.

The Origin of Flame Colours

We have seen that the outer electron (i.e. ns^1 electron) of atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their salts into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic spectrum and hence the colour is imparted by the atoms to the flame. Sine the amount of energy absorbed during the excitation process is different in different atoms, different colour are imparted by the atoms to the flame. The property of alkali metals to give coloration in the Bunsen flame has been used to detect their presence in salts by a test known as flame test.

Quick Quiz

1. Ion of which element among the alkali metals has the greatest polarising power?
2. Justify the placing of Li, Na, K, Rb, and Cs in the same group of the periodic table.
3. Write the electronic configuration for alkali metal atoms.
   Explain the periodicity in ionisation energy, electronegativity and atomic radii on passing from Li to Rb.
4. Among alkali metals atoms which has the largest ionisation potential?
5. Explain the following:
   a) Alkali metals show an oxidation state +1 only
   b) Alkali metals are univalent.
   c) Alkali metals are good reducing agents
   d) Alkali metals have low melting points
   e) Alkali metals give characteristic colour to the Bunsen flame.
   f) Na is stored under kerosene.
   g) alkali metal form M^+ cations instead of M^{2+} cations
   h) Alkali metals have low ionisation potentials.
6. Hydroxides of 1st group are strong bases. Explain why?
7. Explain the following:
   Li_2CO_3, is unstable while other alkali metals carbonates are relatively more stable.

13.3 GROUP 2 ELEMENTS

13.3.1 Atomic and Physical Properties

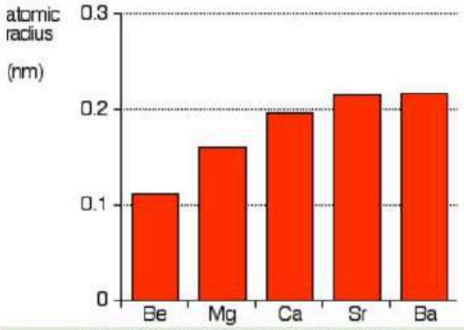


Fig. 13.27 Atomic Radii of the Group 2 elements

This section explores the trends in some atomic and physical properties of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium. You will find separate sections below covering the trends in atomic radius, first ionization energy, electronegativity and physical properties.

Trends in Atomic Radius

You can see that the atomic radius increases as you go down the Group. Notice that beryllium has a particularly small atom compared with the rest of the Group.

Explaining the increase in Atomic Radius

Atomic volume, Atomic and Ionic Radii

Because of the addition of an extra shell of electrons to each elements from Be to Ra, the atomic volume increases from Be to Ra. With the increases of atomic volume the atomic and ionic radii (of M^{2+} ions) also increase from Be to Ra. The atomic radii of these elements are however, smaller than those of alkali metals in the same period. This is due to the fact that the alkaline earth metals have higher nuclear charge which tends to draw the orbit electrons towards the nucleus. The smaller values of atomic radii result in that the alkaline earth metals are harder, have higher densities and higher melting points than alkali metals.

Table 13.4 Some physical properties of alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	6.4x10.4	2.0	3.45	0.915	0.040	1.3X10.10
Density (gm/c.c)	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	763	714	700
Boiling point (°C)	2770	1107	1440	1380	1610	--
Atomic volume (c.c)	4.90	13.97	25.9	34.54	63.7	38.0
Atomic (i.e., metallic radius for coordination number 12 (A°)	1.12	1.60	1.97	2.15	2.22	--
Convalent radius (A°)	0.90	1.36	1.74	1.91	1.98	--
Tonic (crystal radius of M^2 + ion for coordination number + ((A°)	0.31	065	0.99	1.13	1.35	140
Ionisations energies (KJ/mole)						
I_1	899.5	737.7	829.8	547.5	502.9	509.4

I_2	1757.1	1450.7	1145.4	1064.3	965.2	979.06
$I_1 + I_2$	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation stato	+2	+2	+2	+2	+2	+2
Electronegativity	1.5	1.2	1.0	0.9	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for M (s) $M_{(s)} \longrightarrow M^{2+}_{(aq)} + 2e$	1.70 1.70	1.37	2.87	2.89 163.21	2.90 175.77	2.92 --
Heat of atomization at 25 °C and I atm pressure (kJ/mole)	327.26	146.89	181.21	1458.67	1276.42	--
Heat of hydration (kJ/mole)	2385.45	1925.1	1653.07			
Jonic potential of M^{2+} ion (i.e., charge/radius ratio).	6.66	3.08	2.12	1.82	1.55	1.33

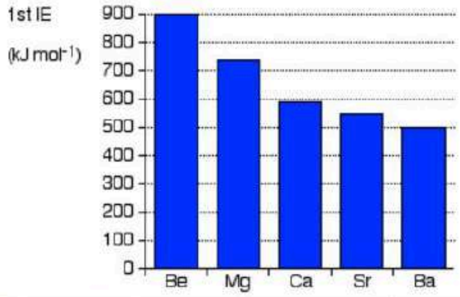


Fig. 13.28 First Ionisation energy of the Group 2 elements

Trends in First Ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly +4I charged gaseous ions - in other words, for 1 mole of this process:

$$X_{(g)} \longrightarrow X^+_{(g)} + e^-$$

Notice that first ionisation energy falls as you go down the group.

Explaining the decrease in first Ionisation Energy

The first and second ionisation energies of these elements decrease with the increase of atomic radii from Be to Ba. However, the values for Ra is slightly higher than those of Ba (for values see table no 13.4)

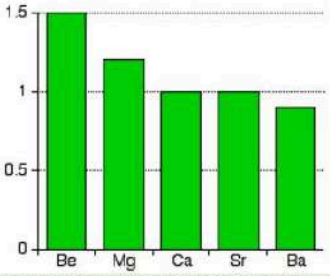


Fig. 13.29 Electronegativity of the Group 2 elements

Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

Notice that electronegativity values fall as you go down the group (for values see table 13.4)

Trends in Melting Point and Boiling Point

Melting Points

Boiling Points

If we look at figure, the ionization energies of carbon at the top of the group that there is no possibility of it forming simple positive ions, while Sn and Pb have low energies so form positive ion easily.

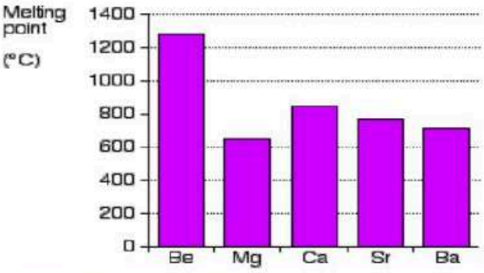


Fig. 13.30: You will see that there is no obvious pattern in boiling points. It would be quite wrong to suggest that there is any trend here whatsoever.

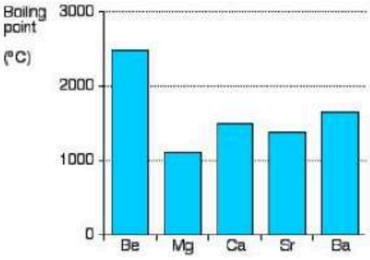


Fig. 13.31: you will see that (apart from where the smooth trend is broken by magnesium) the melting point falls as you go down the Group.

13.3.2 Trends in Reactivity with Water

This section looks at the reactions of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium - with water (or steam). It uses these reactions to explore the trend in reactivity in Group 2.

The Facts

Beryllium

Beryllium has no reaction with water or steam even at red heat.

Magnesium

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

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

Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface, and the coil of magnesium ribbon usually floats to the surface. However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.

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

Summarising the trend down the Group

As the metal atoms get bigger, any bonding pair gets further and further away from the metal nucleus, and so is less strongly attracted towards it. In other words, as you go down the Group, the elements become less electronegative.

As you go down the Group, the bonds formed between these elements and other things such as chlorine become more and more ionic. The bonding pair is increasingly attracted away from the Group 2 element towards the chlorine (or whatever).

Calcium, Strontium and Barium

These all react with cold water with increasing vigour to give the metal hydroxide and hydrogen. Strontium and barium have reactivities similar to lithium in Group 1 of the Periodic Table.

Calcium, for example, reacts fairly vigorously with cold water in an exothermic reaction. Bubbles of hydrogen gas are given off, and a white precipitate (of calcium hydroxide) is formed, together with an alkaline solution (also of calcium hydroxide - calcium hydroxide is slightly soluble).

The equation for the reactions of any of these metals would be:

$$X_{(s)} + 2H_2O_{(l)} \longrightarrow X(OH)_{2(aq\ or\ s)} + H_{2(g)}$$

The hydroxides aren't very soluble, but they get more soluble as you go down the Group. The calcium hydroxide formed shows up mainly as a white precipitate (although some does dissolve). You get less precipitate as you go down the Group because more of the hydroxide dissolves in the water.

Summary of the trend in reactivity The Group 2 metals become more reactive towards water as you go down the Group.

Explaining the trend in Reactivity

Be $(OH)_2$ is not at all basic; in fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

The hydroxides of other metals are basic in character. Their basic character increases on moving down the group. Thus $Mg(OH)_2$ is weakly basic while $B(OH)_2$ is the strongest base. The increase in basic character of the hydroxides on moving down the group is due to the fact that with the increase in size of M^{2+} cation both the polarity of M-OH bond and the internuclear distance between oxygen of OH- ion and the metals atom increase. As a result of this, there is greater ionisation of $M(OH)_2$ and hence basic character increases.

Due to high polarising power of small Be^{2+} in, $Be(OH)_2$ is covalent while other hydroxides are ionic.

$Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in H_2O while the hydroxides of other metals are slightly soluble. Their solubility increases on moving down the group as shown by the increasing value of the solubility products of these hydroxides.

$Be(OH)_2 = 1.6 \times 10^{-26}$; $Mg(OH)_2 = 8.9 \times 10^{-12}$; $Ca(OH)_2 = 1.3 \times 10^{-4}$;

$Sr(OH)_2 = 3.2 \times 10^{-4}$; $Ba(OH)_2 = 5.4 \times 10^{-2}$

13.3.3 Reactions with Oxygen and Nitrogen

I. Reactions of the Group 2 Elements With Air Or Oxygen

This topic looks at the reactions of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium - with air or oxygen.

Formation of Simple Oxides

Preparation: The alkaline earth metals form the normal oxides of MO type which are obtained by heating the metal in O_2 or by heating their carbonates at high temperature e.g.

$$2Ca + O_2 \longrightarrow 2CaO$$
$$CaCO_3 \longrightarrow CaO + CO_2$$

Properties:

(i) These oxides are extremely stable white crystal line solids due to their high crystal lattice energy obtained by packing doubly charged in sin a sodium chloride type of lattice.

(ii) BeO and MgO are quite insoluble in H_2O while H_2O CaO, SrO qand BaO react with H_2O to give soluble hydroxides, $M(OH)_2$ which are strong bases

(iii) BeO is not at all basic in nature; in fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

$$Be(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

The oxides of other metals are basic in character. Their basic character increases on moving down the group.

(iv) Due to small size Be^{2+} ion, BeO is covalent which other oxide are ionic. Although BeO is covalent yet it has a higher melting point and is harder than the oxides of other metals as it is polymeric. Each Be atom is tetrahedrally coordinated by four oxygen atoms.

(b) Peroxides Preparation: The peroxides of heavier metals (Ca, Sr, Ba etc.) can be obtained on heating the normal oxides with O_2 at high temperature.

$$2BaO + O_2 \longrightarrow 2BaO_2$$

Properties: The peroxides are white, ionic solids having peroxide anion, $[O\text{-}O]^{2-}$. They react with acids to produce H_2O_2.

Formation of Nitrides on Heating in Air

All the elements burn in nitrogen to form nitrides, M_3N_2 e.g.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

These react with H_2O to liberate NH_3 e.g.

Be_3N_2 is volatile while other nitrides are not so.

13.3.4 Trends in Solubility of the Hydroxides, Sulphates and Carbonates

This topic looks at the solubility in water of the hydroxides, sulphates and carbonates of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium.

I. Solubility of the Hydroxides

The hydroxides become more soluble as you go down the Group.

This is a trend which holds for the whole Group, and applies whichever set of data you choose. Some examples may help you to remember the trend:

Magnesium Hydroxide appears to be insoluble in water. However, if you shake it with water, filter it and test the pH of the solution, you find that it is slightly alkaline. This shows that there are more hydroxide ions in the solution than there were in the original water. Some magnesium hydroxide must have dissolved.

Calcium Hydroxide solution is used as "lime water". 1 litre of pure water will dissolve about 1 gram of calcium hydroxide at room temperature.

Barium Hydroxide is soluble enough to be able to produce a solution with a concentration of around 0.1 mol dm^{-3} at room temperature.

II. Solubility of the Sulphates

The sulphates become *less soluble* as you go down the Group.

III. Solubility of the Carbonates

The carbonates tend to become less soluble as you go down the Group.

Carbonates are insoluble in water and therefore occur as solid rock minerals in nature. However they dissolve in H_2O containing CO_2 due to the formation of bicarbonates.

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

13.3.5. Trends in Thermal Stability of the Carbonates and Nitrates

This topic looks at the effect of heat on the carbonates and nitrates of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium. It describes and explains how the thermal stability of the compounds changes as you go down the Group.

The effect of heat on the Group 2 Carbonates

All carbonates decompose on heating at appropriate temperature evolving CO_2

$$MCO_3 \longrightarrow CO_2 + MO$$

The stability of the carbonates of these metals increase on moving down the group. This is illustrated by the values of the decomposition temperatures of these carbonates as given below:

$BeCO_3$ = 25°C, $MgCO_3$ = 540°C, $CaCO_3$ = 900°C,
$SrCO_3$ = 1290°C, $BaCO_3$ = 1360°C

The effect of heat on the Group 2 Nitrates

All the nitrates in this Group undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.

The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen. Magnesium and calcium nitrates normally have water of crystallisation, and the solid may dissolve in its own water of crystallisation to make a colourless solution before it starts to decompose.

Again, if "X" represents any one of the elements:

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

As you go down the Group, the nitrates also have to be heated more strongly before they will decompose.

The nitrates also become more stable to heat as you go down the Group.

Summary

Both carbonates and nitrates become more thermally stable as you go down the Group. The ones lower down have to be heated more strongly than those at the top before they will decompose.

13.3.6. How Beryllium Differ from other Members of its Group?

Beryllium, the first elements of the group differs from rest of alkaline earth metals due to its small atomic size and comparatively high electronegativity. The main points of difference are:

1. **Hardness:** Beryllium is the hardest of all the elements of its group.
2. **Melting and Boiling Points:** The melting and boiling points of beryllium are the highest.
3. **Formation of Covalent Compounds:** Beryllium has a tendency to form covalent compounds. Thus when it reacts with other elements the electronegativity difference is not so large and the bond is therefore covalent.
4. **Reaction with Water:** Beryllium does not react with water even at high temperature. Other alkaline earth metals decompose water liberating H_2 gas.

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

5. **Reaction with Hydrogen:** Beryllium does not react with hydrogen directly to form its hydride. Its hydride however has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.
6. **Reaction with Alkalis:** Beryllium reacts with alkalis to form hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$

Other alkaline earth metals do not react with alkalis.

7. **Behaviour of Oxides and Hydroxides:** The oxides and hydroxides of beryllium are amphoteric, i.e. dissolve in both acids and alkalis to form salts.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

8. **Behaviour of Carbides:** Beryllium carbide is decomposed by water to form methane (CH_4).

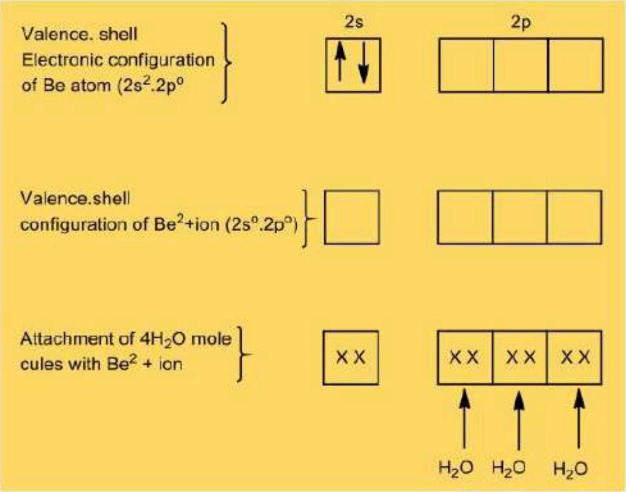
$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

The carbide of other alkaline earth metals are decomposed by water to form acetylene (C_2H_2). For example:

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

9. **Behaviour of Nitrides:** Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. **Number of Molecules of Water of Crystallisation:** The salts of Be^{2+} ion cannot have more than four molecules of water of crystallisation while other alkaline earth metals have more than four molecules of water of crystallisation. This is explained as follows. In case of Be^{2+} ion there are only four orbitals (namely one orbital can accept lone pairs of electrons denoted by O-atoms on each of the water molecules as shown below.



One the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell.

11. **Formation of Complex Compounds:** Be^{2+} ion, on account of its small size, forms stable complex compounds like $[BeF_3]^-$, $[BeF]^{2-}$ while M^{2+} ions derived from other alkaline earth metals form very few complex compounds.

Quick Quiz

1. Among the alkaline earth metals atoms which has the highest ionisation potential?
2. Explain why Ca, Cr, Ba, and Ra are places in one group of the periodic table.
3. Explain the following
   a. Alkaline earth metals form M^{2+} ions but no M^+ ions.
   b. Although the value of 2nd ionisation potential of alkaline earth metals is higher than that of 1st ionisation potential yet these metals form M^{2+} ions instead of M^+ ion.
   c. Beryllium salts have never more than four molecules of water of crystallisation.
   d. The solubility of the sulphates of alkaline earth metals decreases whereas the solubility of their hydroxides increases on moving down the group.
   e. The thermal stability of carbonates of alkaline earth metals increases in atomic numbers.
   f. Alkaline earth metals salts impart colour to the Bunsen flame.
   g. $MgSO_4$ is more soluble in water than $BaSO_4$.
   h. Alkaline earth metals form M^{2+} ions but not M^{3+} ions.
4. How do the elements of group IIA differ from alkali metals
5. Explain the following.
   a. The hydroxides of group IIA metals are weaker than those of group IA metals.
   b. The carbonates of group IIA metals are less stable to heat than those of group IA metals.
   c. KOH is stronger base than $Ba(OH)_2$.

13.4 GROUP 4- ELEMENTS

13.4.1 Physical Properties of the Elements

Melting Points and Boiling Points

As we move down the group from C to Pb, the melting points as well as boiling points generally decrease, although the decrease is not in a regular order. This decrease in melting points as well as in boiling points indicates that inter-atomic forces also decrease in the same direction. The melting and boiling points of C and Si are notably high because of the tendencies of these elements to form giant molecules.

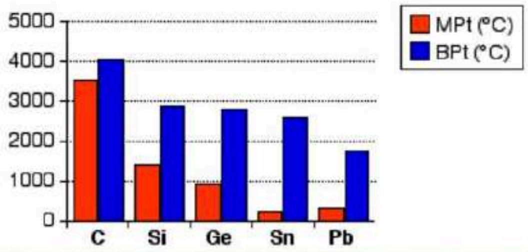


Fig. 13.32 Melting and Boiling Points of Group 4 elements

The low value for tin's melting point compared with lead is presumably due to forming a distorted 12-co-ordinated structure rather than a pure one. The tin values in the chart refer to metallic white tin.

Brittleness

Carbon as diamond is, of course, very hard - reflecting the strength of the covalent bonds. However, if you hit it with a hammer, it shatters. Silicon, germanium and grey tin (all with the same structure as diamond) are also brittle solids. However, white tin and lead have metallic structures. The atoms can roll over each other without any permanent disruption of the metallic bonds - leading to typical metallic properties like being malleable and ductile. Lead in particular is a fairly soft metal.

Electrical Conductivity

Carbon as diamond doesn't conduct electricity. In diamond the electrons are all tightly bound and not free to move. Unlike diamond (which doesn't conduct electricity), silicon, germanium and grey tin are semiconductors. White tin and lead are normal metallic conductors of electricity.

There is therefore a clear trend from the typically non-metallic conductivity behaviour of carbon as diamond, and the typically metallic behaviour of white tin and lead.

Electronegativity

Carbon is the most electronegative elements of this sub-group and the electronegativities decrease with the rise of atomic number but not a regular manner. This is probably due to the filling of the d-orbital in case of Ge and Sn and f-orbitals in case of Pb.

Ionization Energies

The ionisation energy values decrease on moving down the group form C to Pb, although the decrease dos not occur in a regular order. The irregularity in the decrease of these values is due to the filling of intervening d-orbitals in case of Ge and Sn and f-orbitals in case of Pb which are not able to screen the valence electrons effectively in elements following them.

13.4.2 The Trend from Non-Metal to Metal in the Group 4 Elements

Structures and Physical Properties

Structures of the Elements

The trend from non-metal to metal as you go down the Group is clearly seen in the structures of the elements themselves.

This topic explores the trend from non-metallic to metallic behaviour in the Group 4 elements - carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). It describes how this trend is shown in the structures and physical properties of the elements, and finally makes a not entirely successful attempt to explain the trend.

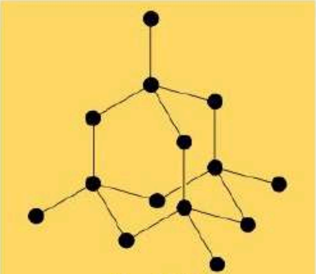


Fig. 13.33

Carbon at the top of the Group has giant covalent structures in its two most familiar allotropes - diamond and graphite.

Diamond has a three-dimensional structure of carbon atoms each joined covalently to 4 other atoms. The diagram shows a small part of that structure.

Exactly this same structure is found in silicon and germanium and in one of the allotropes of tin - "grey tin" or "alpha-tin".

The common allotrope of tin ("white tin" or "beta-tin") is metallic and has its atoms held together by metallic bonds. The structure is a distorted close-packed arrangement. In close-packing, each atom is surrounded by 12 near-neighbours.

There is therefore a clear trend from the typical covalency found in non-metals to the metallic bonding in metals, with the change-over obvious in the two entirely different structures found in tin.

13.4.3 Oxidation State

This topic explores the oxidation states (oxidation numbers) shown by the Group IV elements - carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). It looks at the increasing tendency of the elements to form compounds in which their oxidation states are +2, particularly with reference to tin and lead.

(a). Inert pair effect and positive oxidation states: Carbon and silicon show +4 oxidation states while occurrence of +2 and +4 oxidation states in case of Ge, Sn and Pb is explained as follows: when only two np electrons from the ns^2p^2 configuration are lost, we get the elements in +2 oxidation states ns^2 electron inert and hence are not lost in the formation of M^{2+} cations. This pair of ns^2 electrons is called inert pair of electrons. Since in the group the stability of +2 oxidation state also increases from Ge^{2+} to Pb^{2+} i.e. $Ge^{2+} < Sn^{2+} < Pb^{2+}$

When all the four ns^2p^2 electrons are lost we get the elements in +4 oxidation state, i.e. M^{4+} cations are formed. On descending the group stability of +4 oxidation state decrease i.e. the stability of M^{4+} cations decreases from Ge^{4+} to Pb^{4+} i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$

Compounds of Ge^{2+} are less stable than those of Ge^{4+} and hence the compounds of Ge^{2+} are readily oxidised into those of Ge^{4+}. In other words compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidising agents.

Ge^{2+} compounds	$\longrightarrow$	Ge^{4+} compounds
Less stable		More stable
Reducing agent		Oxidising agent

On similar grounds it can be shown that the compounds of Sn^{2+} are less stable than those of Sn^{4+}. In other words, compounds of Sn^{2+} act as strong reducing agents while those of Sn^{4+} act as oxidising agents.

Sn^{2+} compounds	$\longrightarrow$	Sn^{4+} compounds
Less stable		More stable
Reducing agent		Oxidising agent

When we compare the stability of the compounds of Pb^{2+} and Pb^{4+} ions, we find that Pb^{2+} compounds are more stable than those of Pb^{4+} ($PbCl_4$) and hence the compounds of Pb^{4+} are readily changed (reduced) into those of Pb^{2+}. In other words compounds of Pb^{4+} act as strong oxidising agents while those of Pb^{2+} act as reducing agents.

Pb^{2+} compounds	$\longrightarrow$	Pb^{4+} compounds
Less stable		More stable
Reducing agent		Oxidising agent

Thus when we compare the stability of M^{2+} and M^{4+} cations of Ge, Sn and Pb, we find that their stability is in the order $Ge^{2+} < Ge^{4+}$; $Sn^{2+} < Sn^{4+}$; $Pb^{2+} > Pb^{4+}$

(b). Negative Oxidation State: Since the electronegativities of these elements are low, they do not have much tendency to form the negative ion. However, carbon forms C^{4-} and C_2^{2-} ions in certain compounds, e.g. $Be_4^{2+}C_2^{4-}$ or Be_2C(Be^{2+} and C^{-4} ions), Al_4^{3+} C_3^{4-} (Al^{3+} and C^{4-}ions) Na^{+1} CH_3^{-1} (Na^+, C^{-4} and H^+ ions), Na_2^{2+} C_2^{2-} (Na^+ and C_2^{2-} ions), $Ca^{2+}C_2^{2-}$ (Ca^{2+} and C_2^{2-} ions).

The inert pair effect in the formation of Ionic Bonds

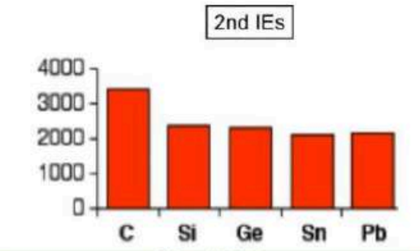


Fig. 13.34

If the elements in Group 4 form 2+ ions, they will lose the p electrons, leaving the s^2 pair unused. For example, to form a lead(II) ion, lead will lose the two 6p electrons, but the 6s electrons will be left unchanged - an "inert pair".

You would normally expect ionization energies to fall as you go down a Group as the electrons get further from the nucleus. That doesn't quite happen in Group 4.

This first chart shows how the total ionization energy needed to form the 2+ ions varies as you go down the Group. The values are all in kJ mol^{-1}.

Notice the slight increase between tin and lead.

This means that it is slightly more difficult to remove the p electrons from lead than from tin.

However, if you look at the pattern for the loss of all four electrons, the discrepancy between tin and lead is much more marked. The relatively large increase between tin and lead must be because the $6s^2$ pair is significantly more difficult to remove in lead than the corresponding $5s^2$ pair in tin. Again, the values are all in kJ mol^{-1}, and the two charts are to approximately the same scale.

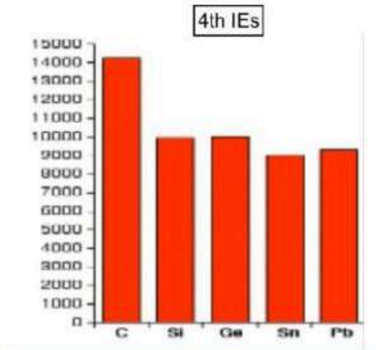


Fig. 13.35

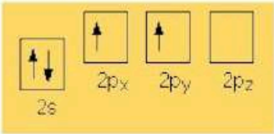
The reasons for all this lie in the Theory of Relativity. With the heavier elements like lead, there is what is known as a relativistic contraction of the orbitals, which tends to draw the electrons closer to the nucleus than you would expect. Because they are closer to the nucleus, they are more difficult to remove. The heavier the element, the greater this effect.

This affects s electrons much more than p electrons. In the case of lead, the relativistic contraction makes it energetically more difficult to remove the 6s electrons than you might expect. The energy releasing terms when ions are formed (like lattice enthalpy or hydration enthalpy) obviously are not enough to compensate for this extra energy. That means that it doesn't make energetic sense for lead to form 4+ ions.

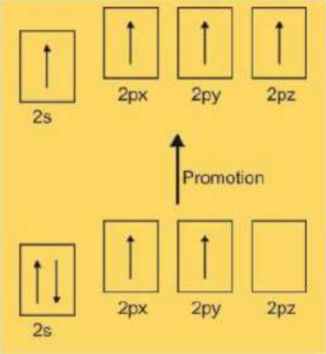
The inert pair effect in the formation of covalent bonds

(a) You need to think about why carbon normally forms four covalent bonds rather than two.

(b) Using the electrons-in-boxes notation, the outer electronic structure of carbon looks like this:



(c) There are only two unpaired electrons. Before carbon forms bonds, though, it normally promotes one of the s electrons to the empty p orbital.



(d) That leaves 4 unpaired electrons which (after hybridisation) can go on to form 4 covalent bonds.

(e) It is worth supplying the energy to promote the s electron, because the carbon can then form twice as many covalent bonds. Each covalent bond that forms releases energy, and this is more than enough to supply the energy needed for the promotion.

(f) One possible explanation for the reluctance of lead to do the same thing lies in falling bond energies as you go down the Group. Bond energies tend to fall as atoms get bigger and the bonding pair is further from the two nuclei and better screened from them.

(g) For example, the energy released when two extra Pb-X bonds (where X is H or Cl or whatever) are formed may no longer be enough to compensate for the extra energy needed to promote a 6s electron into the empty 6p orbital.

(h) This would be made worse, of course, if the energy gap between the 6s and 6p orbitals was increased by the relativistic contraction of the 6s orbital.

13.4.5 The Chlorides of Carbon, Silicon and Lead

This topic takes a brief look at the tetrachlorides of carbon, silicon and lead, and also at lead(II) chloride. It looks at their structures, stability and reactions with water.

Structures and Stability

Structures

Carbon, Silicon and Lead Tetrachlorides

These all have the formula XCl_4.

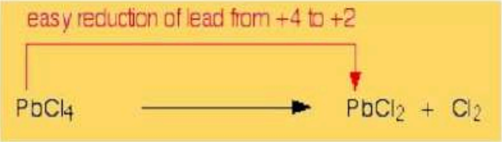
They are all simple covalent molecules with a typical tetrahedral shape. All of them are liquids at room temperature. (Although at room temperature, lead(IV) chloride will tend to decompose to give lead(II) chloride and chlorine gas - see below.)

Lead (II) Chloride, $PbCl_2$

Lead (II) chloride is a white solid, melting at 501°C. It is very slightly soluble in cold water, but more soluble in hot water. You can think of lead(II) chloride as being mainly ionic in character.

Stability

At the top of Group 4, the most stable oxidation state shown by the elements is +4. This is the oxidation state shown by carbon and silicon in CCl_4 and $SiCl_4$. These therefore have no tendency to split up to give dichlorides.



However, the relative stability of the +4 oxidation state falls as you go down the Group, and the +2 oxidation state becomes the most stable by the time you get to lead.

Lead (IV) chloride decomposes at room temperature to give the more stable lead(II) chloride and chlorine gas.

Reaction with water (hydrolysis)

Actually the hydrolysis of tetra halides takes place through the following two steps:

1st step: In this step oxygen atoms of H_2O which acts as a donor attacks the central atoms of the halide to form a coordinate bond with it and thus produces an unstable intermediate compound $MX_4.H_2O$

2nd step: In this step four HX molecules are eliminated from this unstable intermediate compound and hydroxide of the central element is formed. Thus X atoms of MX_4 molecule are replaced by OH^- ions.

Why the tetrahalides of C are not hydrolysed while those of Si, Ge and Sn get readily hydrolysed can be explained as follows:

We know that C atom being a member of 2nd period of the periodic table, has no d-orbitals in its valance shell and hence is unable to accommodate the lone pair donated by the donor oxygen atom of H_2O molecule to form an unstable intermediate compounds. Thus the tetrahalides of C are not hydrolysed. On the other hand Si, Ge and Sn have vacant d-orbitals which can accept the lone pair and thus this tetrahalides get readily hydrolysed.

The ease with which the tetrahalides are hydrolysed by H_2O decreases from Si to Sn as the metallic character of the central atom increase in this order. Thus GeX_4 and SnX_4 tetrahalides are less readily hydrolysed than SiX_4 tetrahalides.

It may be mentioned here that empty orbitals are always available with any atom and they can be utilised if sufficient energy is provided for the reaction to occur, e.g., CCl_4 undergoes hydrolysis when superheated steam is used.

$$CCl_4 + H_2O \text{ (superheated steam)} \rightarrow COCl_2 + 2HCl$$

Hydrolysis of tetrahalides of Pb follows essentially the same pattern but due to the instability of tetravalent compounds of Pb, some decomposition of $PbCl_4$ to $PbCl_2$ also takes place.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

$PbCl_4$ is hydrolysed by H_2O as follows:

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

Excepting the tetrahalides of C, those of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ions like $[SiF_6]^{2-}$, $[GeX_6]^{2-}$. For example

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

13.4.6 Oxides

This topic takes a brief look at the oxides of carbon, silicon, germanium, tin and lead. It concentrates on the structural differences between carbon dioxide and silicon dioxide, and on the trends in acid-base behaviour of the oxides as you go down Group 4.

13.4.7 The Structures of Carbon Dioxide and Silicon Dioxide

There is an enormous difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon (IV) oxide or silica). Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid. The other dioxides in Group 4 are also solids.

This obviously reflects a difference in structure between carbon dioxide and the dioxides of the rest of the Group.

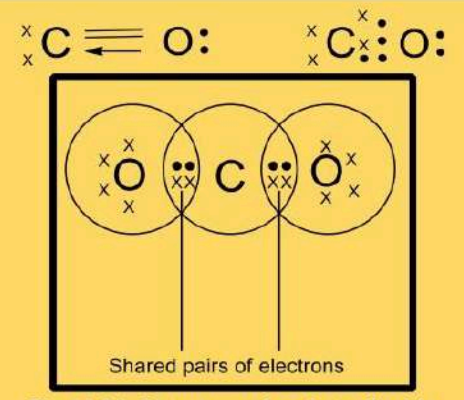


Fig 13.36: Structure of carbon dioxide

The Structure of Carbon Dioxide

The dipole moment of carbon dioxide is zero. Therefore it is a linear molecule.

The Structure of Silicon Dioxide

It is a macromolecular compound, in which silicon and oxygen atoms are linked together covalently in tetrahedral basic unit. In crystobalite, these units are joined as in diamond, while in quartz and tridymite they are arranged spirally around an axis. Because of its structure silicon dioxide is non-volatile and hard unlike carbon dioxide. Triatomic molecules of silicon dioxide and carbon dioxide, carbon and silicon are similar in having.

(i) 4 valence electrons.
(ii) 4 covalent bond formation.

But they show a lot of difference in their physical properties. It is due to the fact that:

(i) Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more oxygen atoms.

(ii) Silicon from only single born with oxygen atoms while carbon forms double bonds.

(iii) Carbon forms a linear molecule of CO_2 with two oxygen atoms while silicon atom is bound to four oxygen atoms in a tetrahedral structure which result in the formation of silicon dioxide crystal The simplest formula for silica is SiO_2. However the whole crystal of silicon can be considered as one molecule.

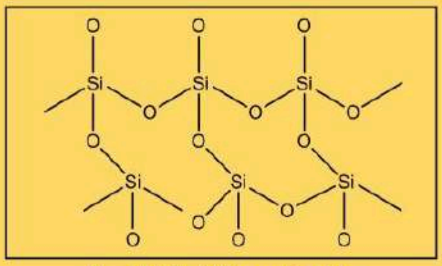


Fig 13.37: Silicon dioxide

The Acid-Base Behaviour of the Group 4 Oxides

The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

An oxide which can show both acidic and basic properties is said to be amphoteric.

The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom.

Carbon and Silicon Oxides

Carbon Monoxide

Carbon monoxide is usually treated as if it was a neutral oxide, but in fact it is very, very slightly acidic. It doesn't react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.

$$NaOH + CO \longrightarrow HCOONa$$

The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic.

Carbon and Silicon Dioxides

These are both weakly acidic.

With Water

Silicon dioxide doesn't react with water, because of the difficulty of breaking up the giant covalent structure.

Carbon dioxide does react with water to a slight extent to produce hydrogen ions (strictly, hydroxonium ions) and hydrogencarbonate ions.

Overall, this reaction is:

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

The solution of carbon dioxide in water is sometimes known as carbonic acid, but in fact only about 0.1% of the carbon dioxide has actually reacted. The position of equilibrium is well to the left-hand side.

With Bases

Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogencarbonate solution - depending on the reacting proportions.

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

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

Silicon dioxide also reacts with sodium hydroxide solution, but only if it is hot and concentrated. Sodium silicate solution is formed.

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

You may also be familiar with one of the reactions happening in the blast furnace extraction of iron (in which calcium oxide (from the limestone which is one of the raw materials) reacts with silicon dioxide to produce a liquid slag, calcium silicate). This is also an example of the acidic silicon dioxide reacting with a base.

$$CaO_{(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(l)}$$

Gernamium, Tin and Lead Oxides

The Monoxides

All of these oxides are amphoteric (they show both basic and acidic properties).

The Basic Nature of the Oxides

These oxides all react with acids to form salts.

For example, they all react with concentrated hydrochloric acid. This can be summarised as:

$$XO_{(s)} + 2HCl_{(aq)} \longrightarrow XCl_{2(aq)} + H_2O_{(l)}$$

. . . Where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

Lead (II) chloride is fairly insoluble in water and, instead of getting a solution, it would form an insoluble layer over the lead (II) oxide if you were to use *dilute* hydrochloric acid - stopping the reaction from going on.

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

However, in this example we are talking about using *concentrated* hydrochloric acid.

The large excess of chloride ions in the concentrated acid react with the lead(II) chloride to produce soluble complexes such as $PbCl_4^{2-}$. These ionic complexes are soluble in water and so the problem disappears.

$$PbCl_{2(s)} + 2Cl_{(aq)} \longrightarrow PbCl_4{}^{2-}{}_{(aq)}$$

The Acidic Nature of the Oxides

All of these oxides also react with bases like sodium hydroxide solution.

$$XO_{(3)} + 2OH^-{}_{(aq)} \longrightarrow XO_2{}^{2-}{}_{(as)} + H_2O_{(l)}$$

Lead(II) oxide, for example, would react to give PbO_2^{2-} - plumbate(II) ions.

The Dioxides

These dioxides are again amphoteric - showing both basic and acidic properties.

The Basic Nature of the Dioxides

The dioxides react with concentrated hydrochloric acid first to give compounds of the type XCl_4:

$$XO_2 + 4HCl \longrightarrow XCl_4 + 2H_2O$$

These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}.

$$XCl_4 + 2H_2O_{(l)} + 2Cl^- \longrightarrow XCl_6^{2-} + 2H_2O$$

In the case of lead(IV) oxide, the reaction has to be done with ice-cold hydrochloric acid. If the reaction is done any warmer, the lead(IV) chloride decomposes to give lead(II) chloride and chlorine gas. This is an effect of the preferred oxidation state of lead being +2 rather than +4.

The Acidic Nature of the Dioxides

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form $[X(OH)_6]^{2-}$.

$$XO_{2(s)} + 2OH^{-1}{}_{(aq)} + 2OH^-{}_{(aq)} + 2H_2O_{(l)} \longrightarrow [X(OH)6]^{2-}{}_{(aq)}$$

Some sources suggest that the lead(IV) oxide needs molten sodium hydroxide. In that case, the equation is different.

$$PbO_{2(s)} + 2NaOH_{(l)} \longrightarrow Na_2PbO_{3(s)} + H_2O_{(g)}$$

Quick Quiz

1. Why tin melting point is low as compared to lead?
2. Give trend of conductivity 4th group element
3. Which of the following metals are semiconductors Pb, C, Si, Ge?
4. Arrange follow cation in increasing order of their stability. Sn^{+4}, Sn^{+2}, Ge^{+4}, Pb^{+2}

13.5 GROUP 7-ELEMENTS: (HALOGENS)

13.5.1 Atomic and Physical Properties

This article explores the trends in some atomic and physical properties of the Group 7 elements (the halogens) - fluorine, chlorine, bromine and iodine. You will find separate sections below covering the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility. There is also a section on the bond enthalpies (strengths) of halogen-halogen bonds (for example, Cl-Cl) and of hydrogen-halogen bonds (e.g. H-Cl)

Trends in Atomic Radius

Trend

Atomic radius increases as we go down the group due to increase in number of shells greater shielding effect and less nuclear change.

Trends in Electronegativity

Halogens have large values of electronegativity. These values decrease as we proceed from F to I in the group. Large electronegativities values of halogen atoms indicate that X atoms have a strong tendency to form X-ions.

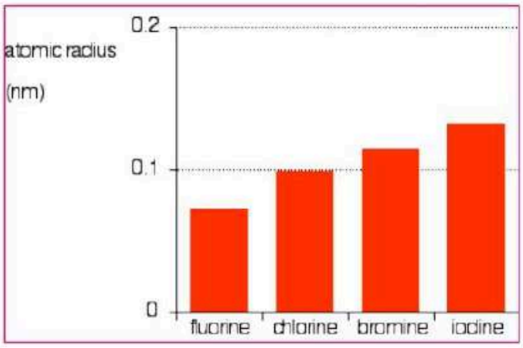


Fig. 13.38

Trends in First Electron Affinity

Electron affinity values decrease from Cl to I. why the electron affinity value of F is less than that of Cl has already been explained.

Trends in Melting and Boiling Points

The melting and boiling points of the halogens regularly increase form F to I. This indicates that the attractive forces between molecules become progressively more prominent as the of molecules increase in halogens. F and Cl are gases at ordinary temperature Br is a heavy liquid while I is a solid.

Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms.

So for chlorine, $Cl_{2(g)}$, it is the heat energy needed to carry out this change per mole of bond:

$$Cl\text{—}Cl_{(g)} \longrightarrow 2Cl_{(g)}$$

For bromine, the reaction is still from gaseous bromine molecules to separate gaseous atoms.

$$Br\text{—}Br_{(g)} \longrightarrow 2Br_{(g)}$$

Note: GAS not liquid!

Bond enthalpy in the halogens, $X_{2(g)s}$

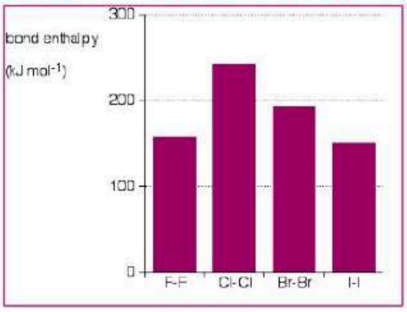


Fig. 13.35

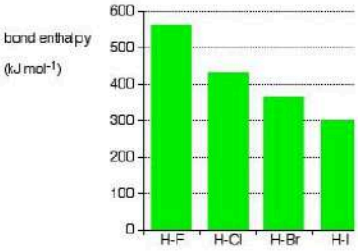


Fig. 13.28

Look at following figure (13.28)

The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds fall just as you would expect, but the F-F bond is deviated from the sequence.

This is because of:

Due to very small F-F bond length very large as compared to other X-X bond lengths. This makes the F atoms in F_2 molecule repel each other and helps the dissociation of F_2 molecule into F atoms. (ii) X-X bond in Cl_2, Br_2 and I_2 molecules is stronger than F-F bond in F_2 molecule. This is due to the possibility of the existence of multiple bonds in X-X bond involving d- orbitals.

Bond Enthalpies in the Hydrogen Halides, $Hx_{(G)}$

Where the halogen atom is attached to a hydrogen atom, this effect doesn't happen. There are no lone pairs on a hydrogen atom.

As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker, exactly what is shown by the data. There is nothing complicated happening in this case.

$$Br_2 + 2X^- \longrightarrow 2Br^- + X_2$$

13.5.2 Strength of Halogens as Oxidising Agents: $F_2>Cl_2>Br_2>I_2$

This section explores the trend in oxidising ability of the Group VII elements (the halogens) - fluorine, chlorine, bromine and iodine. We are going to look at the ability of one halogen to oxidise the ions of another one, and how that changes as you go down the Group.

Facts: A substance that has a tendency to accept one or more electrons is said to show oxidising property. The halogens due to high electron affinity values have a great tendency to accept electron and hence act as strong oxidising agent. The oxidising property of a halogen molecule, X_2 is represented by;

$$X_2 + H_2O \longrightarrow HX + HOX$$

It has been seen that the values of E are decreasing from F_2 to I_2 the oxidising power of halogens is also decreasing in the same direction i.e. the oxidising power of halogen is in the or $F_2 > Cl_2 > Br_2 > I_2$ (weakest oxidising agents). Since F_2 is the strongest oxidising agent in the series, it will oxidise other halide ions to halogens in solution or when dry, F_2, displaces other halogens from their corresponding halides. For example.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2$$

Similarly Cl_2 will displace Br^- and I^- ions from their solutions and Br_2 will displace I^- ions from their solutions.

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$$

13.5.3 The Acidity of the Hydrogen Halides

This topic looks at the acidity of the hydrogen halides - hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide.

The acidity of the Hydrogen Halides

Hydrogen Chloride as an Acid

All the halogen acids in the gaseous states are essentially covalent but in the aqueous solution they ionise to give solvated proton (H_3O^+) and hence acts as acids.

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

HF ionises only slightly while HCl, HBr, and HI ionise completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI, i.e. HF (weakest acid) <HCl<HBr<HI (strongest acid). The weakest acidic nature of HF is due to the fact that the dissociation energy of H-F bond in H-F molecule is the highest and hence this molecule has least tendency to splits up into H^+ and F^- ions in aqueous solution. Another explanation of the above order of the acidic strength of HX acids can be given by finding out the relative order of the acidity of the conjugate bases viz F^-, Cl^-, Br^- and I^- of these acids. The hydrides show no acidic character when perfectly dry.

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

(The Redox Reactions between Halide Ions and Concentrated Sulphuric Acid)

This section describes and explains the redox reactions involving halide ions and concentrated sulphuric acid. It uses these reactions to discuss the trend in reducing ability of the ions as you go from fluoride to chloride to bromide to iodide. Fluorides and Chlorides do not reduce concentrated sulphuric acid.

With Bromide Ions

The bromide ions are strong enough reducing agents to reduce the concentrated sulphuric acid. In the process the bromide ions are oxidised to bromine.

$$2Br- \longrightarrow Br_2 + 2e^-$$

The bromide ions reduce the sulphuric acid to sulphur dioxide gas. This is a decrease of oxidation state of the sulphur from +6 in the sulphuric acid to +4 in the sulphur dioxide.

$$H_2SO_4 + 2H^+ + 2e^- \longrightarrow SO_2 + 2H_2O$$

You can combine these two half-equations to give the overall ionic equation for the reaction:

$$H_2SO_4 + 2H^+ + 2Br^- \longrightarrow Br_2 + SO_2 + 2H_2O$$

With Iodide Ionsd

Iodide ions are stronger reducing agents than bromide ions are. They are oxidised to iodine by the concentrated sulphuric acid.

$$2I^- \longrightarrow I_2 + 2e^-$$

The reduction of the sulphuric acid is more complicated than before. The iodide ions are powerful enough reducing agents to reduce it

- first to sulphur dioxide (sulphur oxidation state = +4)
- then to sulphur itself (oxidation state = 0)
- and all the way to hydrogen sulphide (sulphur oxidation state = -2).

The most important of this mixture of reduction products is probably the hydrogen sulphide. The half-equation for its formation is:

$$H_2SO_4 + 8H^+ + 8e^- \longrightarrow H_2S + 4H_2O$$

Combining these last two half-equations gives:

$$H_2SO_4 + 8H^+ + 8I^- \longrightarrow 4I_2 + H_2S + 4H_2O$$

Summary of the trend in reducing ability

Fluoride and chloride ions won't reduce concentrated sulphuric acid.

Bromide ions reduce the sulphuric acid to sulphur dioxide. In the process, the bromide ions are oxidised to bromine.

Iodide ions reduce the sulphuric acid to a mixture of products including hydrogen sulphide. The iodide ions are oxidised to iodine.

Reducing ability of the halide ions increases as you go down the Group.

Explaining the trend

- When a halide ion acts as a reducing agent, it gives electrons to something else. That means that the halide ion itself has to lose electrons.
- The bigger the halide ion, the further the outer electrons are from the nucleus, and the more they are screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons as you go down the Group because there is less attraction between the outer electrons and the nucleus.

Quick Quiz

1. **Give reasons of the following**
   (a) HI is stronger acid than HF.
   (b) Although H-bonding in HF is stronger than that in H_2O, H_2O has much higher boiling point.
   (c) The acidic character of hydrides of VIIA elements increases on descending the group.
2. Illustrate the oxidising properties of halogens by giving example of two typical reactions.
3. Arrange the halogens in the decreasing order of their oxidising power.
4. Give reasons for the following;
   (a) Chlorine is a stronger oxidising agent than iodine.
   (b) Halogens are the best oxidising agents.
   (c) Fluorine is a batter oxidising than chlorine.
   (d) Electronegativity of halogens decreases in the order F > Cl > Br > I

SOCIETY, TECHNOLOGY AND SCIENCE

Food and Beverage Canning

As early as 1940, can manufacturers began to explore adapting cans to package carbonated soft drinks. The can had to be strengthened to accommodate higher internal can pressures created by carbonation (especially during warm summer months), which meant increasing the thickness of the metal used in the can ends. Otherwise, distortion of the end would strain the seal, creating potential leaks or making cans unstackable for storage and transport.

Another concern for the new beverage can was its shelf life. Even small amounts of dissolved tin or iron from the can could impair the drinking quality of both beer and soft drinks. Fortunately, beer, which is only mildly acidic, is relatively noncorrosive. In addition, beer ages naturally, so it has a limited shelf life of about three months in any package. In contrast, the food acids, including carbonic, citric and phosphoric, in soft drinks present a risk for rapid corrosion of exposed tin and iron in the can. The consequences of off-flavors, color changes and leakage through the metal needed to be addressed. At this point, the can was upgraded by improving the organic coatings used to line the inside, making cans heavier and more encasing.

- **Elements/Metals – Their Mining and Extraction**

Different elements/metals are not obtained such rather these are obtained after passing through different steps.

These steps are discussed as follows:

1. Mining and enrichment
2. Reduction
3. Refining and Casting

In fact some special methods are used to obtain each metal from its ores and to develop it into useful articles, yet few steps are common in the metallurgy of every metal. These are follows.

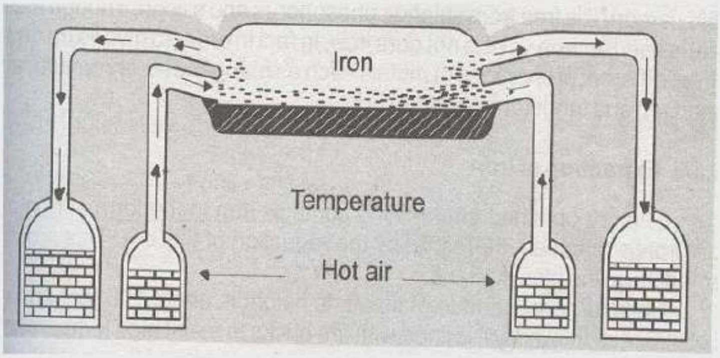
1. **Mining**
   - i. **Crushing**
     Obtaining ores by digging the rocks and hills is called mining. This work is done by engineers and laborers with the help of machines. But prior to this work it is confirmed by survey and analysis that obtaining metals from this is economical or not.
   - ii. **Grinding**
     Breaking of rocks and larger stones into smaller size stones is called crushing. This is done by jaw crushers.
   - iii. **Hand Picking, Jugging and Shaking**
     In Pakistan and other under developed countries where labour is cheap, metallic stones are picked and separated by hands. Heavy metals are separated from useless material i.e. gangue, by shaking with "chaage". In some countries this process is done by pressurized water.
   - iv. **Magnetic Separation**
     The ground ore is passed over a magnetic belt which separates the magnetic metal from gangue. This process is used for metals, which have magnetic properties like iron.
2. **Reduction**
   For the complete separation of a metal from gangue, ores are heated at high temperature. At its melting pint, molten metal is separated from solid gangue. It must be remembered that different metals are mixed with different compounds according to the type of impurities present in the metal ore and then they are passed through the process of reduction. The process of reduction is carried out in the blast furnace.

Blast Furnace

It is lined inside with fire bricks. Its height and capacity are kept according to the requirement. Hot gases enter from lower side and ores are charged from the tope of the furnace. Temperature is maintained at 1500°-3000°C. This furnace is usually used for iron and copper metallurgy.

3. **Refining of Metals**
   Metals extracted in the above process are further refined by the following process.

Open-Hearth Process:



A fire furnace is used to remove the impurities of metal. It is lined inside with fire bricks and is just like a room. Burning gases are entered from one side and exhaust gases are removed from the opposite end. The process is operated form opposite ends after an interval. Metals melt in a shorter time by this two way heating.

Applications of Bleaching Powder

Bleaching powder is actually a mixture of calcium hypochlorite ($Ca(OCl)_2$) and the basic chloride $CaCl_2$, H_2O with some slaked lime, $Ca(OH)_2$.

Bleaching powders take time to dissolve in water and longer to work but have a longer shelf life in comparison to liquid bleaches and can be used on items like upholstery, carpet and some delicate fabrics. However, bleaching powder should never be combined with ammonia or used on colored fabrics as it will cause fading.

- Bleaching powder is highly effective for cleaning inside the home and outdoors. It can be used for removing mildew from fabric, cleaning countertops and for removing mold from grout between tiles, bathmats and shower curtains. Outside, the agent can be used on plastic furniture, unpainted cement, paving and painted surfaces to eliminate mildew and other stubborn stains.
- Bleaching powder can be used to safely disinfect and sterilize many things around the home including secondhand goods, trash cans, pet accessories and baby toys and furniture. Bleaching powder is a highly effective means of returning the luster to white porcelain and glassware. Glassware can regain its sparkle by adding a small amount of powdered bleach to dishwater when washing glasses.
- To kill any annoying weeds growing from cracks and crevices in the garden a strong mixture of bleaching powder and water is applied. Moss and algae on garden walkways can be easily eliminated by scrubbing with bleaching powder diluted in water. Powdered bleach is also useful for sanitizing garden tools to avoid diseases spreading between plants. Adding powdered bleach to the water of cut flowers will help to preserve their freshness by preventing the growth of bacteria in the vase.

Bleaching powder is used for the disinfection of drinking water or swimming pool water. It is used as a sanitizer in outdoor swimming pools in combination with a **cyanuric acid** stabilizer, which reduces the loss of chlorine due to **ultraviolet** radiation. The calcium content hardens the water and tends to clog up some filters; hence, some products containing calcium hypochlorite also contain **anti-scaling agents.**

Bleaching powder is used for bleaching cotton and linen. It is also used in bathroom cleaners, household disinfectant sprays, moss and algae removers, and weedkillers.

In addition, bleaching powder may be used to manufacture **chloroform.**

Bleaching powder is used also in sugar industry for bleaching sugar cane juice before its crystallization.

Commercial Uses of Halogens

1. Chlorine is used as a cheap industrial oxidant in the manufacture of bromine
2. Iodine is dissolved in alcohol, commonly known as tincture of iodine is used as a mild antiseptic for cuts and scratches. Iodine is also mixed with the detergents used in cleaning diary equipment.
3. Small quantities of fluorine are used in rocket propulsion. Much larger quantities are used make uranium (VI) fluoride for the separation of ^{238}U and ^{235}U:

$$UF_4\,(s) + F_2\,(g) \longrightarrow UF_6\,(s)$$

4. Fluorine is also used to make a wide range of fluorocarbon compounds for use as refrigerants, aerosol propellants, anaesthetics and fire-extinguisher fluid. One of the most important fluorocarbons is poly (tetrafluoroethene), PTFE, frequently sold under the trade name Fluon or Teflon.

Iodine Deficiency and Goiter

Iodine Deficiency

Iodine is an element that is needed for the production of thyroid hormone. The human body cannot synthesize iodine, so it is an essential element.

1. The deficiency of iodine leads to enlargement of thyroid a condition called goiter.

Hypothyroidism and mental retardation in children and infants is observed if their mothers suffer from iodine deficiency during pregnancy.

Before 1920, iodine deficiency was common in Appalachian, north-western US regions, and in most of Canada. Approximately, 40% of the world's population remains at the risk of iodine deficiency.

Goiter:

The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet. It results in swelling in neck. It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism). A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

Fluoride Deficiency and Toxicity

Fluoride Toxicity

Fluoride toxicity or fluoride poisoning is a condition in which more fluoride is taken than the amount required for normal growth, development and metabolism. Fluoride toxicity is characterised by a variety of signs and symptoms. Poisoning most commonly occurs following ingestion of conspicuous amount of fluoride containing products. Symptoms appear within minutes of exposure. Fluoride is found in many common household products e.g. toothpaste, dietary supplements, insecticides, rodenticides etc. fluoride toxicity results,

1. Arthritis
2. Stiff painful joints with or wistful swelling
3. Asthma, especially after showering
4. Painful bony lumps where tendons and ligaments attach to bones

Fluoride Deficiency

Fluoride deficiency results when the amount of its up take is less than required.
Fluoride deficiency results in Brittle bones or demineralization of bones

Cavities

Weakened tooth enamel

Fluoride deficiency can lead to a higher likelihood of developing bone fractures and possibly even steoporosis. Halogens and their compounds are used for bleaching, refrigeration and as aerosols, etc.

Quick Quiz

1. How different metals are extracted
2. What problems are caused by fluorides deficiency
3. What is goiter.
4. What problem is caused by examining
5. How fluoride is useful for uranium separation

Key Points

- 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.
- Alkaline earth metals have two electrons in s-orbital of their valence shell.
- They lose two electrons forming dipositive ions M^{2+}.
- Lithium behaves different from the other alkali metals.
- Beryllium is the only member of group 2 which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

- Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
- The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
- The electronic configuration of group 4 elements show that they have four electron in their valence shells, tow electron of which are in s-orbital and the remaining two are in p-orbitals.
- The halogens are very reactive. Intermolecular forces in halogens increase down the group, fluorine is a gas but iodine is solid.
- Halogens form ionic compounds with s-block metals, covalent compound with p-block elements and complex ions with d-block metals. Fluorides are usually ionic.
- Halogens show oxidation states -1, +1, +3, +5, +7 but fluorine shows the oxidation state of -1 only.
- Oxidizing power of halogens decreases down the group in the following order: $F_2 > Cl_2 > Br_2 > I_2$.
- Reducing power of halide ions decrease form I^- to Br^-. Chloride and fluoride ions are not reductants.

Exercise

1. Select the right answer from the choices given with each question.

i. Oxides and hydroxides of Group I elements are:

(a) acidic (b) alkaline (c) neutral (d) amphoteric

ii. The flame colour of sodium metal or its compounds is

(a) bright crimson (b) violet (c) golden yellow (d) bright blue

iii. When sodium burn in air, it forms sodium:

(a) monoxide (b) peroxide (c) oxide (d) superoxide

iv. The carbonates of alkali metals are not affected by heat except:

(a) Li_2CO_3 (b) Na_2CO_3 (c) K_2CO_3 (d) Rb_2CO_3

v. Green is characteristic flame color of

(a) calcium (b) barium (c) strontium (d) sodium

vi. All the carbonates, sulphates and phosphates of alkaline earth metals are .... In water.

(a) sparingly soluble (b) soluble (c) insoluble (d) less soluble

vii. The first ionization energy is higher for the

(a) alkaline earth metals (b) alkali metals

(c) halogens (d) noble gases

viii. Which one of the element has the maximum electron affinity?

(a) F (b) Cl (c) Br (d) I

ix. Which pair has both members from same period of periodic table?

(a) Na-Ca (b) Na-Cl (c) Ca-Cl (d) Cl-Br

x. Melting points and boiling points of alkali metals

(a) decreases from top to bottom (b) increase from top to bottom

(c) first increases then decreases (d) remains unchanged

xi. Which one of the following oxides is amphoteric in nature

(a) rubidium oxide (b) barium oxide

(c) antimony oxide (d) sulphur oxide

xii. Oxidising power of halogen depends upon

(a) energy of dissociation (b) electron affinity

(c) heat of vaporization (c) all of above

xiii. Which of following oxide is Amphoteric in nature?

(a) MgO (b) BeO (c) CO_2 (d) SnO_2

xiv. Select the correct increasing order of atomic radius?

(a) Ne>O>S>Al (b) Ne<O>S>Al (c) Ne<O<S<Al (d) Ne>O<S>Al

xv. Due to inert pair effect .... Oxidation state is more stable than .... for Sn and Pb.

(a) 2+, 4+ (b) 1+ , 4+ (c) 4+, 2+ (d) 2+, 3+

xvi. Highest electron affinity is shown by?

(a) F_2 (b) I_2 (c) Br_2 (d) Cl_2

xvii. Which is the strongest reducing agent?

(a) HF (b) HCl (c) HI (d) HBr

xviii. Substance boiling at higher temperature among following is?

(a) HI (b) HF (c) HCl (d) HBr

xix. Group VII-A elements are generally called:

(a) Halogens (b) Noble gases (c) Inert gases (d) Metalloids

xx. The radioactive element in halogen group is:

(a) Radon (b) Radium (c) Astatine (d) Bromine

2. Give brief answers for the following questions.

i. Although Na and P are present in the same period yet their oxides are different in nature Na_2O is basic while P_2O_5 is acidic why?

ii. How acidic basic and amphoteric behaviour of oxides is explained?

iii. Why the elements of group 1 are called alkali metals?

iv. Why all group 1 metals have low ionization energies?

v. Why do the group 1 metals show strong electropositive character?

vi. Why do group 1 metals show strong reducing properties?

vii. Why different colours are imparted by the atoms of the group 1 metals to the flame?

viii. Why the elements of group 2 are called alkaline earth metals?

ix. Why do the group 2 earth metals have high melting and boiling points than alkali metals?

x. How do group 1 metals resemble with group 2 metals.

xi. How do group 1 metals differ form group 2 metals?

xii. Discuss the metallic and non-metallic character of group 4 elements.

xiii. Discuss the general group trends of group 7 elements.

xiv. Why the term halogen is used for group 7 elements?

xv. Why does fluorine differ from other members of its group?

xvi. What is the structure of CO_2 and SiO_2 and why they differ?

xvii. CO_2 is a gas while SiO_2 is a solid although C and Si belong to the same group?

xviii. Explain why nitrates and carbonates of Li are not stable?

xix. Differentiate the behaviour of Li and Na with atmospheric oxygen.

xx. Alkali metal carbonates are more soluble that alkaline earth metal carbonates. Why?

xxi. Explain why solubility of alkaline earth metal carbonates decrease down the group?

xxii. Oxidising power of F_2 is greater than I_2. Why?

xxiii. HF is weak acid than HI. Why?

xxiv. On what factors does the oxidising power of halogens depend?

3. Give detailed answers for the following questions.

i. (a) The pattern of first ionization energy and melting and boiling point is not smooth. Justify it.

(b) Why atomic radius increases in group and decreases along the period.

(c) Describe the trends in reaction of period 3 elements with water.

(d) The melting and boiling pints of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?

ii. Discuss the metallic oxides and silicon dioxide under the following headings:

(i) Structures (ii) Melting and Boiling points

(iii) Electrical conductivity.

iii. Discuss acid-base behaviour of (i) Aluminium oxide (ii) Sodium oxide

iv. (a) Why are different types of oxides formed as you go down the group?

(b) How Beryllium differs from other members of its group?

(c) Why is Beryllium chloride covalent and not ionic?

v. (a) Why do some metals form peroxides on heating in oxygen?

(b) Why do group 2 elements form nitrides on heating in air?

(c) Discuss the trend in solubility of hydroxide of group 2 elements.

vi. Discuss the trends in thermal stability of the carbonates and nitrates.

vii. Explain with examples that Beryllium hydroxide in Amphoteric?

viii. Explain the trends in oxidation states with suitable examples.

ix. Discuss the inert pair effect in the:

(i) formation of ionic bonds (ii) formation of covalent bonds

x. Discuss in detail acid-base trend in group 4 oxides.

xi. Explain in detail the trends in group 7 of following physical properties.

(i) Electronegativity (ii) Electron affinity

xii. (a) Why is the bond enthalpy of F-F less as compared to Cl-Cl and Br-Br?

(b) Explain the order F>Cl>Br>I with respect to oxidizing agent/power.

xiii. (a) Why is fluorine much stronger oxidising agent than chlorine?

(b) HCl is strong acid as compared to HF. Why?

14

d AND f - BLOCK ELEMENTS TRANSITION ELEMENTS

After completing this lesson, you will be able to:

This is 8 days lesson (period including homework)

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

Reading

14.1 INTRODUCTION

- **Definition of Transition Elements:**

"The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements." They are called d-block or f-block elements.

- **Why are they called Transition Elements?**

They are called transition elements because they show such properties which are transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which form covalent compounds.

- **Series of Transition Elements:**

The d=block elements consist of following three series of ten elements each:

1. From Scandium (Sc =21) to Zinc (Zn =30) – 3d-series
2. From Yttrium (Y =39) to Cadmium (Cd = 48) – 4d-series
3. From Lanthanum (La = 57) to Mercury (Hg = 80) – 5d-series
   [Omitting Lanthanides (rare-earths)]

The f-block elements constitute two series which are:

1. From Cerium (Ce = 58) to Lutetium (Lu = 71) – 4f-series
2. From Actinium (Ac = 89) to Lawrentium (Lr = 103) which are called actinides. – 5f-series

General outermost configurations:

1. First series (d-block elements) = $(n-1)d^{1-10}ns^2$
2. Second series (f-block elements) = $(n-1)d^1(n-2)f^{1-14}ns^2$

- **Why is Zn-group included in Transition Elements?**

Zn, Cd and Hg are not regarded as transition elements because they have completely filled d-orbitals. It is appropriate to include these in transition elements because they form complexes with ammonia, halide ions and amines and their chemical behaviors is similar to transition elements.

- **"Coinage Metals are Transition Elements." Justify the Statement.**

Coinage metals are transition elements since Cu^{2+} has $3d^9$ configuration, Ag^{2+} has a $4d^9$ and Au^{3+} has $5d^8$ configuration, although all these metals have d^{10} configuration in atomic states.

- **Position of d-Block Elements in the Periodic Table:**

Following diagram show the position of d-block elements in the periodic table.

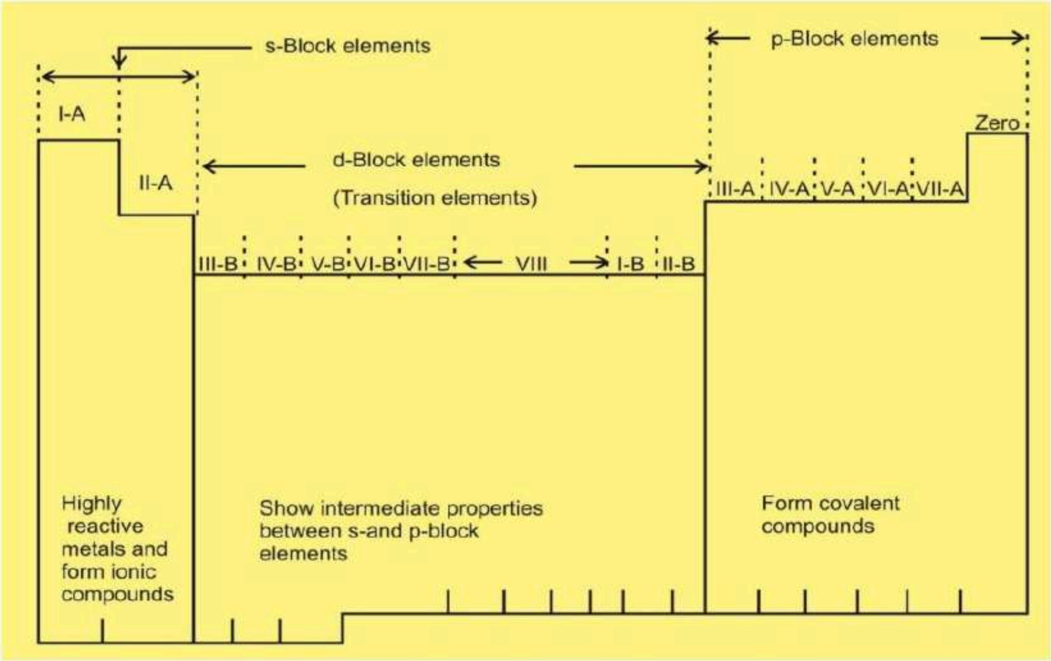


Fig. 14.1: Position of d-block elements in the periodic table

- **Typical and non-Typical Transition Elements:**

The elements of the group II-B and III-B have the electronic distribution as follows:

II-B	III-B
Zn_{30} = …..$4s^23d^{10}$	Sc_{21} = …..$4s^23d^1$
Cd_{48} = …..$5s^24d^{10}$	Y_{39} = …...$5s^24d^1$
Hg_{80} = …..$6s^25d^{10}$	La_{57} = ….$6s^25d^1$

It is clear that the elements of II-B i.e. Zn, Cd and Hg do not have partially filled d-subshell in the elemental state or ionic state.

They do not show the typical properties of the transition elements to an appreciable extent.

The elements of the group III-B are Sc_{21}, Y_{31} and La_{57}. They do not show many of their properties typical of transition elements. In the compound state, they show tri-positive ion i.e. Sc^{+3}, Y^{+3} and La^{+3}. In this way they do not have any electron in d-orbital.

For the reason, that the elements of group II-B and III-B are non-typical transition elements.

Non-Typical Transition Elements	Typical Transition Elements
II-B and III-B	IV-B, V-B, VI-B, VII-B, VIII-B and I-B

14.2 GENERAL FEATURES

14.2.1 General Features of Transition Elements

1. They are all metallic in nature.
2. Some of the transition elements play an important role in the industry. These metals are Ti, Cr, Fe, Ni, Cu, Mo, W, Zr, Nb, Ta and Th etc.
3. They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
4. They form alloys with one another and other elements of periodic table as well.
5. With a few exceptions, they show variable oxidation states.
6. Their ions and compounds are colored in the solid state and the solution state.

Quick Quiz

1. Give the electronic configuration of the elements of first transition series.
2. Write the general state electronic configuration (s, p, d, f) of the elements of the first transition series (z=21 to 30) indicating the number of unpaired electrons in each case.
3. Give the names, symbols and electronic configuration of the elements of second transition series.
4. Discuss the trends and variation in oxidation states (valency) of transition metals.
5. Explain the magnetic properties of transition metals.
6. What do you understand by diamagnetism and paramagnetism.

14.2.2 Electronic Structure

Electronic distribution of d-block elements:

Table14.1

$Sc_{21} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^0_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Ti_{22} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$V_{23} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Cr_{24} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Mn_{25} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Fe_{26} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Co_{27} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Ni_{28} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Cu_{29} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

$Zn_{30} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

Table14.2 – Detailed electronic configuration of the valence shell of first series of transition elements:

		$3d_{xy}$	$3d_{yz}$	$3d_z$	$3d_{x^2-y^2}$	$3d_{z^2}$	4s
Sc_{21} =	(Ar)	↑					↑↓
Ti_{22} =	(Ar)	↑	↑				↑↓
V_{23} =	(Ar)	↑	↑	↑			↑↓
Cr_{24} =	(Ar)	↑	↑	↑	↑	↑	↑
Mn_{25} =	(Ar)	↑	↑	↑	↑	↑	↑↓
Fe_{26} =	(Ar)	↑↓	↑	↑	↑	↑	↑↓
Co_{27} =	(Ar)	↑↓	↑↓	↑	↑	↑	↑↓
Ni_{28} =	(Ar)	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu_{29} =	(Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn_{30} =	(Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Electronic Distribution of 4d and 5d-Series:

The following table shows the electronic distribution of 4d and 5d-block elements. The elements of the group number VI-B, i.e. Cr group shows the same deviation except W_{74}.

Similarly, the elements of the group I-B that is Cu-family also show the deviated distribution. Following table shows the electronic distribution of 3d, 4d, 5d series

Table 14.3: Electronic Configurations of three Series of d-Block Elements

3d-block elements		4d-block elements		5d-block elements	
Elements	**Electronic Configuration**	**Elements**	**Electronic Configuration**	**Elements**	**Electronic Configuration**
Sc (21)	$[Ar]3d^14s^2$	Y (39)	$[Kr]4d^15s^2$	La (57)	$[Xe]5d^16s^2$
Ti (22)	$[Ar]3d^24s^2$	Zr (40)	$[Kr]4d^25s^2$	Hf (72)	$[Xe]4f^{14}5d^26s^2$
V (23)	$[Ar]3d^34s^2$	Nb (41)	$[Kr]4d^45s^1$	Ta (73)	$[Xe]4f^{14}5d^36s^2$
Cr (24)	$[Ar]3d^54s^1$	Mo (42)	$[Kr]4d^55s^1$	W (74)	$[Xe]4f^{14}5d^46s^2$
Mn (25)	$[Ar]3d^54s^2$	Te (43)	$[Kr]4d^65s^2$	Re (75)	$[Xe]4f^{14}5d^56s^2$
Fe (26)	$[Ar]3d^64s^2$	Ru (44)	$[Kr]4d^75s^1$	Os (76)	$[Xe]4f^{14}5d^66s^2$
Co (27)	$[Ar]3d^74s^2$	Rh (45)	$[Kr]4d^85s^1$	Ir (77)	$[Xe]4f^{14}5d^76s^2$
Ni (28)	$[Ar]3d^84s^2$	Pd (46)	$[Kr]4d^{10}$	Pt (78)	$[Xe]4f^{14}5d^96s^1$
Cu (29)	$[Ar]3d^{10}4s^1$	Ag (47)	$[Kr]4d^{10}5s^1$	Au (79)	$[Xe]4f^{14}5d^{10}6s^1$
Zn (30)	$[Ar]3d^{10}4s^2$	Cd (48)	$[Kr]4d^{10}5s^2$	Hg (80)	$[Xe]4f^{14}5d^{10}6s^2$

14.2.3 Binding Energy

In order to understand the mechanical properties of transition elements, we should understand the binding energies. Transition elements are tough, malleable and ductile. The toughness of the metals is due to greater binding energies.

Reason:

The s-electron of outermost shell takes part in chemical bonding. Anyhow, along with that the electrons of underlying half filled d-orbitals also participate in bonding.

Variation in Binding Energies:

When we move from left to the right in any d-block series, the number of electrons increase up to group V-B; that is vanadium family and VI-B i.e. Cr family. After that the pairing of electron starts. The unpaired electrons become zero at group II-B. It means that binding forces go on increasing up to Cr and then decrease after that. This is shown for the elements of 3d and 5d series in the following graph.

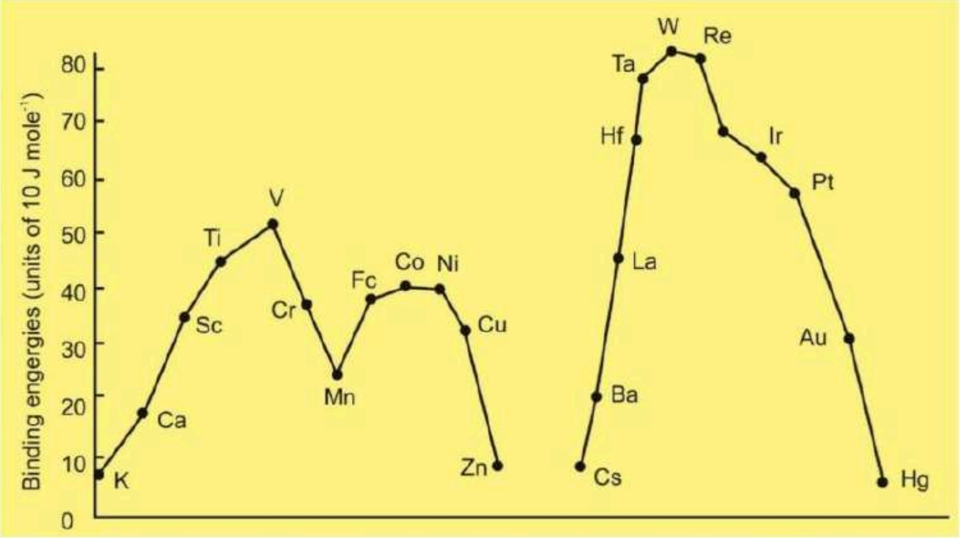


Fig. 14.2: Atomic number of elements Graphical picture of binding energy of 3 d and 5 d series of transition elements (qualitative view)

14.2.4 Variable Oxidation States

Transition elements are electropositive, so they have positive oxidation states. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.

They show variable oxidation states. The reason is that they have d-electrons in addition to s-electron for the purpose of bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons. In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.

Among the 3d series, Mn has maximum oxidation states, and goes up to +7. The following table shows oxidation numbers +2 and +3 are more common. Positive oxidation states increase up to the middle of series and after that they decrease.

			3d					4s	Oxidation states						
Sc	[Ar]	$3d^1 4s^2$	↑					↑↓		2	3				
Ti	[Ar]	$3d^2 4s^2$	↑	↑				↑↓		2	3	4			
V	[Ar]	$3d^3 4s^2$	↑	↑	↑			↑↓		2	3	4	5		
Cr	[Ar]	$3d^5 4s^1$	↑	↑	↑	↑	↑	↑		2	3	4	5	6	
Mn	[Ar]	$3d^5 4s^2$	↑	↑	↑	↑	↑	↑↓	1	2	3	4	5	6	7
Fe	[Ar]	$3d^6 4s^2$	↑↓	↑	↑	↑	↑	↑↓	1	2	3	4	5	6	
Co	[Ar]	$3d^7 4s^2$	↑↓	↑↓	↑	↑	↑	↑↓		2	3	4	5		
Ni	[Ar]	$3d^8 4s^2$	↑↓	↑↓	↑↓	↑	↑	↑↓		2	3	4			
Cu	[Ar]	$3d^{10} 4s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑	1	2	3				
Zn	[Ar]	$3d^{10} 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		2					

Table 14.3

14.2.5 Catalytic Activity

Most of the transition elements are used as catalysts. The compounds of transition metals are also catalysts.

The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.

They also form interstitial compounds which can absorb an activator to the reacting species. Some of the important examples of catalysts are as follows:

1. A mixture of ZnO and Cr_2O_3 is used for the manufacture of methyl alcohol.
2. Ni, Pt and Pd are catalysts for the hydrogenation of vegetable oil and saturation of alkenes and alkynes to alkanes.
3. MnO_2 can be used as a catalyst for the decomposition of H_2O_2.
4. $TiCl_4$ is used as catalyst for the manufacture of plastics.
5. V_2O_5 is used to oxidize SO_2 to SO_3 in the manufacture of H_2SO_4.
6. Fe is used as a catalyst for synthesis of NH_3 in Haber's process about 1% of Na_2O or K_2O and about 1% SiO_2 or Al_2O_3 are added as promotors. Mo is also sometimes used as a promotor.

14.2.6 Magnetic Behaviour

Many transition elements and their compounds are paramagnetic. The compounds attracted into the magnetic field are called paramagnetic. Paramegnetism is due to the unpaired electrons present in the metals and their compounds. The substances which can be magnetized are called ferromagnetic. For example, Fe, Co and Ni are ferromagnetic. Some substances in which even number of electrons are present, and have paired spins are diamagnetic. They are slightly repelled by magnetic field. The magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation:

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

It is measured in Bohr magneton, BM. By measuring magnetic moment, the nature of transition metal compound and oxidation state of transition metal can be calculated.

14.2.7 Alloy Formation

Alloy is mixture of two or more than two metals. Transition metals form alloys with each other.

Reason:

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the other. They form substitutional alloys among themselves.

Example:

1. Alloy steels are the materials in which the iron atoms are substituted by Cr, Mn and Ni. Steel has more useful properties than iron.
2. Brass, bronze and coinage alloys are the best alloys.

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	It is a strong alloy of copper which is soft and flexible. It does not corrode. Due to low melting point, it is easy to use. It is used to make locks, keys, water taps, pipes, artificial jewellery, door handles and parts of machines
Bronze	Cu 90 - 95 % Sn 5 - 10 %	It is strong, brilliant and long lasting. It does not corrode. It is used to prepare medals, coins, badges and bullets etc. besides these; decorative articles are also made from this alloy.
Nichrome	Ni = 60 % Cr = 15 % Fe = 25 %	It is used in electric heaters and filaments of furnaces.

Properties:

As alloys are prepared according to the requirements, their characteristics are different, yet few properties are common which are as follows:

1. Alloys are comparatively cheap.
2. They are strong and flexible but hard alloys can also be prepared.
3. They have long life because they do not corrode.
4. They are durable.
5. They have high melting points.
6. They are better conductor but non-conductor alloys are also prepared.

Quick Quiz

1. How magnetic moment is measured
2. Give unit of magnetic moment
3. Give difference between nichrome and bronze
4. Name the catalyst use for (i) decomposion of H_2O_2 (ii) manufacturing of CH_3OH
5. On which factor binding energy depends
6. Why transition element shows variable oxidation state.
7. Which property of transition elements enable them to serve as catalyst
8. Why alloys are prepared?

14.3 COORDINATION COMPOUNDS

Definition:

Those compounds which contain complex molecules or complex ions capable of independent existence are called coordination compounds or complex compounds.

Such compounds are formed by the coordination of an electron pair donor to metal atom or an ion.

Explanation:

In order to understand the complex compounds, let us mix two substances that is KCN and $Fe(CN)_2$. When this mixture is evaporated, a new compound is obtained. This compound when dissolved in water ionizes into K^+ and $[Fe(CN)_6]^{-4}$. On this basis the new compounds has been given the formula $K_4[Fe(CN)_6]$ (potassium ferrocyanide).

$$4KCN + Fe(CN)_2 \longrightarrow K_4Fe(CN)_6$$

$$K_4Fe(CN)_6 \longrightarrow 4K^+ + [Fe(CN)6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is called complex ion.

Parts of Complex Compound after Dissociation in a Solvent:

A complex compound is mostly made up of two parts:

1. Positively charged ion or cation.
2. Negatively charged ion or anion.

For example in $K_4Fe(CN)_6$, K+ is a cation and $[Fe(CN)_6]^{-4}$ is the anion.

Complex ion as cation:

In some of the complexes the positively charged ion is complex ion

$$\left[Cu(NH_3)_4\right]SO_4 \longrightarrow \left[Cu(NH_3)_4\right]^{+2} + SO_4^{-2}$$

Complex cation

Complex Ion as anion:

In some of the complexes the negatively charged ion is the complex ion

$$K_4Fe(CN)_6 \longrightarrow 4K+ + [Fe(CN)_6]^{-4}$$

14.3.1 Components of Complex Compounds

Complex compound is consisted of three components:

1. A positively or negatively charged ion which is not complex.
2. A central metal atom or ion which is consisted of transition element.
3. Electron pair donor which is negatively charged, positively charged or neutral.

Let us discuss them one by one.

a) Central Metal Atom or Ion

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

1. In $K_4[Fe(CN)_6]$, Fe^{+2} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
2. In $K_3[Fe(CN)_6]$, Fe^{+3} is the central metal ion. Six ligands (CN^- ions) are surrounding it.

3. In $[Cu(NH_3)_4]SO_4$, Cu^{+2} is the central metal ion. Four ligands (NH_3 ions) are surrounding it.
4. In $[Ag(NH_3)_2]Cl$, Ag^+ is the central metal ion. Two ligands (NH_3) are surrounding it.

b) Ligand

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples:

1) In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.
2) In $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]$ Cl, NH_3 is the ligand.

Types of Ligands:

Depending upon number of donatable electron pairs, ligands are of many types:

1) Monodentate Ligands:

Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral.

Examples:

1) Negatively charged ligands F^-, Cl^-, Br^-, I^-, OH^-, CN^-
2) Neutral ligands H_2O, NH_3, CO

2) Bidentate Ligands:

Those ligands which have two donatable electron pairs are called bidentate ligands.

CO_3^{-2}, SO_4^{-2}, $(COO)_2^{-2}$, $NH_2\text{-}NH_2$, $NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

Examples:

Carbonate ion, Sulphate ion, Oxalate ion, Hydrazine, Ethylene diamine

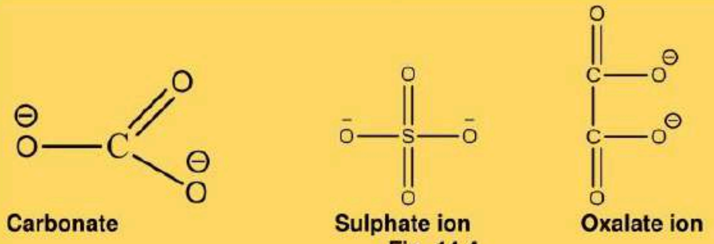

Carbonate
Sulphate ion
Oxalate ion

Fig. 14.4

3) Tridentate Ligands:

Those ligands which have three donatable electron pairs

Examples

Diethylene triammine

$H_2NCH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2$

Fig. 14.5

4) Hexadentate Ligands:

Those ligands which have six donatable electron pairs.

Example:

Ethylenediamenetetracetate (EDTA)

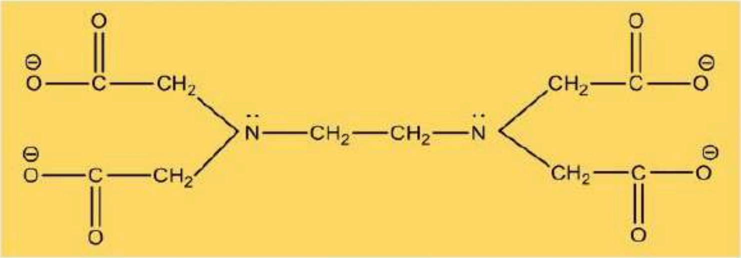


Fig. 14.6

C) Coordination Number or Ligancy:

It is the total number of the atoms of the ligands that can coordinate to the central metal atom or ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal atom or ion and the donor atoms of the ligands.

Example:

1) In $K_4[Fe(CN)_6]$, the coordination number of Fe^{+2} is six.
2) In $[Cu(NH_3)_4]SO_4$, the coordination number of Cu^{+2} is four
3) In $[Ag(NH_3)_2]$, the coordination number of Ag^+ is two
4) In $[Ni(CO)_4]$, the coordination number of Ni^0 is four

D) Coordination Sphere

The central neutral metal atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples:

1) In $K_4[Fe(CN)_6]$, the $[Fe(CN)_6]^{-4}$ is the coordination sphere of this complex compound
2) In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{+2}$ is the coordination sphere of this complex compound
3) In $K_3[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-3}$ is the coordination sphere of this complex compound
4) In $[Ag(NH_3)_2]Cl$, the ion $[Ag(NH_3)_2]^{+1}$ is the coordination sphere of this complex compound
5) In $[Ni(CO)_4]$, the $[Ni(CO)_4]$ is the coordination sphere of this complex compound

E) Charge on the Coordination Sphere

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands.

Example:

In $K_4[Fe(CN)_6]$ the charge on the coordination sphere can be calculated as follows.

Since charge on each ligand is	= -1
Charge on $6CN^-$	= -6
Charge on iron	= +2
So the charge on the coordination sphere	= -6+2
	= -4

14.3.2 Nomenclature of Complex Compounds

Complex compounds are named according to following rules give by IUPAC

1) Order of Ions:

Cations are named first and then the anions. For example in $K_4[Fe(CN)_6]$, we will call K^+ first and then $[Fe(CN)_6]^{-4}$

In naming $[Cu(NH_3)_4]\ SO_4$, we will call $[Cu(NH_3)_4]^{+2}$ first and then SO_4^{-2}.

2) Naming of Ligands:

a) The ligands which are negatively charged end in O. For example

F^- = Fluoro
Cl^- = Chloro
Br^- = Bromo
I-$^-$ = Iodo
CN^- = Cyno
$CH_3\text{-}COO^-$ = Acetato
$C_2O_4^{-2}$ = Oxalato

b) Neutral ligands are called as such. For example

H_2O	Aquo or Aqua
NH_3	Ammine
CO	carbonyl

c) Positively charged ligands end in “ium”. For example

$NH_2NH_3^+$	Hydrazinium
NO^+	Nitrosylium
NH_4^+	Ammonium

3) Order of Ligands

All ligands are arranged alphabetically without any preference order. The numerical prefixes (di, tri, etc) are not considered.

4) More than one same type of Ligands

In order to indicate more than one ligands, use prefixes as di for two, tri for three, tetra for four, penta for five and hexa for six.

5) Termination of name of Metal

If the complex ion is negatively charged then the name of the metal ends in “ate”. For example

In $K_4[Fe(CN)_6]$, the name is potassium hexacyanoferrate (II).

6) Oxidation Number of Metal Ion

The oxidation number of the metal ion is represented by roman numeral in parenthesis following the name of the metal.

7) More than one Polydentate Ligands

If polydentate ligands are there, then in order to indicate their number, use bis for two, tris for three and tetrakis for four.

Examples:

Keeping in view all the above rules the following names are proposed for the complex compounds according to IUPAC system:

(a) In the following Complexes, the Complex Ion has Negative Charge. So, the name of the Metal ends in "ate".

(1) $K_4[Fe(CN)_6]$ Potassium hexacyanoferrate (II)

(2) $K_3[Fe(CN)_6]$ Potassium hexacyanoferrate (III)

(3) $Na[Mn(CO)_5]$ Sodium Pentacarbonylmanganate (-I)

(4) $K_2[PtCl_6]$ Potassium hexachloroplatinate (IV)

(5) $Na_2[Ni(CN)_4]$ Sodium tetracyanonickelate

(b) In the following Complexes the Complex Ion has Positive Charge. So the name of the Metal is called as such:

(6) $[Co(NH_3)_6]Cl_3$ Hexaamminecobalt (III) chloride

(7) $[Co(F)_6]Cl_3$ Hexafluorocobalt (III) chloride

(8) $[Cr(H_2O)_6]Cl_3$ Hexaaquochromium (III) chloride

(9) $[Co(en)_2Cl_2]Cl$ Dichlorobisethylendiamminecobalt (III) chloride

(10) $Ni(CO)_4$ Tetracarbonylnickel (O)

(11) $[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro platinum (IV) sulphate

(12) $[Co(NO_2)_3(NH_3)_3]$ Triamminetrinitrocobalt (III)

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

The coordination number shown by metals in complexes are 2 to 9. The most common are 2, 3 and 6. Geometries corresponding to C.N's =2, 3, 4 and 5 are shown in Fig. 14.3

1) Coordination Number 2

The complexes having C.N=2 are linear, since this geometry provides minimum ligand-ligand repulsion. Cu^+, Ag^+ and in some cases Hg^{+2} form such complexes, e.g. $Cu(CN)_2$, $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Au(CN)_2]^-$, $[Hg(NH_3)_2]^{2+}$, $Hg(CN)_2$.

2) Coordination Number 4

Complexes with CN=4 may be tetrahedral or square planar in geometry. Complexes like

$[ZnCl_4]^{2-}$, $[Cu(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$, $[Ni(CO)_4]^0$, $[FeCl_4]^-$,

$[ZnBr_4]^{2-}$, $[CuX_4]^{2-}$, ($X = Cl^-$, Br^-, CNS^-)

$[Zn(CN)_4]^{2-}$,

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

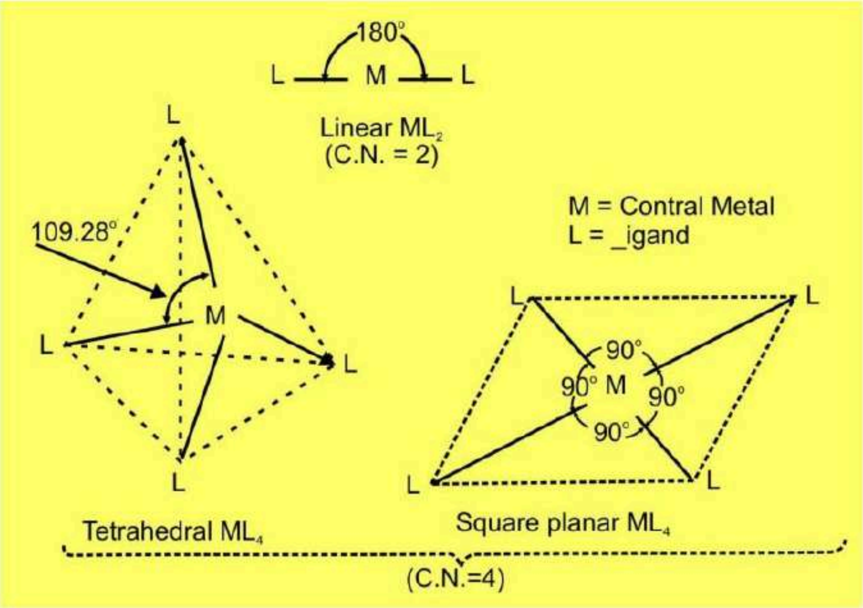


Fig. 14.7

are tetrahedral. Oxyanions such as VO_4^{3-}, CrO_4^{2-}, FeO_4^{2-} and MnO_4^- are also tetrahedral.

Square planar geometry is found in complexes of Cu^{2+} Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+} etc ions e.g. $[Ni(NH_3)_4]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Ni(dmg)_2]^0$, $[Pt(NH_3)_4]^{2+}$, $[PdCl_4]^{2-}$, $[AuCl_4]^-$, $[Cu(en)_2]^{2+}$,$[Cu(NH_3)]^{2+}$ etc.

3) Coordination Number 6

Complexes with C.N = 6 are the most common ones formed by transition metal ions.

Six ligands in a 6-coordination compound may be arranged round the central metal ion, M, either at the corners of hexagonal plane or at the apices of a trigonal prism or at the apices of a regular octahedron. These arrangements together with numbers designating substitution positions may be depicted as shown in fig. 14.4. An extensive study of the geometrical and optical isomers of complexes with C.N = 6 has however, shown that arrangement of six ligands in a 6- coordination compound is always octahedral and that the arguments concerning other possible geometries (i.e. hexagonal planar and trigonal prismatic geometries) are of historical interest only.

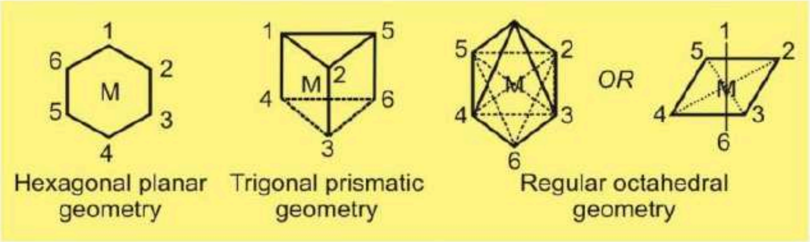


Fig.14.8

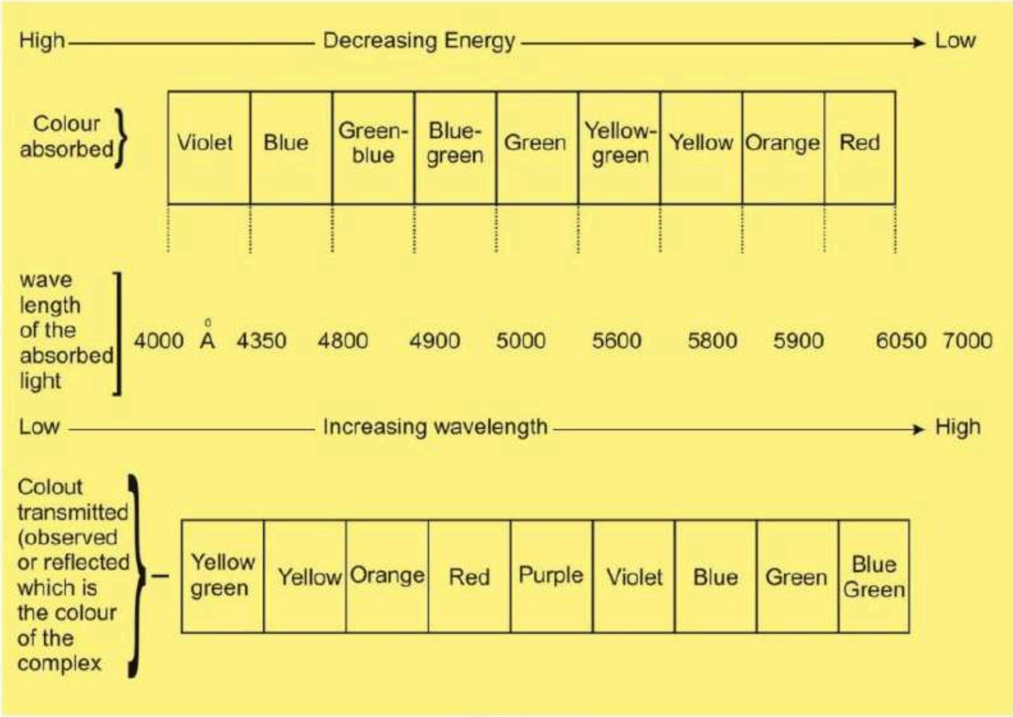
14.3.4 Color of Complexes

When white light is allowed to fall on a complex. The following things may occur:

(i) The complex may absorb the whole of white light. In this case complex appears black.

(ii) The complex may reflect or transmit the whole light. In this case it appears white.

(iii) The complex may absorb some of it and may reflect or transmit the remaining light. In this case the complex has some color. i.e. it is colored. The absorption of light by the colored complexes takes place in the visible region of the spectrum which extends from 4000Å to 7000Å in wavelengths. The color of the absorbed light is different from that of the transmitted light. The relation between the colors of the absorbed and reflected light is shown in Fig. 14.5 the color of the transmitted light is called the complementary color of that of the absorbed light and is in fact the color of the complex.



High — Decreasing Energy → Low

Colour absorbed	Violet	Blue	Green-blue	Blue-green	Green	Yellow-green	Yellow	Orange	Red

wave length of the absorbed light: 4000 Å 4350 4800 4900 5000 5600 5800 5900 6050 7000

Low — Increasing wavelength → High

Colout transmitted (observed or reflected which is the colour of the complex	Yellow green	Yellow	Orange	Red	Purple	Violet	Blue	Green	Blue Green

Fig.14.9

Thus:

(i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is blue color of the transmitted light because it absorb yellow light.

(ii) Cuprammonium sulphate containing $[Cu(NH_3)_4]^{2+}$ ions is violet because it absorbs yellow green light.

(iii) $[Ti(H_2O)_6]^{3+}$ absorbs green light in the visible region and hence it is purple which is the color of the transmitted light.

The complex ions which absorb light in the infrared or ultraviolet regions of the spectrum are colorless, e.g. (i) anhydrous cupric sulphate is colorless since it absorbs light in the infrared region. (ii) $[Cu(CN)_4]^{4-}$ ion absorbs light in the ultraviolet region and hence is colorless.

With the help of visible absorption spectrum of a complex ion it is possible to predict the color of the complex. For example, $[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000Å which corresponds to the wave number $v = 20000\ cm^{-1}$ as shown below:

Since $1Å = 10^{-8} cm$. wavelength, $\lambda = 5000Å = 5000 \times 10^{-8} cm$

Consequently wave number,

$$v = 1/\lambda = 1/5000 \times 10^{-8}$$

$$= 1/5 \times 10^{-5}\ cm^{-1} = 0.2 \times 10^{5} cm^{-1} = 20000 cm^{-1}$$

Light of this wavelength (5000Å) is green (Fig 14.5) and is absorbed by the complex ion. Thus the transmitted light is purple, which is in fact, the color of the ions.

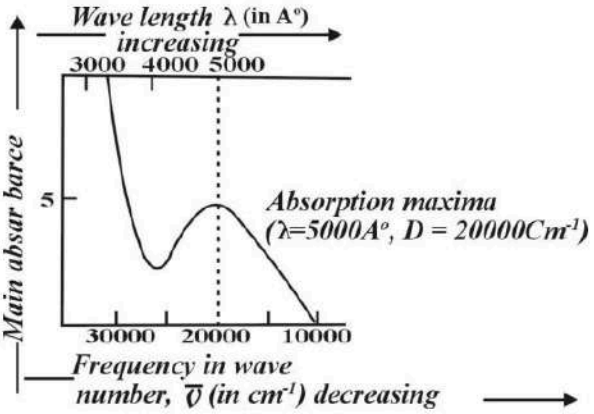


Fig.14.10

Quick Quiz

1. Why do most of the transition metal ions posses a definite color?
2. What is wavelength of green color
3. When complex compound appear black
4. What will be geometry of complex compound having co-ordination number 2, 4 and 6.
5. Give examples of hexadentate and tridentate ligand.

14.4 CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

14.4.1 Vanadium

In this topic we will discuss:

i) The conversion between various Vanadium Oxidation states and

ii) The use of Vanadium (V) oxide as a catalyst in the contact process.

Vanadium's Oxidation States

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).

Observing the changes in the Lab

Reducing Vanadium (V) in stages to Vanadium (II)

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate, NH_4VO_3. This isn't very soluble in water and is usually first dissolved in sodium hydroxide solution. The solution can be reduced using zinc and an acid - either hydrochloric acid or sulphuric acid, usually using moderately concentrated acid.

The exact vanadium ion present in the solution is very complicated, and varies with the pH of the solution. The reaction is done under acidic conditions when the main ion present is **VO_2^+** - called the dioxovanadium (V) ion.

The reduction from +5 to +4

Note: The ion is usually written as VO_2^+, but is more accurately $[VO_2(H_2O)_4]^+$.

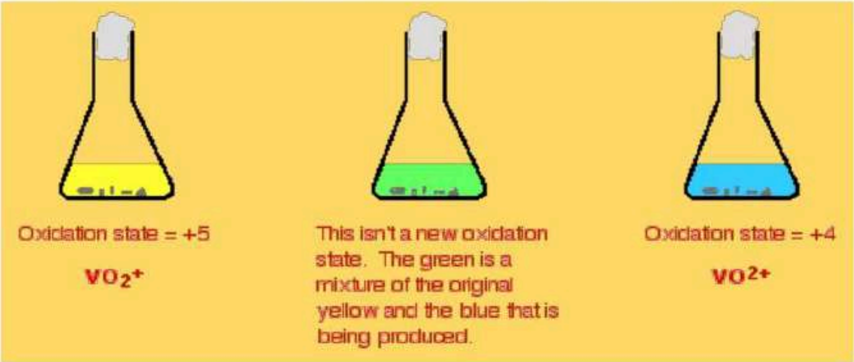


Fig.14.11

It is important to notice that the green colour you see isn't actually another oxidation state. it is just a mixture of the original yellow of the +5 state and the blue of the +4.

Do you know? Just like the VO^{2+} ion, the VO^{2+} ion will have water molecules attached to it as well - $[VO(H_2O)_5]^{2+}$. We usually use the simpler form.

The reduction from +4 to +2

The colour changes just continue.

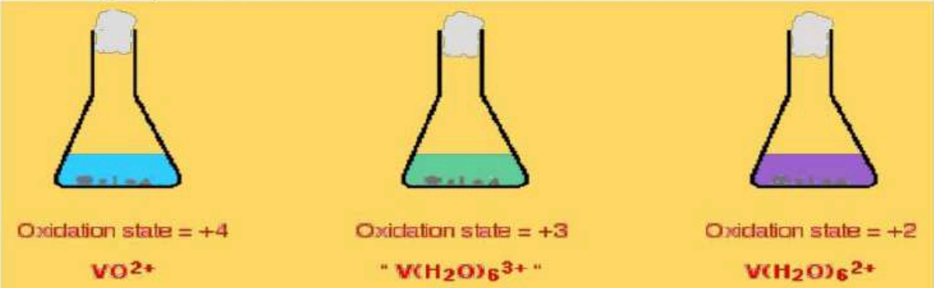


Fig.14.12

The reason for the inverted commas around the vanadium (III) ion is that this is almost certainly a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. The simplification is probably reasonable at this level.

Re-Oxidation of the Vanadium (II)

The vanadium (II) ion is very easily oxidized. If you remove the cotton wool from the flask and pour some solution into a test tube, it turns green because of its contact with oxygen in the air. It is oxidized back to vanadium (III).

If it is allowed to stand for a long time, the solution eventually turns blue as the air oxidizes it back to the vanadium (IV) state - VO^{2+} ions.

Adding nitric acid (a reasonably powerful oxidizing agent) to the original vanadium (II) solution also produces blue VO^{2+} ions. The vanadium (II) is again oxidized back to vanadium (IV).

Re-Oxidation of the Vanadium (II)

The vanadium (II) oxidation state is easily oxidized back to vanadium(III) - or even higher.

Oxidation by hydrogen ions

You will remember that the original reduction we talked about was carried out using zinc and an acid in a flask stoppered with a piece of cotton wool to keep the air out. Air will rapidly oxidize the vanadium (II) ions - but so also will the hydrogen ions present in the solution!

The vanadium (II) solution is only stable as long as you keep the air out, and in the presence of the zinc. The zinc is necessary to keep the vanadium reduced.

What happens if the zinc isn't there? Look at these E° values:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$

The reaction with the more negative E° value goes to the left; the reaction with the more positive (or less negative) one to the right.

That means that the vanadium (II) ions will be oxidized to vanadium (III) ions, and the hydrogen ions reduced to hydrogen.

Will the oxidation go any further - for example, to the vanadium (IV) state?

Have a look at the E° values and decide:

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$

In order for the vanadium equilibrium to move to the left, it would have to have the more negative E° value. It *hasn't* got the more negative E° value and so the reaction doesn't happen.

Oxidation by Nitric Acid

In a similar sort of way, you can work out how far nitric acid will oxidize the vanadium (II). Here's the first step:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

The vanadium reaction has the more negative E° value and so will move to the left; the nitric acid reaction moves to the right.

Nitric acid will oxidize vanadium (II) to vanadium (III).

The second stage involves these E° values:

The nitric acid again has the more positive E° value and so moves to the right. The more negative (less positive) vanadium reaction moves to the left.

Nitric acid will certainly oxidize vanadium (III) to vanadium (IV).

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

Will it go all the way to vanadium (V)?

$$VO_2^+{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +1.00\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

No, it won't! For the vanadium reaction to move to the left to form the dioxovanadium (V) ion, it would have to have the more negative (less positive) E° value. It hasn't got a less positive value, and so the reaction doesn't happen.

You can work out the effect of any other oxidizing agent on the lower oxidation states of vanadium in exactly the same way. But do not assume that because the E° values show that a reaction is *possible*, it will *necessarily* happen.

Vanadium (V) Oxide as a Catalyst in the Contact Process

The Overall Reaction

During the Contact Process for manufacturing sulphuric acid, Sulphur dioxide has to be converted into Sulphur trioxide. This is done by passing Sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst.

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

How the Reaction works

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number).

The Sulphur dioxide is oxidized to Sulphur trioxide by the vanadium (V) oxide. In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide.

$$SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$$

The vanadium (IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + \frac{1}{2}O_2 \longrightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

Quick Quiz

1. Give source of vanadium in +5 oxidation state
2. How solution of NH_4VO_3 is prepared?
3. How re-oxidation of lower oxidation state of vanadium is prevented?
4. How V_2O_5 use as catalyst for oxidation of $SO_{2(g)} \rightarrow SO_{3(g)}$

14.4. 2 Chromium

In this topic we will discuss;

i) The interconversion of the various oxidation states of chromium.

ii) The chromate (VI)-dichromate (VI) equilibrium;

iii) The use of dichromate (VI) ions as an oxidizing agent (including titrations).

The Oxidation of Chromium(Iii) to Chromium(Vi)

An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium(III) ions to produce a solution of green hexahydroxochromate(III) ions.

This is then oxidised by warming it with hydrogen peroxide solution. You eventually get a bright yellow solution containing chromate (VI) ions.

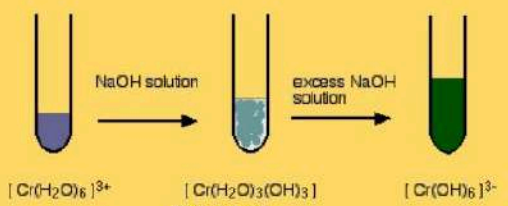


Fig.14.13

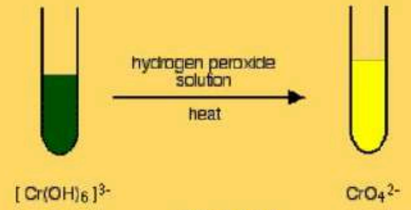


Fig.14.14

The equation for the oxidation stage is:

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \longrightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$$

Some Chromium(VI) Chemistry

The Chromate(VI)-Dichromate(VI) Equilibrium

You are probably more familiar with the orange dichromate(VI) ion, $Cr_2O_7^{2-}$, than the yellow chromate(VI) ion, CrO_4^{2-}.

Changing between them is easy:

If you add dilute sulphuric acid to the yellow solution it turns orange. If you add sodium hydroxide solution to the orange solution it turns yellow.

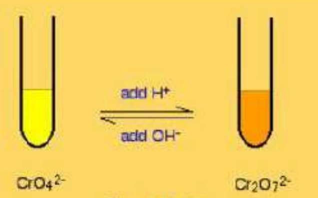


Fig.14.15

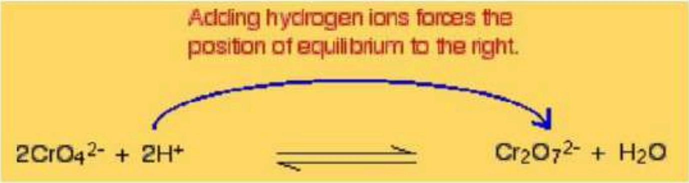
The most important: If you had just produced the yellow chromate (VI) ions by oxidising chromium (III) ions using hydrogen peroxide, you can't convert them into dichromate (VI) ions without taking a precaution first.

In the presence of acid, dichromate (VI) ions react with any hydrogen peroxide which is left in the solution from the original reaction. To prevent this, you heat the solution for some time to decompose the hydrogen peroxide into water and oxygen before adding the acid.

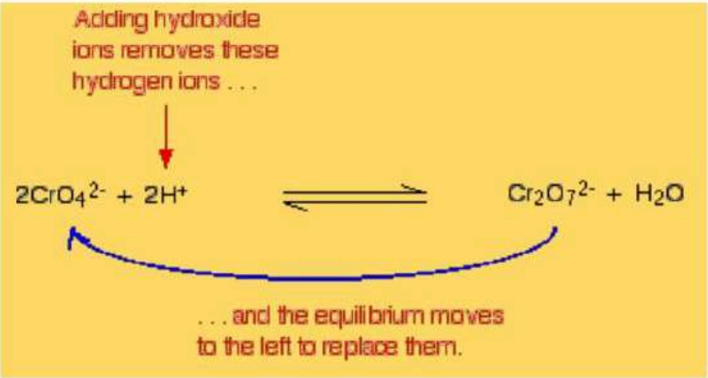
The equilibrium reaction at the heart of the interconversion is:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

If you add extra hydrogen ions to this, the equilibrium shifts to the right. This is consistent with Le Chatelier's Principle.



If you add hydroxide ions, these react with the hydrogen ions. The equilibrium tips to the left to replace them.



The Reduction of Di-chromate (VI) Ions with Zinc and an Acid

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

Hydrogen is produced from a side reaction between the zinc and acid. This must be allowed to escape, but you need to keep air out of the reaction. Oxygen in the air rapidly re-oxidises chromium (II) to chromium(III).

An easy way of doing this is to put a bit of cotton wool in the top of the flask (or test-tube) that you are using. This allows the hydrogen to escape, but stops most of the air getting in against the flow of the hydrogen.

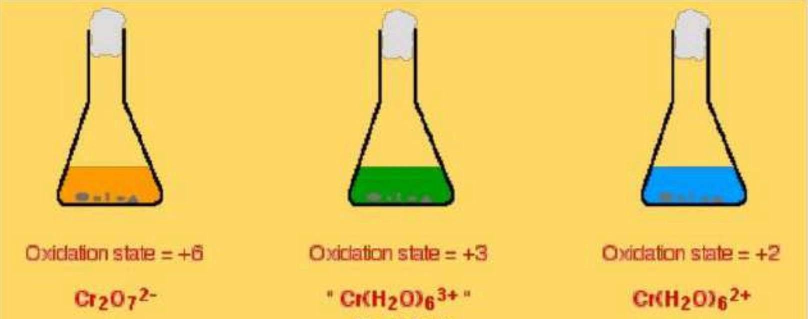


Fig.14.16

The reason for the inverted commas around the chromium (III) ion is that this is a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. This has already been discussed towards the top of the page. The equations for the two stages of the reaction are:

For the reduction from +6 to +3:

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

For the reduction from +3 to +2:

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

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

Potassium dichromate (VI) solution acidified with dilute sulphuric acid is commonly used as an oxidising agent in organic chemistry. It is a reasonably strong oxidising agent without being so powerful that it takes the whole of the organic molecule to pieces! (Potassium manganate(VII) solution has some tendency to do that.)

It is used to:

- oxidise secondary alcohols to ketones;
- oxidise primary alcohols to aldehydes;
- oxidise primary alcohols to carboxylic acids.

For example, with ethanol (a primary alcohol), you can get either ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions.

- If the alcohol is in excess, and you distil off the aldehyde as soon as it is formed, you get ethanal as the main product.

$$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2OH \longrightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

- If the oxidising agent is in excess, and you do not allow the product to escape - for example, by heating the mixture under reflux (heating the flask with a condenser placed vertically in the neck) - you get ethanoic acid.

$$2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \longrightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$$

In organic chemistry, these equations are often simplified to concentrate on what is happening to the organic molecules. For example, the last two could be written:

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$
$$CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$$

The oxygen written in square brackets just means "oxygen from an oxidising agent".

Using Potassium Dichromate(VI) as an Oxidising Agent in Titrations

Potassium dichromate(VI) is often used to estimate the concentration of iron(II) ions in solution. It serves as an alternative to using potassium manganate(VII) solution.

In practice

There are advantages and disadvantages in using potassium dichromate(VI).

Advantages

- Potassium dichromate(VI) can be used as a primary standard. That means that it can be made up to give a stable solution of accurately known concentration. That isn't true of potassium manganate(VII).
- Potassium dichromate(VI) can be used in the presence of chloride ions (as long as the chloride ions aren't present in very high concentration).

  Potassium manganate(VII) oxidises chloride ions to chlorine; potassium dichromate(VI) isn't quite a strong enough oxidising agent to do this. That means that you do not get unwanted side reactions with the potassium dichromate(VI) solution.

Disadvantage

- The main disadvantage lies in the colour change. Potassium manganate(VII) titrations are self-indicating. As you run the potassium manganate(VII) solution into the reaction, the solution becomes colourless. As soon as you add as much as one drop too much, the solution becomes pink - and you know you have reached the end point.

  Unfortunately potassium dichromate(VI) solution turns green as you run it into the reaction, and there is no way you could possibly detect the colour change when you have one drop of excess orange solution in a strongly coloured green solution.

  With potassium dichromate(VI) solution you have to use a separate indicator, known as a *redox indicator*. These change colour in the presence of an oxidising agent.

  There are several such indicators - such as diphenylamine sulphonate. This gives a violet-blue colour in the presence of excess potassium dichromate(VI) solution. However, the colour is made difficult by the strong green also present. The end point of a potassium dichromate(VI) titration isn't as easy to see as the end point of a potassium manganate(VII) one.

The Calculation

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

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

. . . and for the iron(II) ions is:

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

Combining these gives:

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

You can see that the reacting proportions are 1 mole of dichromate(VI) ions to 6 moles of iron(II) ions.

Once you have established that, the titration calculation is going to be just like any other one.

Testing for Chromate(VI) Ions in Solution

Typically, you would be looking at solutions containing sodium, potassium or ammonium chromate(VI). Most chromates are at best only slightly soluble; many we would count as insoluble.

The bright yellow colour of a solution suggests that it would be worth testing for chromate(VI) ions.

Testing by adding an Acid

If you add some dilute sulphuric acid to a solution containing chromate(VI) ions, the colour changes to the familiar orange of dichromate(VI) ions.

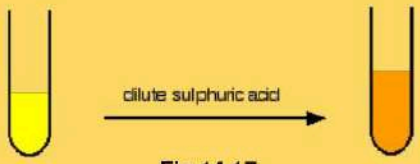


Fig.14.17

You can't rely on this as a test for chromate(VI) ions, however. It might be that you have a solution containing an acid-base indicator which happens to have the same colour change!

Testing by adding Barium Chloride (or Nitrate) Solution

Chromate(VI) ions will give a yellow precipitate of barium chromate(VI).

$$Ba^{2+}{}_{(aq)} + CrO_4{}^{2-}{}_{(aq)} \longrightarrow BaCrO_{4(s)}$$

Fig.14.18

Testing by adding Lead(II) Nitrate Solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI). This is the original "chrome yellow" paint pigment.

$$Pb^{2+}{}_{(aq)} + CrO_4{}^{2-}{}_{(aq)} \longrightarrow PbCrO_{4(s)}$$

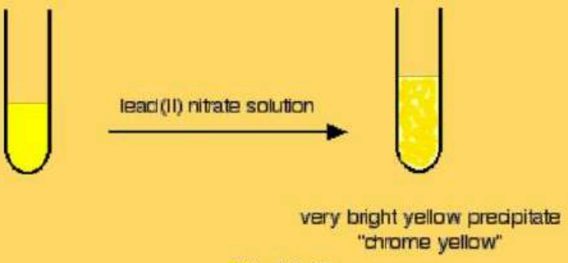


Fig.14.19

Quick Quiz

1. How dichromate ion is converted into chromate and vice versa
2. What happens when chromate ion reacts with barium chloride
3. Why potassium dichloride is preferred over potassium magnetic in titration.
4. In which titration end point is clear potassium dichromate or potassium magnate
5. What color changes obscure when (i) Acid (ii) Lead nitrate solution are added separately in potassium chromate solution

14.4.3 Manganese

In this topic we will discuss:

(II) The Oxidation States
(III) Two simple reactions of manganese (II) ions in solution).
(IV) The use of potassium manganate(VII) (potassium permanganate) as an oxidizing agent - including its use in titrations.

The Oxidation States

Manganese can exist in a number of oxidation states, but is most stable in an oxidation state of +2, +4 or +7

In the +7 oxidation state it exists as the intense purple ion MnO_4^{-1}. This can be reduced to the pale pink Mn^{2+} by Fe^{2+} in acidic solution:

$$MnO^{-1}_{4(aq)} + 8H^{+}_{(aq)} + 5Fe^{2+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{\ell}$$

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^{-}$$

Overall:

$$MnO^{-1}(aq) + 8H^{+}(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

Reactions of Manganese (II) Ions in Solution/ Oxidation States

I - The Reaction of Hexaaquamanganese(II) Ions with Hydroxide Ions

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

Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

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

In the test-tube, the colour changes are:

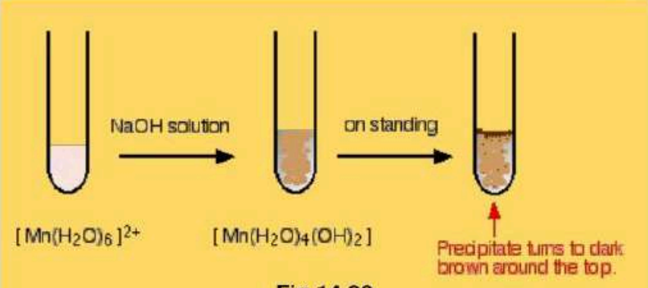


Fig.14.20

It has been shown the original solution is very pale pink, but infact it is virtually colourless. The pale brown precipitate is oxidised to darker brown manganese(IV) oxide in contact with oxygen from the air.

II - The Reaction of Hexaaquamanganese(ii) Ions with Ammonia Solution

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

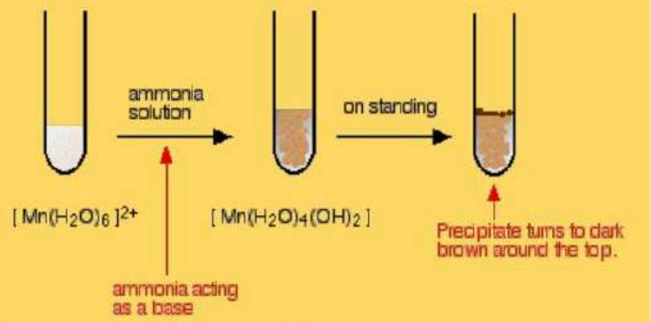


Fig.14.21

Ammonia can act as both a base and a ligand. In this case, at usual lab concentrations, it simply acts as a base - removing hydrogen ions from the aqua complex.

Again, it has been shown the original solution as the palest pink I can produce, but in fact it is virtually colourless. The pale brown precipitate is oxidised to darker brown manganese(IV) oxide in contact with oxygen from the air.

There is no observable difference in appearance between this reaction and the last one.

Some Potassium Manganate(VII) Chemistry

Potassium manganate(VII) (potassium permanganate) is a powerful oxidising agent.

Using Potassium Manganate(VII) as an Oxidising Agent in Organic Chemistry

Potassium manganate(VII) is usually used in neutral or alkaline solution in organic chemistry. Acidified potassium manganate(VII) tends to be a rather destructively strong oxidising agent, breaking carbon-carbon bonds.

The potassium manganate(VII) solution is usually made mildly alkaline with sodium carbonate solution, and the typical colour changes are:

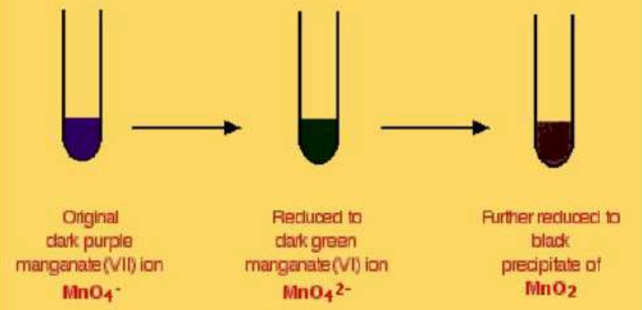
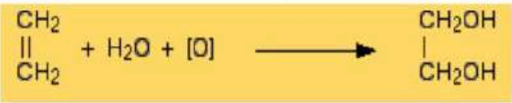


Fig.14.22

In Testing for a C=C Double Bond

Potassium manganate(VII) oxidises carbon-carbon double bonds, and so goes through the colour changes above.

Ethene, for example, is oxidised to ethane-1,2-diol.



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + H_2O + [O] \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

The oxygen in square brackets is taken to mean "oxygen from an oxidising agent". This abbreviated form of the equation is most commonly used in organic chemistry. You are very unlikely to have to write the complete ionic equation for this reaction at this level.

To be honest, this isn't a good test for a carbon-carbon double bond, because anything which is even mildly reducing would have the same effect on the potassium manganate(VII) solution.

You could, however, use this reaction simply as a means of making the diol.

In the Oxidation of Aromatic side Chains

Alkaline potassium manganate(VII) solution oxidises any hydrocarbon side chain attached to a benzene ring back to a single -COOH group. Prolonged heating is necessary.

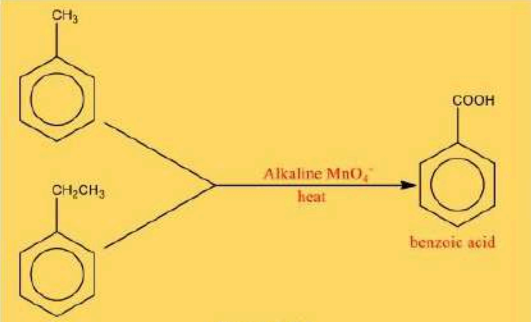


Fig.14.21

For example:

In the case of the ethyl side chain, you will also get carbon dioxide. With longer side chains, you will get all sorts of mixtures of other products - but in each case, the main product will be benzoic acid.

Using Potassium Manganate(VII) as an Oxidising Agent in Titrations

Background

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

For example, it oxidises

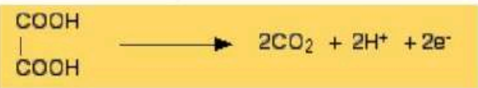
- iron(II) ions to iron(III) ions

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

- hydrogen peroxide solution to oxygen

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

- ethanedioic acid to carbon dioxide (This reaction has to be done hot.)



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \longrightarrow 2CO_2 + 2H^+ + 2e^-$$

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

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

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

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

These equations can be combined to give you an overall ionic equation for each possible reaction. That, of course, also gives you the reacting proportions.

For example, when the equations are combined, you find that 1 mole of MnO_4^- ions react with 5 moles of Fe^{2+} ions. Having got that information, the titration calculations are just like any other ones.

Doing the Titration

The potassium manganate(VII) solution always goes into the burette, and the other solution in the flask is acidified with dilute sulphuric acid.

As the potassium manganate(VII) solution is run into the flask it becomes colourless. The end point is the first faint trace of permanent pink colour in the solution showing that there is a tiny excess of manganate(VII) ions present.

Problems with the use of Potassium Manganate(VII) Solution

There are two things you need to be aware of:

- Potassium manganate(VII) can't be used in titrations in the presence of ions like chloride or bromide which it oxidises. An unknown amount of the potassium manganate(VII) would be used in side reactions, and so the titration result would be inaccurate.

  This is why you do not acidify the solution with hydrochloric acid.

Potassium manganate(VII) isn't a primary standard. That means that it can't be

- made up to give a stable solution of accurately known concentration.

  It is so strongly coloured that it is impossible to see when all the crystals you have used have dissolved, and over a period of time it oxidises the water it is dissolved in to oxygen.

  Bottles of potassium manganate(VII) solution usually have a brown precipitate around the top. This is manganese(IV) oxide - and is produced when the manganate(VII) ions react with the water.

You have to make up a solution which is approximately what you want, and then standardise it by doing a titration. This is often done with ethanedioic acid solution, because this *is* a primary standard.

Quick Quiz

1. Give half equation for manganate (VII) ion in acid solution.
2. Write equation for oxidation of oxalic acid.
3. How can you convert toluene into benzoic acid?
4. Write equation of reactin of hexaaquamanganate(II) with –OH ion. What color change is ovserved.

14.4.4 Iron

In this topic we will discuss:

(i) Oxidation state

(ii) Iron as catalyst in Haber's Process and in reaction between per sulphate and iodide ions.

(iii) Reaction of Hex aqua Iron (II) and (III) with water, ammonia, Carbonate and Thiocyanate ions.

Oxidation State

Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+}). In aqueous solution, the Fe is readily oxidized from Fe^{2+} to Fe^{3+}:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

The Fe^{2+} ion is thus a reducing agent. Concentrations of Fe^{3+} in solution can be determined by titration with oxidizing agents.

Iron as Catalyst in the Haber Process

The Haber Process combines nitrogen and hydrogen into ammonia. The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane). Iron is used as a catalyst.

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

Iron Ions as a Catalyst in the Reaction between Persulphate Ions and Iodide Ions

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

The overall equation for the reaction is:

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

For the sake of argument, we'll take the catalyst to be iron(II) ions. The reaction happens in two stages.

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$
$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

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

This is a good example of the use of transition metal compounds as catalysts because of their ability to change oxidation state.

Reactions of Iron Ions in Solution

The simplest ions in solution are:

- the hexaaquairon(II) ion - $[Fe(H_2O)_6]^{2+}$.
- the hexaaquairon(III) ion - $[Fe(H_2O)_6]^{3+}$.

(a) Reactions of the Iron Ions with Hydroxide Ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the iron ions.

When enough hydrogen ions have been removed, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

In the iron(II) case:

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

In the iron(III) case:

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

In the test-tube, the colour changes are:

In the iron(II) case:

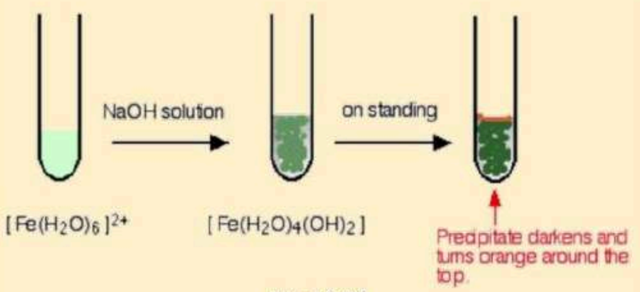


Fig.14.23

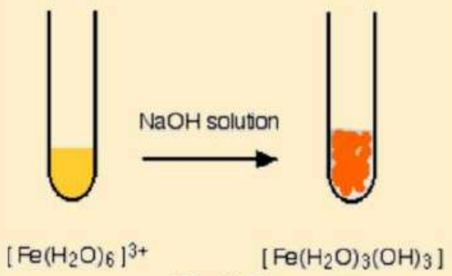


Fig.14.24

Iron is very easily oxidised under alkaline conditions. Oxygen in the air oxidises the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect.

In the iron(III) case:

(b) Reactions of the Iron Ions with Ammonia Solution

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

In the iron(II) case:

The appearance is just the same as in when you add sodium hydroxide solution. The precipitate again changes colour as the iron(II) hydroxide complex is oxidised by the air to iron(III) hydroxide.

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

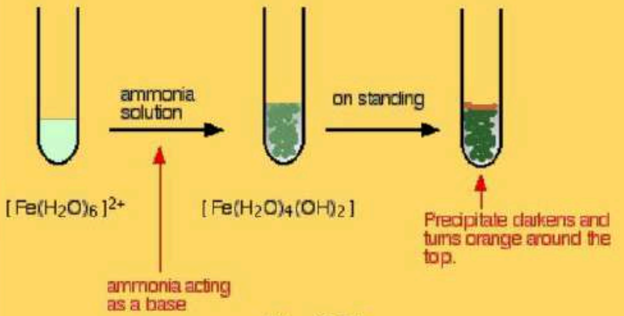


Fig.14.25

In the iron(III) case:

The reaction looks just the same as when you add sodium hydroxide solution.

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

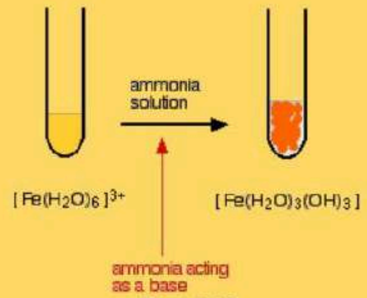


Fig.14.26

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

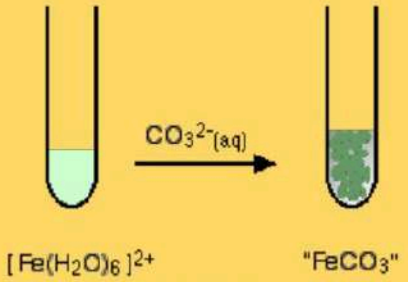


Fig.14.27

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

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

(a) Iron(II) Ions and Carbonate Ions and Thiocyanate Ions

You simply get a precipitate of what you can think of as iron(II) carbonate.

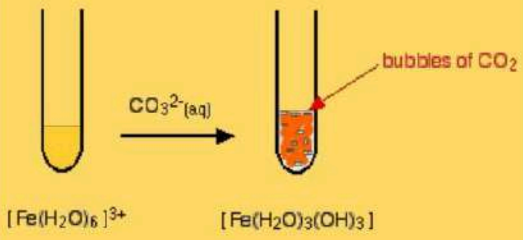


Fig.14.28

Iron(III) Ions and Carbonate Ions

The hexaaquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.

If you add sodium carbonate solution to a solution of hexaaquairon(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution.

This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex.

$$2\,[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \longrightarrow \underset{\text{(orange)}}{2\,[Fe(H_2O)_3(OH)_3]} + 3CO_2 + 3H_2O$$

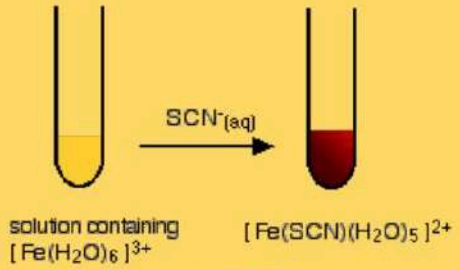


Fig.14.29

Depending on the proportions of carbonate ions to hexaaqua ions, you will get either hydrogencarbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

Apart from the carbon dioxide, there is nothing new in this reaction:

(b) Testing for Iron(III) Ions with Thiocyanate Ions

This provides an extremely sensitive test for iron(III) ions in solution.

If you add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.

$$[Fe(H_2O)6]_3^+ + SCN^- \longrightarrow [Fe(SCN)(H_2O)_5]^{2+H_2O}$$

Quick Quiz

1. Give role of ammonia in reaction of it with iron ion solution.
2. In which form iron ion are present in aqueous solution?
3. Write reaction equation between persulphate ion and iodide ion.
4. How thiocyanate in is used for testing of Fe?

14.4.5 Copper

(i) The Oxidation States

(ii) The reaction of hexaaquacopper (II) ions with hydroxide ions, Ammonia and Carbonate ion

The Oxidation States

Copper exists in two common oxidation states, +1 (Cu^{1+}) and +2 (Cu^{2+}). In aqueous solution, the Cu is readily oxidized from Cu^{1+} to Cu^{2+}:

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

The Cu^{1+} ion is thus a reducing agent. Concentrations of Cu^{2+} in solution can be determined by titration with oxidizing agents.

The Reaction of Hexaaquacopper(II) Ions with Hydroxide Ions

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

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

(blue)

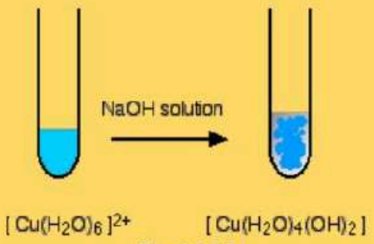


Fig.14.30

Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

In the test-tube, the colour change is shown in figure 14.28:

Reactions of Hexaaquacopper(II) Ions with Ammonia Solution

The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

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

That precipitate dissolves if you add an excess of ammonia.

The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Notice that only 4 of the 6 water molecules are replaced.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The colour changes are:

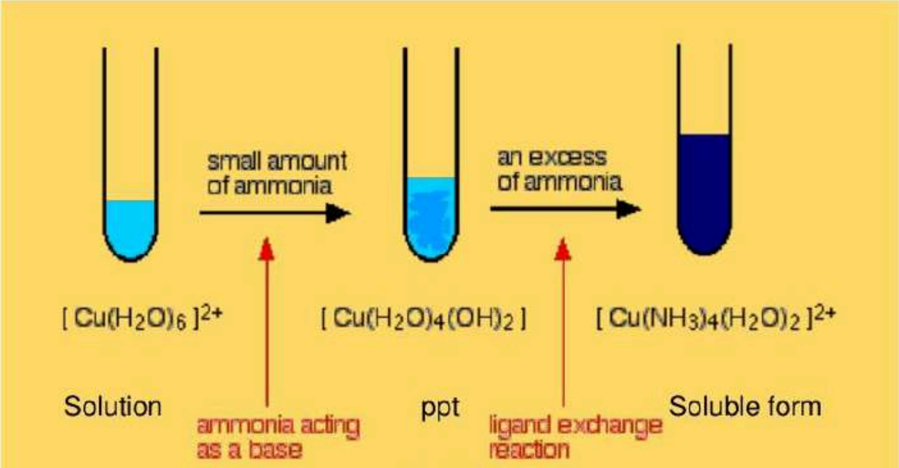


Fig.14.31

The Reaction of Hexaaquacopper(II) Ions with Carbonate Ions

You simply get a precipitate of what you can think of as copper(II) carbonate.

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

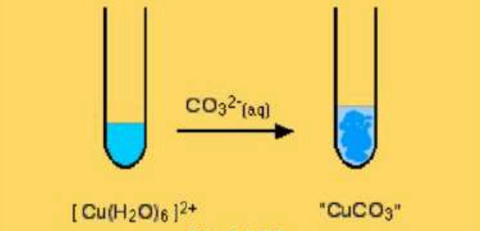


Fig.14.32

Quick Quiz

1. Ammonia acts as base as well as ligand. Prove above statement by reaction with copper ion.
2. When copper ion reacts with carbonate. What you expect. Which types of precipitate are formed?
3. Cu^{+1} ion is reducing/oxidizing agent and why.

Society, Technology and Science

Transition Elements and Paints

Certain transition elements such as Cu, Cr, etc are used in Paints. Mostly copper and its different compounds are used in paints.

Name of compound	Uses
Lead Monoxide (PbO)	1. It is used in paints, vulcanizations of rubber and for the preparation of red lead. 2. It is used in the manufacture of varnished, glazes, plasters and enamels. 3. It is used in the manufacture of flint glass.
Lead Suboxide (Pb_2O)	1. It is black in color and found in powder form 2. It is used as pigment in paints 3. It is used in lead storage.
Lead Dioxide (PbO_2)	Lead dioxide is a reddish brown powder and used as pigment in paints.
Triplumbic Tetra oxide Red Lead (Pb_3O_4)	1. It is used as red paint when mixed with linseed oil 2. It is used in glass industry for making glazes 3. It is used in match industry
Basic Lead Carbonate [$2PbCO_3 . Pb(OH)_2$]	1. It is used as white paint for wood because of its good covering power and protection 2. It is used in making pottery glazes.
Lead Chromate ($PbCrO_4$)	1. It is used as a pigment under the name of chrome yellow. 2. On heating with dilute alkali hydroxide it forms orange or red basic lead chromat.

Key Points

- Transition elements have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states.
- 2 and 3 group elements are called non-typical transition elements.
- Binding energies, melting points, paramagnetism and oxidation states of transition metals increase with increasing number of unpaired electrons.
- Such compounds containing complex molecule or complex ions a capable of independent existence are called coordination.
- When a complex ion absorbs a wavelength from visible light, it transmits a set of radiation that imparts color.
- General outermost configurations:
  1. First series (d-block elements) = $(n-1)d^{1-10}ns^2$
  2. Second series (f-block elements) = $(n-1)d^1(n-2)f^{1-14}ns^2$

Exercise

1. Select the right answer from the choices given with each question.

i. Coinage metals are actually:

(a) halogens (b) alkali metals

(c) transition metals (d) alkaline earth metals

ii. Zinc is a transition elements but it does not show variable valency because:

(a) it does not form colored salts

(b) it has incomplete d-subshell

(c) it has completely filled d-subshell

(d) it has two electrons in the outermost orbit

iii. Which of the following is non-typical transition element?

(a) Fe (b) Mn (c) Zn (d) Cr

iv. Which elements form alloy

(a) Alkali metals (b) alkaline earth metals

(c) Halogens (d) Transition elements

v. Which are repelled by magnetic filed?

(a) Paramagnetic (b) Ferromagnetic

(c) Diamagnetic (d) None

vi. Magnetic moment (μ) of an atom or ion is the measure of its number of unpaired

(a) Electron (b) Proton

(c) Neutron (d) Nucleons

vii. The unit of Magnetic moment is:

(a) Coulombs (Q) (b) Amperes (A)

(c) Bohr magneton (BM) (d) Watts (W)

viii. Bronze alloy contains:

(a) Cu and Sn (b) Ni and Cr

(c) Cu and Zn (d) Cr and Fe

ix. Give the systematic name for $Fe(CO)_5$

(a) Pentacarbonyl iron (III) (b) Pentacarbonyl iron (o)

(c) Pentacarbonyl iron (II) (d) Pentacarbonyl ferrate (III)

x. Give the chemical formula of a complex compound sodium monochloropnetacyanoferrate (III).

(a) $[Na_3FeCl(CN)_5)]$ (b) $Fe_3[NaCl(CN)_5)]$

(c) $Na_3[FeCl(CN)_5)]$ (d) $Na_2[FeCl(CN)_5)]$

xi. The complexes having coordination number (C.N) = 4 have geometry:

(a) Tetrahedral (b) Linear

(c) Square plane (d) both a and c

xii. If we add HNO3 to the original vanadium (II) solution, it produces

(a) blue ions (b) green ions

(c) dull grey blue ions (d) pink ions

xiii. Which metal oxide is used in contact process as a catalyst:

(a) Cr (b) Mn (c) V (d) Cu

xiv. In oxidation of chromium (III) to chromium (VI) the green color will change into

(a) colorless (b) bright yellow

(c) pink (d) None

xv. Acidified potassium permanganate act as a strong

(a) oxidizing agent (b) reducing agent

(c) electrolytic agent (d) hydrolyzing agent

xvi. Following element shows maximum number of oxidation states?

(a) Mn (b) Fe (c) Cr (d) Cr

xvii. The color of Mn^{2+} in hydrated form is:

(a) Blue (b) Yellow (c) Light Pink (d) Green

xviii. Which of the following metals show more than one oxidation state?

(a) Al (b) Mg (c) Fe (d) Ca

xix. Iron is used as a catalyst in:

(a) Brikland Process (b) Contact Process

(c) Haber Process (d) both b and c

xx. During the reaction of Ammonia with iron, it acts as both a base and a:

(a) Ligand (b) Acid (c) Iron (d) Salt

2. Give brief answers for the following questions.

i. Why are d-block elements called transition elements?

ii. Why do the d-block elements show different oxidation states?

iii. Why does Mn show the maximum number of oxidation states in 3d-series?

iv. What is the difference between double salts and coordination or complex compounds?

v. Explain the following terms: (a) Ligand (b) Coordination Sphere (c) Central Metal.

vi. How chromate ions are converted into dichromate ions?

vii. What is the difference between paramagnetism and diamagnetism?

viii. What are advantages of Potassium dichromate in titrations?

ix. How does dichromate ion converted in to chromate ions.

3. Give detailed answers for the following questions.

i. (a) What is the valence shell configuration of transition elements? How does it affect the following properties? (i) Binding energy (ii) Paramagnetism (iii) oxidation states

(b) What are typical and non-typical transition elements?

(c) Explain catalytic Activity of transition elements.

(d) Write composition, properties and uses of: Brass, Bronze and Nichrome alloys.

ii. (a) Explain different types of ligand with examples

(b) Describe the rules for naming the coordination complexes with examples.

iii. (a) Explain shapes and origin of colors of coordination compounds.

(b) Relate the coordination number of ions to the crystal structure of the component of which they are a part.

iv. (a) Write systematic names to following complexes:

(i) $[Co(NH_3)_6]Cl_3$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $Na_3[CoF_6]$

(iv) $[Cr(OH)_3(H_2O)_3]$ (v) $K_2[PtCl_6]$ (vi) $[Pt(OH)_2(NH_3)_4]SO_4$

(vii) $K_2[Cu(CN)_4]$ (viii) $Na_2[NiCl_4]$ (ix) $Pt(NH_3)_2Cl_4$ (x) $[Ag(NH_3)_2]Cl$

(b) Write chemical formulae of following complexes:

(i) Potassiumhexacyanoferrate (II)

(ii) Sodium tetrachloronickelate (II)

(iii) Tetrammine copper (II) Sulphate

(iv) Potassium hexachloroplatinate (IV)

(v) Dichlorotetrammine cobalt (III) Chloride

v (a) Discuss vanadium (V) oxide as a catalyst with example.

(b) How does chromium (III) changes to chromium (VI)?

(c) Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry.

15

ORGANIC COMPOUNDS

After completing this lesson, you will be able to:

This is 5 days lesson (period including homework)

- define organic chemistry and organic compounds.
- explain why there is such a diversity and magnitude of organic compounds.
- classify organic compounds on structural basis.
- explain the use of coal as a source of both aliphatic and aromatic hydrocarbons.
- explain the use of plants as a source of organic compounds.
- explain that organic compounds are also synthesized in the lab
- define functional groups and homologous series.

Reading

INTRODUCTION

There are two main classes of chemical compounds, inorganic and organic. They are classified on the basis of source from which they were derived. The compounds which were of mineral origin were known as inorganic such as table salt, marble, carbon dioxide etc. and those of vegetable or animal origin were called organic for example; acetic acid (from vinegar), alcohol (from wine), tartaric acid (from grapes) etc.

Organic chemistry is concerned with the chemistry of living material or substances which were at one time alive. It is therefore concerned with living plants or animals or substances like coal and oil which are derived from living plants (coal), or from microscopic sea organisms (oil).

Organic chemistry is now defined as the chemistry of compounds of carbon as carbon is the essential element in all organic compounds. However there are several compounds like carbon monoxide (CO), carbon dioxide (CO_2), carbon disulphide (CS_2), carbonates (CO_3^{-2}), bicarbonates (HCO_3^{-1}), Cyanides (CN^{-1}), thiocynates (SCN^{-1}) etc are studied in inorganic chemistry because of their properties.

Modern definition of organic chemistry:

Organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (Hydrocarbons) and their derivatives.

15.1 SOURCES OF ORGANIC COMPOUNDS

15.1.1 Fossil Remains

The main sources of organic compounds are coal, petroleum and natural gas. These are called fossil fuels.

I – Coal

Coal is one of major source of organic compounds. It yields coke and coal-tar on pyrolysis or destructive distillation. More than 200 organic compounds have been directly isolated from coal-tar. These coal-tar products form the starting materials for the manufacture of thousands of useful aromatic compounds, including perfumes, drugs, dyes, photographic developers, and others.

Points to Remember
Important products prepared from petroleum
Methane (CH_4)
Ethylene ($CH_2{=}CH_2$)
Acetylne ($CH{\equiv}CH$)
Propene ($CH_3CH{=}CH_2$)
Benzene C_6H_6
Toluene $C_6H_5CH_3$
Xylene $C_6H_4(CH_3)_2$

II - Petroleum

In some parts of the world, a black thick sticky liquid seeps out of the ground. This liquid is called petroleum or crude oil. Petroleum is a complex mixture of hydrocarbons whose composition varies according to its place of occurrence.

III - Natural Gas:

It is a mixture of low boiling hydrocarbons. Major portion of the natural gas is methane (CH_4 about 85%); other gases include ethane, propane and butane. It is formed by the decomposition of organic matter.

In Pakistan there are vast reserves of gas at Sui in Baluchistan, Sind and Punjab.

15.1.2 Plants and Natural Product Chemistry

Many organic compounds are obtained directly from plant and animal sources by suitable methods of isolation. A few familiar examples are carbohydrates (cellulose, sugars, starches), proteins (silk, wool, casein, food proteins, fats and oils (cottonseed, soybeans oils, lard, butter), alkaloids (quinine, morphine, strychnine), hormones, vitamins, perfumes, flavors, resins.

15.1.3 Partial and Total Synthesis

Simple organic compounds derived from petroleum or coal has been converted into thousands of useful materials by synthetic methods. Many examples might be cited of synthetic organic compounds replacing those obtained from natural sources, such as dyes, rubber, fibers plastics, drugs, vitamins. In many cases the synthetic materials are superior to the natural compounds. For example, synthetic dyes are superior to those of natural origin. In other cases the synthetic material are entirely unknown in nature and fill the requirements not satisfied from any other source. Examples are ether, glycol, mercurochrome, aspirin, and the sulpha drugs. Synthetic organic chemistry touches almost every phase of life.

15.1.4 Fermentation

Fermentation is defined as the production of chemicals by the action of micro-organism. By employing appropriate organism hosts of useful substances are produced including alcohols, acids, vitamins and antibiotics.

Quick Quiz

1. Define modern defination of oraganic chemistry.
2. Inlist different sources of organic compounds.
3. Write important prodcuts from petroleum.
4. What are alkaloids?
5. Define fermentation?

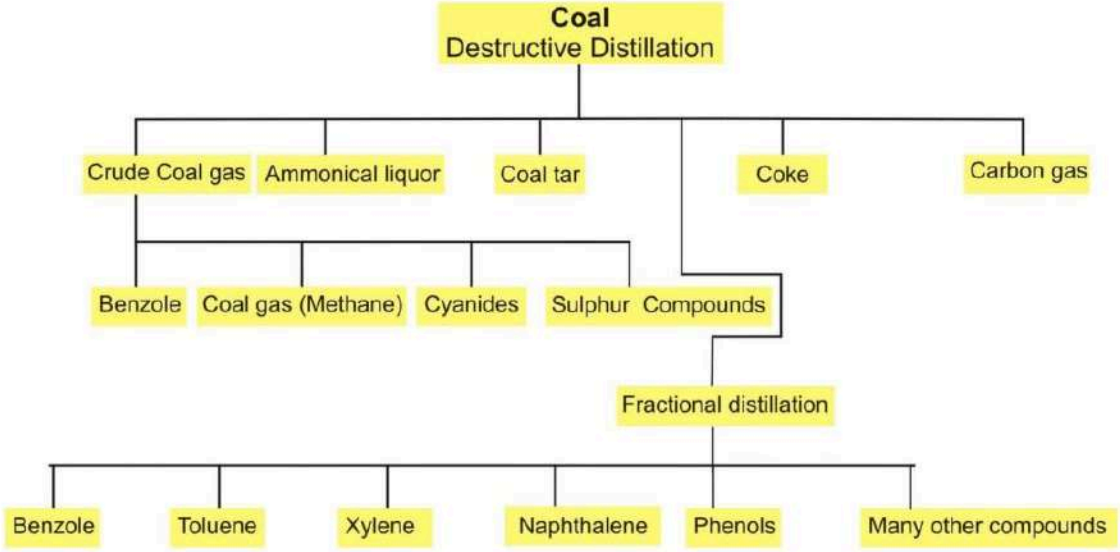
15.2 Coal (as a source of organic compound)

Coal is produced by the decaying of trees buried under the earth crust under the influence of temperature and pressure. These trees got converted into coal.

15.2.1 Destructive Distillation of Coal

When coal is heated in the absence of air (temperature ranging from 500-1000^{0}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 reserves of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tones.



15.3 CHARACTERISTICS OF ORGANIC COMPOUNDS

Organic compounds have entirely different properties from inorganic compounds. Some of their general properties are described below:

1. **Composition**
   Carbon is an essential constituent of all organic compounds.
2. **Combustion**
   Organic compounds with high percentage of carbon are generally combustible in nature.

3. **Melting and Boiling Points**
   Organic compounds generally have low melting and boiling points and are volatile in nature.
4. **Solubility**
   Organic compounds with non polar linkages are generally soluble in organic solvents such as alcohol, ether, benzene, etc. They are less soluble in water.
5. **Stability**
   Since organic compounds have low melting and boiling points. They generally decompose at high temperature into simple substances.
6. **Electrical Conductivity**
   Due to the presence of covalent bonds, organic compounds are poor conductor of electricity both in fused state and in solution form.
7. **Source**
   Most of organic compounds are obtained from plants and animal sources
8. **Rate of Reaction**
   Their rates of reaction very slow and need specific conditions.

Quick Quiz

1. What is coal?
2. What are the products of fractional distillation of coal tar?
3. What we obtain by fractional distillation of coal gas?

15.4 USES OF ORGANIC COMPOUNDS

No field of science is so closely related with our daily activities as is organic chemistry. The food we eat is mainly organic in nature. The changes which this food undergoes in our bodies are organic chemical reactions. Metabolism growth and maintenance of our body functions involve organic chemistry as do the analogous changes taking place throughout the entire living world, plants and animals.

The clothes we wear, the dyes that color them, the soap and starch used to launder them the leather in our shoes as well as the dye and shoe polish, are products of organic chemical industry. Many of the structural materials in our houses and furniture, as well as the paints and varnishes used for finishing them are all organic. Many of the equipments in our motor cars, their fuels and lubricants and the fuels which power our industrial plants are all organic in nature.

The tremendous importance of organic compounds in modern everyday life is illustrated by the following list:

1. ***Food:*** (proteins, fats, carbohydrates, oils,)
2. ***Clothing:*** (cotton, silk, wool, nylon, rayon, dacron)

The natural fiber like cotton, silk and wool have plant and animal origin. Synthetic fiber like rayon, dacron and nylon are prepared in the industry.

3. ***Shelter:*** (wood, paints, varnishes)
4. ***Power and Transportation:*** (natural gas, petroleum products, coal)

Natural gas, petroleum and gas used for power and transportation are organic substances.

5. ***Medicines and Drugs:*** (Penicillin, streptomycin,)

All types of the medicines used in the allopathy, homeopathy and desi-tib involve the organic compounds.

6. ***Insecticides:*** Insecticides like DDT, which are being widely used are organic substances
7. ***Hormones and Steroids:*** Hormones and steroids are complex organic compounds.
8. ***Vitamins and Enzymes:*** All the vitamins which are dietary factors are organic compounds. Similarly enzymes are organic substances.
9. ***Antiseptics and Anesthetics:*** These are the families of the medicines and are organic in nature.
10. ***Pigments and Dyes:*** Pigments and dyes are used for paints and are organic in nature
11. ***Paper and Inks:*** Paper and inks are the sources of civilization and organic materials.
12. ***Perfumes and Flavors:*** Perfumes flavors and all cosmetics are organic in nature.
13. ***Plastics, Rubbers, and Resins:*** Plastics, rubber and resins are organic in nature.
14. ***Propellants and Explosives:*** Propellants, explosives and refrigerants are well-known organic materials.
15. ***Soaps and Detergents:*** Soaps and detergent are organic compounds
16. ***Herbicides:*** Teflon,
17. ***Photographic films and Developers***
18. **Biological Problems in Organic Chemistryu:**

Most of the biological problems are concerned with organic chemistry. For example, organic reactions are involved in formation of tissues and foods. These changes happen in metabolism and growth process etc.

15.5 NEW ALLOTROPES OF CARBONS: BUCKY BALLS

The full name of Bucky Balls is Buckminister Fullerenes. Scientists named it after an architect Buckminister, who designed a Bucky balls shaped building in Montreal. Bucky balls are used as semi-conductors and lubricants.

Fig. 15.1: Bucky balls

In 1985, a new group of allotropic forms of carbon was discovered. These have carbon atoms ranging from forty to hundred. The carbon atoms are arranged in a hollow cage like structure. They are called Bucky Balls. The simplest of them is C_{60} and its molecule is made up of sixty carbon atoms. The carbon atoms fold around and make a ball shaped molecule. The new molecule looks just like a football. The carbon atoms join together to form pentagon and hexagon structures.

Quick Quiz

1. What are allotropes?
2. Why it was given the name Bucky balls?

15.6 FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

15.6.1 Functional Group

The basic idea of the functional group is at the heart of much of the organic chemistry we shall study. We will carry out many transformations of organic molecules. In most cases the change will occur at one "spot" in the original reacting molecule. That spot is the *functional group*.

A functional group is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties. Double and triple bonds are functional groups. Other examples include -Cl, -Br, -OH, -NH2 groups. Remember that the functional group is the action group. The hydrocarbon portion remains inert.

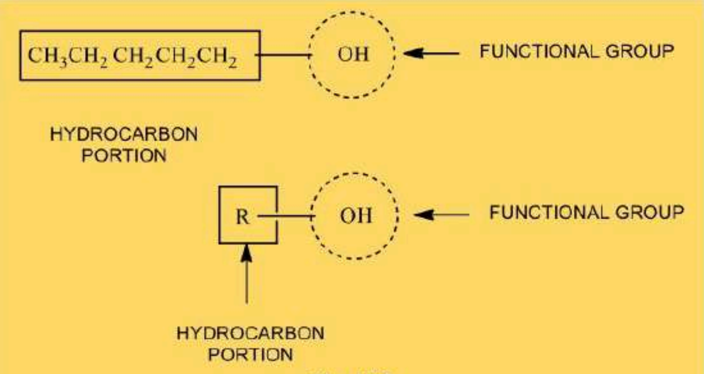


Fig. 15.2

We often use the symbol R- to represent the hydrocarbon portion to which the functional group is attached. Thus R- can CH_3- , CH_3CH_2-, $(CH_3)_2CH$- or any other group of C and H atoms with one free valence by which the functional group is attached. The table 15.1 shows some common functional groups and the corresponding classes of compounds.

Each functional group undergoes characteristic reactions. By recognizing the functional group in a molecule, it is possible to predict the reactions which that molecule will undergo. The concept of functional group is important to organic chemistry for three reasons:

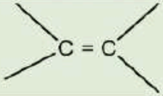
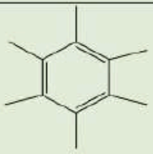
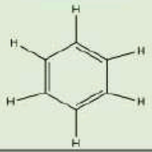
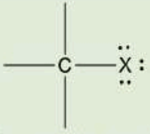
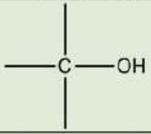
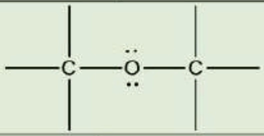
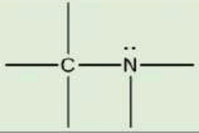
1) Functional groups serve as basis for nomenclature (naming) of organic compounds.
2) Functional groups serve to classify organic compounds into classes/families. All compounds with the same functional group belong to the same class.
3) A functional group is a site of chemical reactivity in a molecule containing the functional group.

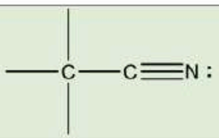
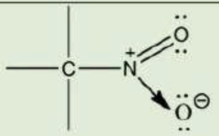
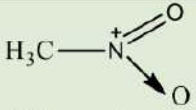
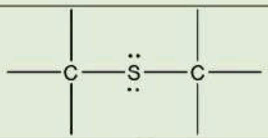
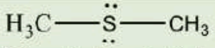
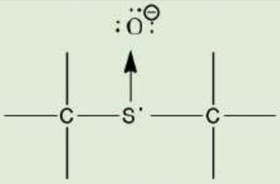
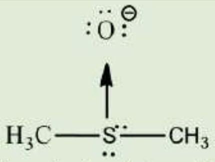
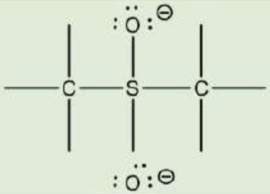
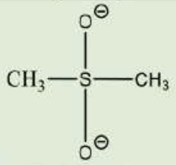
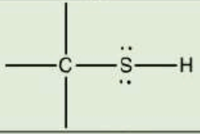
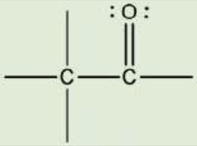
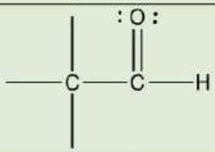
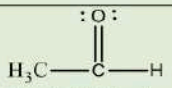
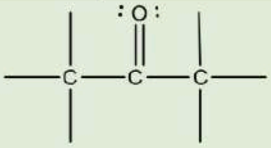
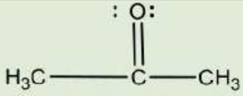
A molecule can contains more than one functional group. It is then said to be **Polyfunctional**, and the properties of each functional group may be modified by the presence of the others.

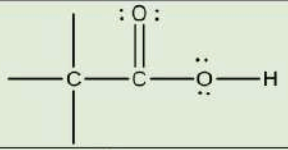
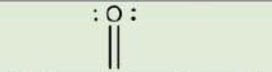
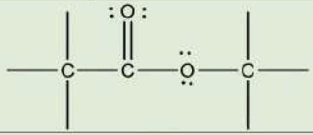
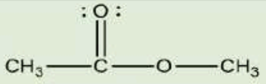
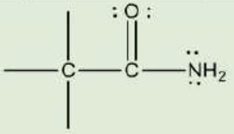
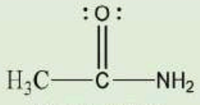
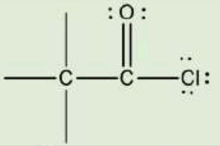
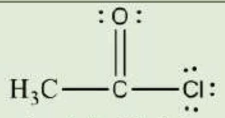
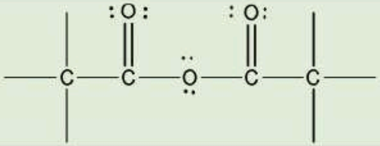
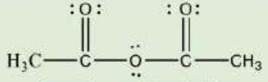
Quick Quiz

What is organic compound?
What is meant by a functional group?
Define sublimation.
How many types of distillation used in the laboratory?
Define the third allotropic forms of Carbon?

Table: 15.1: Some common functional groups are:

Family	Structure of functional group	Simple example
Alkane	Containing only C – H and C – C single bond Contain no functional group	$CH_3 - CH_3$ Ethane
Alkene		$H_2C = CH_2$ Ethene
Alkyne	$- C \equiv C -$	$H - C \equiv C - H$ Ethyne (Acetylene)
Arene		Benzene 
Halide	 (X = F_2 Cl_2 Br_2 I_2)	$H_3C - \ddot{\underset{\cdot\cdot}{Cl}}:$ Methyl chloride
Alcohol		$H_3C - OH$ Methanol (Methyl alcohol)
Ether		$H_3C - \ddot{\underset{\cdot\cdot}{O}} - CH_3$ dimethyl ether
Amine		$H_3C - NH_2$ Methyl amine

Nitrile		$H_3C-C\equiv N$ Methyle Cyanide (Methyl nitrile)
Nitro		 Nitromethane
Sulphide		 Dimethyl sulphide
Sulphoxide		 Dimethyl sulphoxide
Sulphone		 Dimethyl sulphone
Thiol		 Methane thiol (Mehylthiol)
Carbonyle		Aldehydes, ketones, acids and derivatives of acids.
Aldehyde		 Acetaldehyde
Ketone		 Dimethyl Ketone (Acetone)

Carboxylic Acid		 Acetic acid
Ester		 Methyl acetate
Amide		 Acetamide
Carboxylic acid chloride		 Acetyl chloride
Carboxylic acid anhydride		 Acetic anhydride

15.6.2 Homologous Series

A homologous series is a series of compound in which adjacent members differ by a CH_2 unit. The individual members are called Homolog. For example, the homologous series of alcohols can be represented as:

General Formula is ROH or $C_nH_{2n+1}OH$

n	R	Formula
1	CH_3^-	CH_3OH
2	$CH_3CH_2^-$	CH_3CH_2OH
3	$CH_3CH_2CH_2^-$	$CH_3CH_2CH_2OH$
4	$CH_3CH_2CH_2CH_2^-$	$CH_3\ CH_2CH_2CH_2OH$

The general characteristics of a homologous series are:

1. All compounds in the series contain the same elements and the functional group.
2. All compounds in the series can be represented by a general formula. For example; The general formula for Alkane is C_nH_{2n+2} , for alkene C_nH_{2n} and for alkyne C_nH_{2n-2}.
3. The molecular formula of each homolog differs from one above and one below it by a CH_2 unit.
4. All compounds in the series can be prepared by similar methods.
5. They have same set of properties.

6. There is a gradual variation in physical properties with increasing molecular weight.

Quick Quiz

1. What are general formulas for alkanes, alkenes and alkyne
2. What are homologs?
3. Why we arrange compounds in homologous series?

15.7 DETECTION OF ELEMENTS IN ORGANIC COMPOUNDS

Carbon is an essential constituent of all organic compounds. Hydrogen is also present in almost all organic compounds but some of them may contain nitrogen sulphur, and halogen, Oxygen, Phosphorus and Metals.

A) Detection of Carbon and Hydrogen:

Carbon hydrogen can be detected by heating small amount of organic compound with CuO in a glass test tube as shown in the Fig. on heating the mixture carbon and hydrogen are oxidized to CO_2 and H_2O respectively. CO_2 turns lime water milky which proves the presence of carbon and the water vapors turn white anhydrous copper sulphate blue shows the presence of hydrogen in the organic compound.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$CO_2 + \underset{\text{Lime water}}{Ca(OH)_2} \longrightarrow CaCO_3 + H_2O$$

$$H_2 + CuO \longrightarrow Cu + H_2O$$

$$\underset{\text{anhydrous(white)}}{CuSO_4 + 5H_2O} \longrightarrow \underset{\text{Hydrous(blue)}}{CuSO_4.5H_2O}$$

B) Detection of Nitrogen, Sulphur and Halogens

Preparation of Lassaigne's Solution/Sodium Extract

1) Cut a small piece of sodium metal with the help of knife
2) Put this piece of sodium metal in a fusion tube.
3) Heat the fusion tube in a flame to melt sodium metal.
4) When sodium metal is melted, then add a small amount of powdered organic compound into fusion tube.
5) Then Heat the fusion tube again till its bottom become red hot.
6) Break this fusion tube in a China dish containing 20cm^3 of distilled water.
7) Mixed, boil and then filter the solution.
8) The filtrate obtained is called Lassainge's solution or sodium extract.
9) Divide this filtrate into three portion and test, the presence of N, S ad (X) halogens respectively.

Reactions:

$$2Na + S \rightarrow Na_2S$$
$$Na + N + C + S \rightarrow NaSCN$$
$$Na + X \rightarrow NaX \qquad \text{where } X = Cl, Br, I$$

Nitrogen Test:

To one portion of Lassaigne's filtrate a few drops of NaOH is added to make it alkaline, then freshly prepared ($FeSO_4$) solution is added to it. The solution is boiled and a few drops of $FeCl_3$ solution and HCl are added to it. The appearance of blue or greenish blue (Prussian blue) color or ppt. proves the presence of nitrogen in the organic compound.

$$Na + C + N \longrightarrow NaCN$$
$$6NaCN + FeSo_4 \longrightarrow Na_4\left[Fe(CN)_6\right] + Na_2SO_4$$
$$3Na_4\left[Fe(CN)_6\right] + 4FeCl_3 \longrightarrow \underset{\text{prussion blue}}{Fe_4\left[Fe(CN)_6\right]_3} + 12NaCl$$

Note: if a blood red color is produced instead of prussian blue color then it proves that nitrogen and sulphur both are present in the organic compound.

$$2Na + 2C + N_2 + 2S \longrightarrow 2NaSCN$$

$$6NaSCN + FeSO_4 \longrightarrow Na_4\left[Fe(CNS)_6\right] + Na_2SO_4$$
$$3Na_4\left[Fe(CNS)_6\right] + 4FeCl_3 \longrightarrow \underset{\text{Blood red ppt.}}{Fe_4\left[Fe(CNS)_6\right]} + 12NaCl$$

Sulphur Test:

The second portion of Lassaigne's filtrate is acidifiedس with acetic acid and boiled to expel H_2S gas which turns lead acetate paper black that indicates the presence of Sulphur in the compound.

$$S^{2-} + 2CH_3COOH \longrightarrow H_2S + 2CH_3COO^-$$
$$H_2S + 2CH_3COO^- + Pb \longrightarrow \underset{\text{Black ppt.}}{PbS} + 2CH_3COOH$$

Halogen Test:

A third portion of Lassaigne's solution is boiled with nitric acid to expel cyanide ion and sulphide ions and $AgNO_3$ solution is added. The formation of precipitate shows the presence of a halogens, white ppt soluble in NH_4OH shows the presence of chlorine, a pale yellow ppt. partially soluble in NH_4OH shows the presence of bromine and a deep yellow ppt. insoluble in NH_4OH indicated iodine.

$$X^- + Ag^+ \rightarrow AgX \ (X^- = Cl^-, Br^- \ I^-)$$

C) Detection of Oxygen

There is no conclusive test for oxygen, though its presence in organic compounds is often inferred by indirect methods.

1) The substance is heated alone in a dry test-tube, preferably in an atmosphere of nitrogen. Formation of droplets of water on cooler parts of the tube obviously shows the presence of oxygen. A negative result, however, does not necessarily show the absence of oxygen.

2) The second method is to test for the presence of various oxygen containing groups such as hydroxyl (OH), carboxyl (COOH), aldehyde (CHO), nitro (NO_2) etc. if any of these is detected, the presence of oxygen is confirmed.

3) The sure test for oxygen depends on the determination of the percentage of all other elements present in the given compound. If the sum of these percentages fall short of hundred the remainder gives the percentage of oxygen and thus confirms.

D) Detection of Phosphorus

The solid substance is heated strongly with an oxidizing agent such as concentrated nitric acid and mixture of sodium carbonate and potassium nitrate. The phosphorus present in the substance has oxidized to phosphate. The residue is extracted with water, boiled with some nitric acid, and then a hot solution of ammonium molydebate is added to it in excess. A yellow coloration of precipitate indicated the presence of phosphorus.

E) Detection of Metals

The substance is strongly heated in a crucible, preferably of platinum, till all reaction ceases. An incombustible residue indicated the presence of a metal in the substance. The residue is extracted with dilute acid and the solution is tested for the presence of metallic radical by the usual scheme employed for inorganic salts.

Society, Technology and Science

ORGANIC COMPOUNDS OBTAINED FROM PLANTS AND ANIMALS.

Most Sugars, Some alkaloids (a naturally occurring nitrogenous organic molecule), Some terpenoids (a large class of natural products consisting of isoprene (C5) units)
Certain nutrients such as vitamins,
Antigens, Carbohydrates, Enzymes, Hormones, Lipids and fatty acids, fats and oils, Neurotransmitters, Nucleic acids, Proteins, peptides and amino acids, Lectins (sugar-binding proteins)

Quinine- an antimalarial and antipyretic medicine- is obtained from Cinchona ledgeriana (quinine tree).

Nicotine-an insecticide- is obtained from Nicotiana tabacum (tobacco).

Menthol-a rubefacient(a substance for topical application that causes dilation of the capillaries and an increase in blood circulation)-is obtained from Mentha species (mint).

Camphor- a rubefacient- is obtained from Cinnamomum camphora (camphor tree).

Rutin - used for the treatment of capillary fragility- is obtained from citrus species e.g. orange, grapefruit etc.

Hesperidin- used for the treatment of capillary fragility- is obtained from citrus species e.g. orange.

Curcumin- a choleretic- is obtained from Curcuma longa (turmeric).

Cocaine- a local anaesthetic- is obtained from Erythroxylum coca (coca plant).

Caffeine- a CNS stimulant- is obtained from Camellia sinensis (tea, coffee and cocoa).

Bromelain-an anti-inflammatory drug- is obtained from Ananas comosus (pineapple).

Key Points

- Coal, petroleum and natural gas are important sources of organic compounds.
- The study of organic chemistry organized around functional groups. Each functional group defines as organic family.
- Organic chemistry is concerned with the chemistry of living material or substances which were at one time alive. It is therefore concerned with living plants or animals or substances like coal and oil which are derived from living plants (coal), or from microscopic sea organisms (oil).
- Coal is produced by the decaying of trees buried under the earth crust under the influence of temperature and pressure. These trees got converted into coal.
- The word petroleum is derived from the Latin words “Petra” meaning rock and “Oleum” meaning oil. It is also called mineral oil.
- Bacterial decay at high pressure with little oxygen changed the organic matter into crude oil and natural gas.
- The refining of petroleum is carried out by the process of fractional distillation. In this process various fractions are separated according to the difference in their boiling points.
- The clothes we wear, the dyes that color them, the soap and starch used to launder them the leather in our shoes as well as the dye and shoe polish, are products of organic chemical industry.

Exercise

1. Select the right answer from the choices given with each question.

i. The major portion of natural gas is

(a) ethane (b) propane (c) butain (d) methane

ii. In organic compounds carbon atoms form;

(a) ionic bond (b) metallic bond (c) covalent bond (d) non of these

iii. Which of the following is an aromatic compound.
(a) Propanol (b) Cyclohexane (c) Acetone (d) Benzene

iv. There are a few homologous series of compounds. The existence of homologous series is due to;
(a) Functional group (b) Cracking (c) Isomerism (d) Polymerization

v. Which of the following compound is heterocyclic?
(a) Pyridine (b) Pyrole (c) Thiphene (d) All of the above

vi. 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

vii. Lassaigne's solution is prepared in the detection of elements of organic compound. Which metal is used for the reaction with organic compound?
(a) Aluminium (b) Sodium (c) Iron (d) Copper

viii. When $AgNO_3$ is added to the Lassaigne's solution which colour is formed for Iodine?
(a) Blue (b) Violet (c) Green (d) Deep Yellow

ix. When water vapours are passed over white anhydrous copper sulphate, which colour is formed?
(a) White (b) Deep blue (c) Yellow (d) Brown

x. The simplest molecule of Bucky Ball contain carbon atoms;
(a) 20 (b) 8 (c) 60 (d) 100

xi. If a molecule contains more than one functional group, it is known as;
(a) Derivative (b) Polyfunctional (c) Heterocyclic (d) Isomer

2: Give brief answers for the following questions.

i. What is functional group?
ii. What is the difference between partial and total synthesis of organic compounds?
iii. How organic compounds are derived by fermentation process?
iv. What is coal? How is coal used as source of organic compounds?
v. What is name of new allotropic form of carbon? Give its definition?
vi. What is Homologous series?
vii. How sulphur can be detected in organic compounds?

3: Give detailed answers for the following questions.

i. What are the main sources of organic compounds?
ii. Write down the characteristics of organic compound from inorganic compounds.
iii. How organic compounds are used in our daily life?
iv. Write down any ten functional groups of organic compounds? Give reasons for the importance of organic chemistry.
v. Give the chemical tests for the detection of elements in organic compounds.

16

HYDROCARBONS

After completing this lesson, you will be able to:

This is 20 days lesson (period including homework)

- Classify hydrocarbons as aliphatic and aromatic.
- Describe nomenclature of alkanes and cycloalkans.
- Describe the mechanism of free radical substitution in alkanes exemplified methane and ethane.
- Describe the structure and reactivity of alkenes as exemplified by ethane.
- Describe the chemistry of alkenes by the following reaction of ethene
- Describe what is meant by the term delocalized electrons in the context of the benzene ring.
- Describe addition reactions of benzene and methyl benzene.
- Describe the mechanism of electrophilic substitution in benzene
- Describe the preparation of alkynes using eliminain reactins.
- Describe acidity of alkyens.
- Describe and differentiate between substitution and addition reactions.
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane.
- Explain unreactive nature of alkanes towards polar reagents.
- Explain what is meant by a chiral center and show that such a center gives rise to optical isomerism.
- Explain the nomenclature of alkenes.
- Explain shape of ethane molecule in terms of sigma and pi C-C bonds.
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethane.
- Explain the shape of benzene molecule (molecular orbital aspect).
- Explain isomerism in alkanes, alkenes, alkynes and substituted benzene.
- Define hemolytic and heterolytic fission, free radical initiation, propagation and termination.
- Identify organic redox reaction.
- Define and explain with suitable examples the terms isomerism, stereoisomerism and structural isomerism.
- Define resonance, resonance energy and relative stability.
- Hydrogenation, hydrohalogenation, hydration, halogenation, halohydration, epoxidation, ozonolysis, polymerization.
- Compare the reactivity of benzene with alkanes and alkenes
- Compare the reactivity of alkynes with alkanes, alkene and arenes.
- Discuss chemistry of benzene and ethyl benzene by nitration, sulphonation, halogenaion, Friedal Craft's alkylation and acylation.
- Discuss the shape of alkyens in terms of sigma and pi C-C bonds.
- Discuss chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonolysis, and reaction with metals.
- Apply the knowledge of position of substituents in the electrophilic substitution of benzene.
- Use the IUPAC naming system for alkynes.

Reading

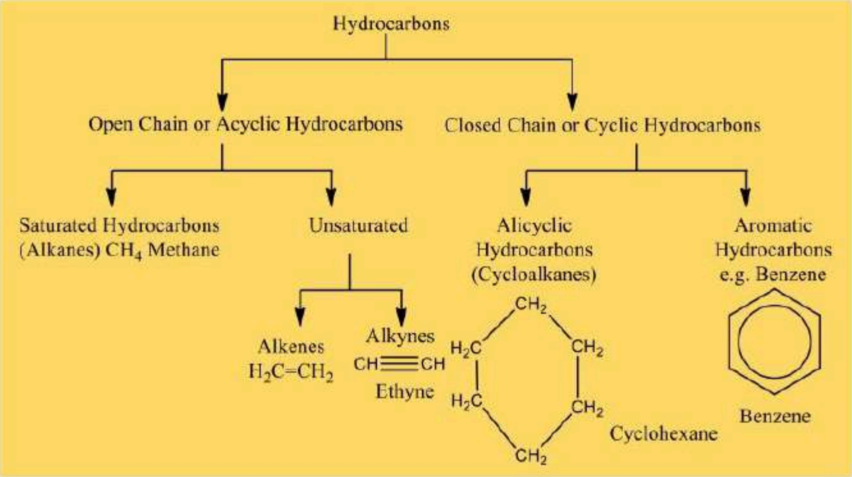
Definition

"Organic compounds which contain carbon and hydrogen only are called hydrocarbons."

The ability of carbon atoms to attach with each other to form a chain or ring is called Catenation.

16.1 TYPES OF HYDROCARBONS

Hydrocarbons have been divided into various classes on the basis of their structure as shown below:



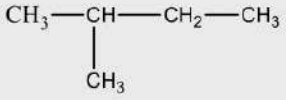
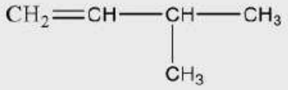
Open Chain Hydrocarbons

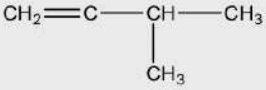
The hydrocarbons in which carbon atoms attached with each other to form open chains are called open chain hydrocarbons.

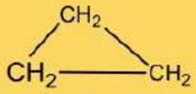
Types:

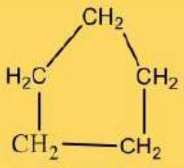
1. Saturated hydrocarbons: (Alkanes or Paraffins)
2. Unsaturated hydrocarbons: (Alkenes or Olefins) and (Alkynes or Acetylenes)

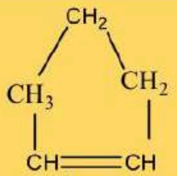
Explanation and Examples:

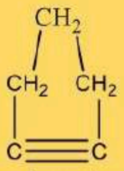
(1) Saturated Hydrocarbons	(2) Unsaturated Hydrocarbons
These are the hydrocarbons in which carbon atoms are attached with each other through single bonds. Each carbon atom is sp^3 hybridized. For example, Alkanes. These may have straight chain or branched chain. $CH_3-CH_2-CH_2-CH_2-CH_3$ pentane (Straight Chain)  $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_3$ 2- Methyl butane (Branched Chain) No further atoms or groups of atoms can be attached to the carbon atoms of such hydrocarbons. This is why they are known as saturated hydrocarbons.	These are the hydrocarbons in which at least two carbon atoms are attached through double or triple bonds, and are sp^2or sp hybridised. For example, alkenes and alkynes. **(i) Alkenes or Olefins:** These are the unsaturated hydrocarbons in which at least two carbon atoms are sp^2hybridized, which cause to from a double bond between these carbon atoms. Alkenes may be straight chain or branched chain. $CH_2=CH-CH_2-CH_3$ 1- pentene (Straight Chain)  $CH_2=CH-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$ 3-Methyl-1-butene (Branched Chain) **(ii) Alkynes or acetylenes:** These are the unsaturated hydrocarbons in which at least two carbon atoms are sp hybridised, which cause

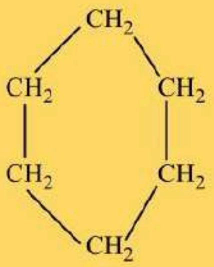
	to form a triple bond between these carbon atoms. Alkynes may be straight chain or branched chain. $CH_2{=}C-CH_2-CH_2-CH_3$ 1 - pentene (Straight Chain)  $CH_2{=}C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$ **3-Methyl-1-butyne (Branched Chain)**


cyclopropane


cyclopentane


cyclopentene


cyclopentyne


cyclohexane

Closed Chain Hydrocarbons:

These are the hydrocarbons in which carbon atoms attach with each other to form rings.

Types: These hydrocarbons are of two types.

1. Alicyclic Hydrocarbons.
2. Aromatic Hydrocarbons.

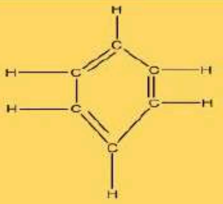
(1) Alicyclic Hydrocarbons:

Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons.

Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons.

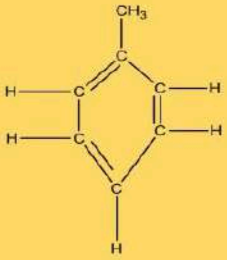
(2) Aromatic Hydrocarbons:

Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons. In these compounds all the carbon atoms present in the ring are sp^2hybridized. Benzene, which is the simplest aromatic hydrocarbon, has a regular hexagonal structure with alternate single or double bonds between carbon atoms.



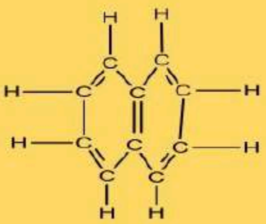
or

benzene



or

toluene



or

naphthalene

Quick Quiz

1. What is catenation?
2. What are hydrocarbons?
3. Why saturated hydrocarbons are called paraffins?
4. Why unsaturated hydrocarbons are called olefins?
5. What is hybridization?
6. Why benzene is called aromatic hydrocarbons?
7. What is hexagonal structure?

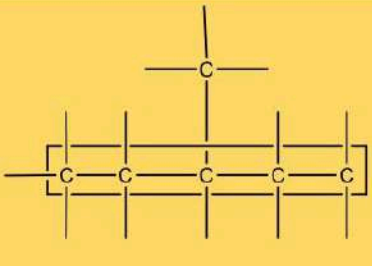
16.2 ALKANES AND CYCLOALKANES

Alkanes

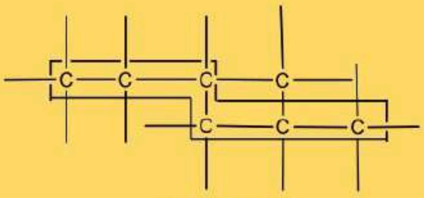
Simplest organic molecules with only C and H atoms. Commercially important as fuels and oils.

16.2.1. Nomenclature

The I.U.P.A.C rules of naming alkanes are as:-

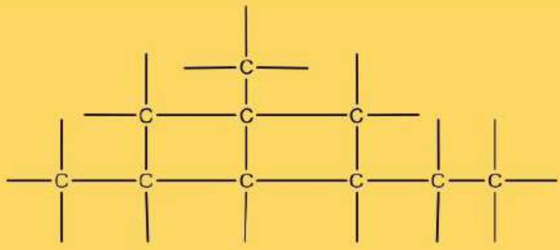


Longest chain
(Horizontal)

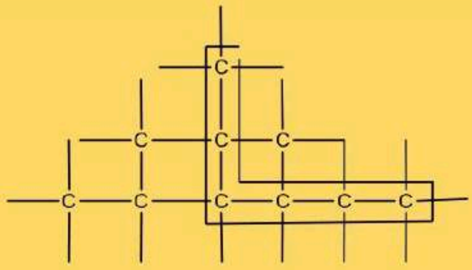


Longest chain
(zig - zag)

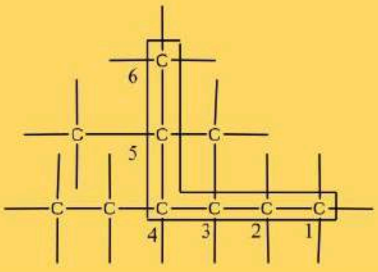
1. Locate the largest continuous chain of carbon atoms independent of direction of the chain. It is called main chain, stem, principal chain or parent chain.
2. If there are two or more chains of equal lengths, the chain with larger number of branches is selected as main chain.
3. Number the main chain starting from the end nearest to the substituent.



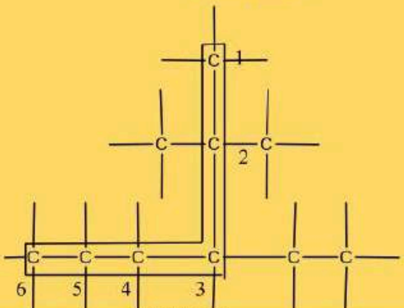
One Branch
(Not main chain)



Three Branches
(main chain)



(Incorrect)

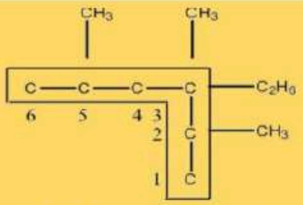


(Correct)

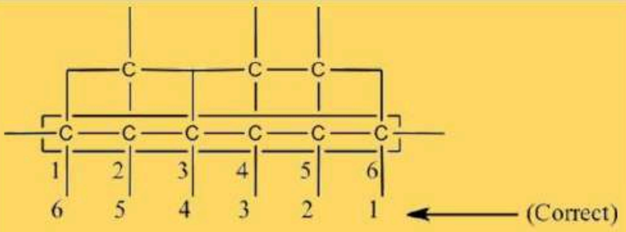
4. When two identical substituents are present at equal distance from either end, number the chain starting with end which gives their minimum sum.

Since the sum of number 2+3+5=10, is less than 2+4+5=11, the correct numbering starts from the right.

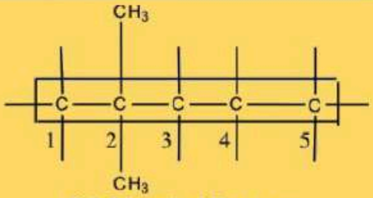
5. The position of substituent is indicated by the number of e-atom to which it is attached. The number is prefixed to the name of group separated by hyphen.



3-Ethyl-2,3,5-tri methyl hexane

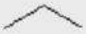


6. Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical order or in order of increasing size, separated by hyphen.
7. When two or more like groups are present, their numbers are indicated by prefixes di, tri-,tetra-, etc. Their numbers are grouped together and are separated by commas.
8. If two identical groups appear at the same C-atom, the number is separated twice, separated by commas.
9. The longest chain of the substituent is numbered starting with the carbon attached directly to the main chain. Parentheses are used to separate the numbering of the substituent and the main chain.



2,2-Dimethyl Pentane

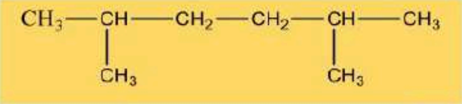
The structural formula and names for the simple alkanes are shown in the following table.

Number of C atoms	Formula	Line Drawing	Alkane Name
1	CH_4	N/A	methane
2	C_2H_6		ethane
3	C_3H_8 or $CH_3CH_2CH_3$		propane
4	C_4H_{10} or $CH_3(CH_2)_2CH_3$		butane
5	C_5H_{12} or $CH_3(CH_2)_3CH_3$		pentane
6	C_6H_{14} or $CH_3(CH_2)_4CH_3$		hexane
7	C_7H_{16} or $CH_3(CH_2)_5CH_3$		heptane
8	C_8H_{18} or $CH_3(CH_2)_6CH_3$		octane
9	C_9H_{20} or $CH_3(CH_2)_7CH_3$		Nonane
10	$C_{10}H_{22}$ or $CH_3(CH_2)_8CH_3$		Decane

Activity

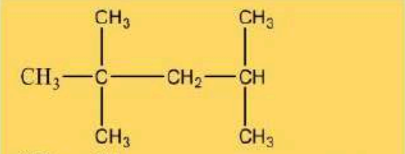
1:- **Name each of the following compounds according IUPAC System.**

a)



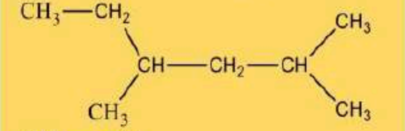
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

b)

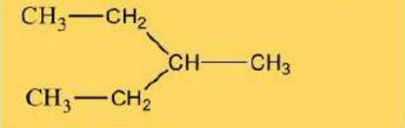


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}$

c)



d)



2:- Indicate what is wrong with each of the following names. Give the correct IUPAC name if possible.

(a) 2-Dimethyl Propane

(b) 2,2,3-Methyl Butane

(c) 3,3-Dimethyle-5,5-Dimethyl Heptane

(d) 2,2-Diethyl-4,4-Dimethyl Pentane

(e) **2**,4-Diethyl Pentane

(f) 3-Ethyl-4-,Methyl Pentane

3:- Write the structures of the following compounds.

(a) Neo heptane

(b) Iso Heptane

(c) Trimethyl Ethyl Methane

(d) Dimethyl Ethyl Isopropyl Methane

(e) Dimethyl Propyl Ethyl Methane

(f) 3-Ethyl Hexane

16.2.2 Physical Properties:

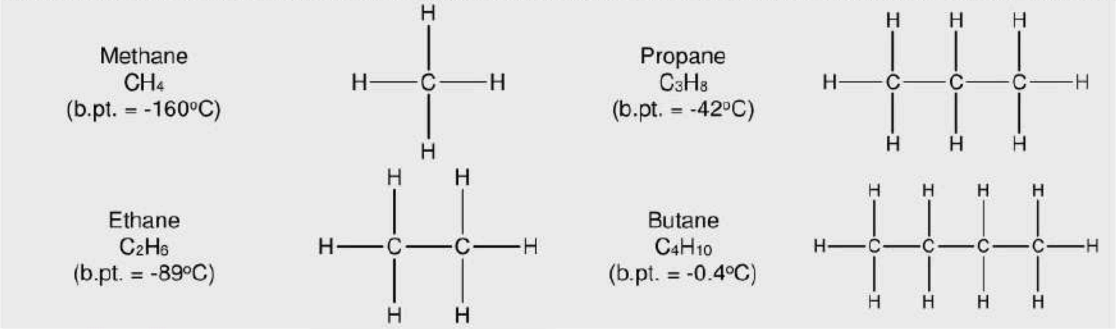
(a) Methane to Butane is colorless, odorless gases while pentane to heptadecane (C_5 to C_{17}) is colorless, odorless liquids. The higher members from C_{18} onwards are waxy solids, which are also colorless and odorless.

(b) 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.

(c) Their boiling points, melting points, density etc increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in mass. The boiling points increases by 20 to 30°C for addition of each CH_2 group to the molecule. However 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 55°C) then iso-butane (-10.2°C).

16.2.3. Structure

Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by single bond. They have a generic formula of C_nH_{2n+2} (a relationship that also defines the maximum number of hydrogen atoms that can be present for a given number of C atoms). Structures of the simple C_1 to C_4 alkanes are shown below in a variety of representations. As the number of C atoms increases then other isomeric structures are possible



Methane
CH_4
(b.pt. = -160°C)

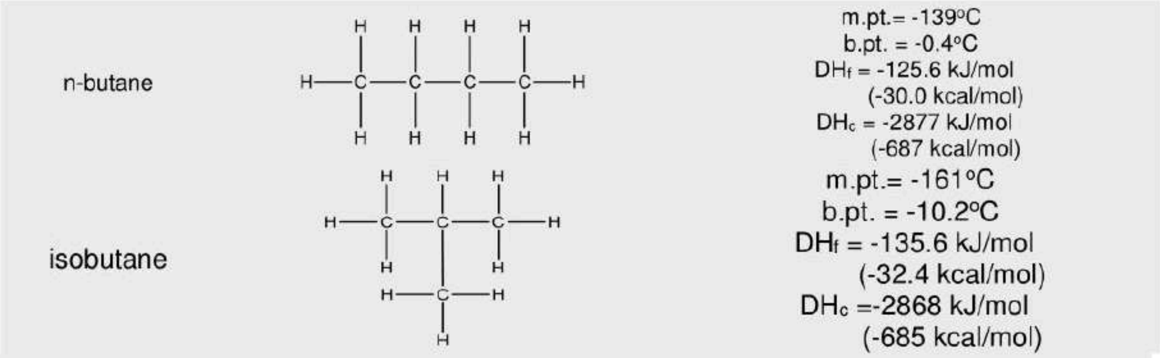
Propane
C_3H_8
(b.pt. = -42°C)

Ethane
C_2H_6
(b.pt. = -89°C)

Butane
C_4H_{10}
(b.pt. = -0.4°C)

Isomeric Alkanes

The molecular formula for the C1 to C3 alkanes lead to single, unique structures. However for C_4H_{10}, there are two possible constitutional isomers. It is important to be able to recognize isomers because there can have different chemical, physical properties and biological properties. The constitutional isomers of C_4H_{10} are shown below along with some properties:



n-butane

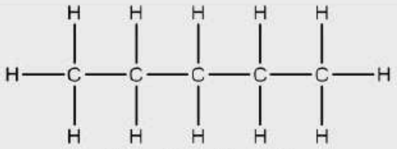
m.pt.= -139°C
b.pt. = -0.4°C
DH_f = -125.6 kJ/mol
(-30.0 kcal/mol)
DH_c = -2877 kJ/mol
(-687 kcal/mol)

isobutane

m.pt.= -161°C
b.pt. = -10.2°C
DH_f = -135.6 kJ/mol
(-32.4 kcal/mol)
DH_c =-2868 kJ/mol
(-685 kcal/mol)

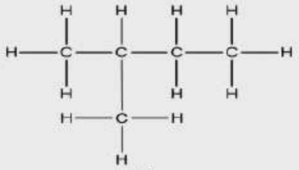
C_5H_{12} has three possible constitutional isomers:

n-pentane



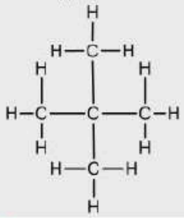
b.pt. = 36.1 °C
DH$_f$ = -147 kJ/mol
(-35.1 kcal/mol)
DH$_c$ = - 3509 kJ/mol
(- 839 kcal/mol)

isopentane



b.pt. = 30 °C
DH$_f$ = -154.1 kJ/mol
(-36.8 kcal/mol)
DH$_c$ = -3502 kJ/mol
(-837 kcal/mol)

neopentane



b.pt. = 9.5 °C
DH$_f$ = -168.0 kJ/mol
(-40.1 kcal/mol)
DH$_c$ = -3493 kJ/mol
(- 835 kcal/mol)

16.2.4. Relative Stability

Branched alkanes are more stable than linear alkanes, *e.g.* 2-methylpropane is more stable than n-butane.

16.2.5 Reactivity

The Alkanes or Paraffins are inert towards acids, alkalies, oxidizing and reducing agents under normal conditions.

Explanation:

The unreactivity of Alkanes can be explained on the basis of inertness of a δ bond and non-polar C-H/C-C bonds.

(i) Inertness of δ bond

In a δ bond the electrons are very tightly held between the nuclei. A lot of energy is required to break it. Moreover, the electrons present in a δ bond can neither attack on any electrophile nor a nucleophile can attack on them. Hence Alkanes are less reactive.

(ii) Non-polar Bonds:

The electronegativity 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 nonpolar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc find no reaction in the alkane molecules to which they could be attached.

However, under suitable condition, Alkanes give two types of reactions.

(i) Thermal and Catalytic Reactions

(ii) Substituted Reactions.

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

II. Cycloalkanes

Another type of molecule containing only sp^3 hybridized C and H atoms connected by single bonds is possible with a ring of 3 or more C atoms. These are the **cycloalkanes** which are fairly common in the world of organic chemistry, both man-made and natural.

1. Nomenclature

According to IUPAC system, cyclo alkanes with one ring are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring, e.g.

Cyclo propane

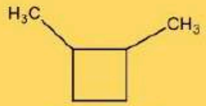
Cyclo butane

Cyclo pentane

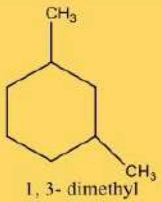
The substituents are numbered in such a way that the sum of numbers is kept minimum, e.g.

If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond) are used, e.g,

Methyl cyclo propane

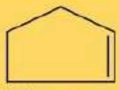


1, 2- dimethyl cyclo butane



1, 3- dimethyl cyclo hexane

Multiple bonds are given the lowest possible number.



Cyclo pentene

Cyclo1, 4 hexadiene

cyclo 1, 3-pentadiene

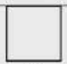
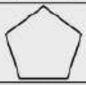
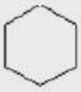
2. Physical Properties

Like alkanes, the low polarity of all the bonds in cycloalkanes means that the only intermolecular forces between molecules of cycloalkanes are the very weak induced dipole - induced dipole forces, also known as **London forces** which are easily overcome. Like alkanes, cycloalkanes also to have low melting and boiling points.

3. Structure

They have a generic formula of C_nH_{2n}, (note: there 2 less H atoms compared to the analogous alkane).

The C3 to C6 cycloalkanes are shown below in a variety of representations.

Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	

4. Reactivity

Very similar reactivity to the closely related alkanes which have the same types of bonds.

Since C and H atoms have very similar electronegativities, both the C-H and C-C bonds are non-polar. As a result, cycloalkanes, like alkanes, are not a very reactive functional group.

Quick Quiz

1. What are polar, non polar and weakly polar compounds?
2. What are isomers?
3. What are inert compounds?
4. What is sigma bond?
5. What are intramolecular and intermoleualr forces.

16.3 RADICAL SUBSTITUTION REACTIONS

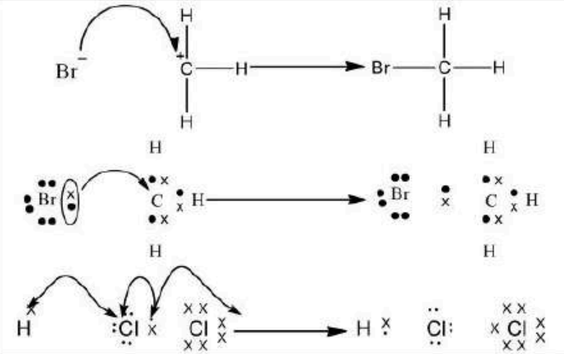
16.3.1 Overview

- Substitution of R-H by X provides the alkyl halide, R-X and HX.
- Alkane R-H relative reactivity order: 3° > 2° > 1° methyl.
- Halogen reactivity $F_2 > Cl_2 > Br_2 > I_2$.
- Only chlorination and bromination are useful in the laboratory.
- Reaction proceeds via a radical chain mechanism

16.3.2 Reaction Mechanism

Interesting information:

When reaction mechanisms are being described, a 'curly arrow' is sometimes used to show the movement of a pair of electrons. The beginning of the arrow shows where the electron pair starts from and the arrow head shows where the pair ends up. Figure 16.1. shows a pair of electrons moving from the Br- ion to the region between the bromine and the carbon, where it forms a covalent bond between the atoms. The same reaction is



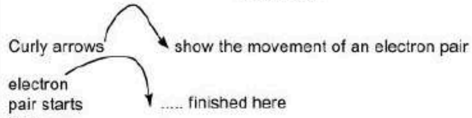
shown again below, with all the bonding electrons indicated.

A half-arrow is used to show the movement of a single electron in reactions involving free radicals. The beginning of the arrow shows where the single electron starts from and the half-arrow head shows where it ends up.

For example, figure 16.3 summarizes the way curly arrows and half-arrows are used.

The mechanism for the bromination of methane is shown below, but the mechanism for chlorination or higher alkanes is the same. Note that it contains three distinct types of steps, depending on the net change in the number of radicals that are present.

Fig. 16.3



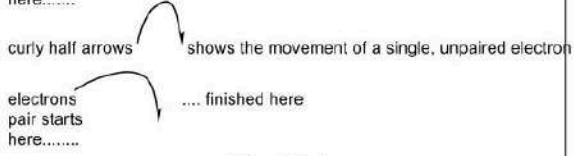


Fig. 16. 4

RADICAL CHAIN MECHANISM FOR REACTION OF METHANE WITH Br_2

Step 1 (Initiation)

Heat or uv light cause the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.

Step 2 (Propagation)

(a) A bromine radical abstracts a hydrogen to form HBr and a methyl radical, then (b) The methyl radical abstracts a bromine atom from another molecule of Br_2 to form the methyl bromide product and ***another*** bromine radical, which can then itself undergo reaction 2 (a) creating a cycle that can repeat.

Step 3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.

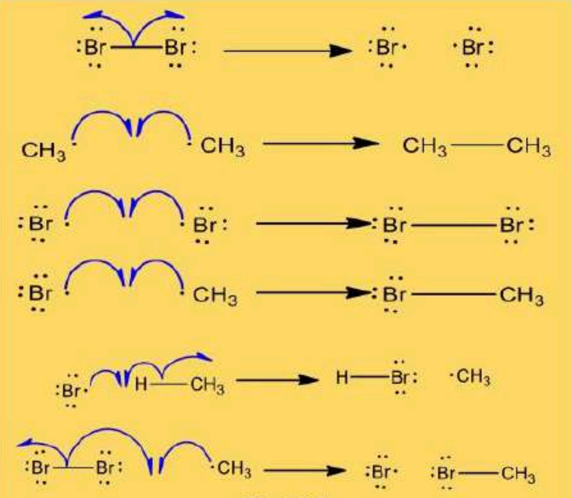


Fig. 16.5

16.4 OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

Oxidation, [O], and reduction, [R], are opposites and both must occur simultaneously, hence ***redox reactions.***

Organic chemists will normally describe a reaction as either oxidation or reduction depending on the fate of the major organic component.

Oxidation:

- more C-O bonds (or other atoms more electronegative than C)
- less C-H bonds
- loss of electrons
- increased oxidation state, *e.g.* +1 to +3

Reduction:

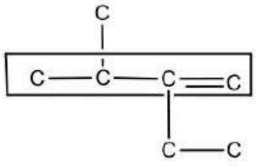
- more C-H bonds
- less C-O bonds (or other atoms more electronegative than C)
- gain of electrons
- decreased oxidation state, *e.g.* +1 to -1

16.5 ALKENES

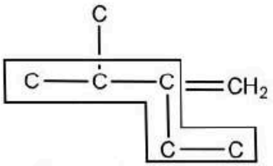
16.5.1. Nomenclature

IUPAC system for naming Alkenes are as:-

1) The longest continuous chain containing double bond is selected as parent chain.
2) The ending 'ane' is replaced by 'ene'.
3) The chain is numbered in such a manner as to give minimum number to the doubly bonded C-atoms.

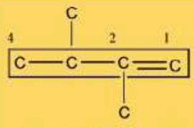


The parent chain containing double bond (correct)

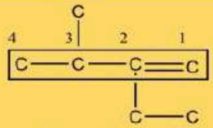


Longest chain with no double bond (incorrect)

4) The position of double bond is indicated by the lower number of C-atom.

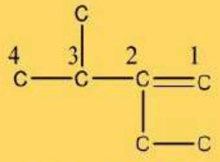


2 - ene (incorrect)



1 - ene (correct)

5) The lower number of C-atom is placed before the name of parent alkene.
6) The presence of more than one double bond is indicated by the suffix -diene for two double bonds, -triene for three double bonds and so on.
7) Alkyl groups are indicated by the methods mentioned in alkane.



2-Ethyl-3-methyl-1-butene

Activity

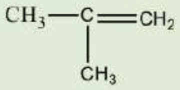
1. Name the following Olefins by the IUPAC Systems

a. $CH_2=CH_2$

b $CH_3-CH=CH_2$

c $CH_3-CH_2-HC=CH-CH_2-CH_3$

d

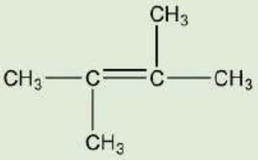


$CH_3-\underset{\substack{|\\CH_3}}{C}=CH_2$

e $CH_2=CH-CH=CH-CH_3$

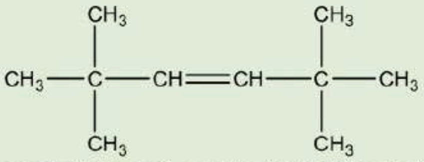
f $CH_2=C=C=CH-CH_2-CH_3$

g.



$CH_3-\underset{\substack{|\\CH_3}}{C}=\overset{\substack{CH_3\\|}}{C}-CH_3$

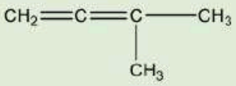
h



$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH=CH-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3$

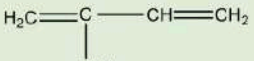
2. Name the compounds (a) and (b) by IUPAC nomenclature and compounds (c) and (d) by their trivial/common names and (e) by its derived name.

(a).



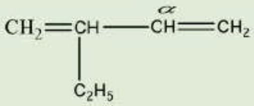
$CH_2=C=\underset{\substack{|\\CH_3}}{C}-CH_3$

(b)



$H_2C=\underset{\substack{|\\C_2H_5}}{C}-CH=CH_2$

(c)



$CH_2=\underset{\substack{|\\C_2H_5}}{CH}-\overset{\alpha}{CH}=CH_2$

(d) $\overset{\alpha}{CH_3}-\overset{\beta}{CH_2}-\overset{\lambda}{CH}=CH-CH_2-CH_2-CH_3$

(e) $CH_2=CH-CH_3$

3. Write structural formulas for the following compounds and discuss the geometric isomerism in each case.

(a) 1,3-Buta dience

(b) 1,2- Penta diene

(c) 2,4 -Hexa dience

(d) 2-Methyl-1,3-buta diene

(e) 3-Methyl-1,3-pentadiene

16.5.2. Relative Stability

There are 3 factors that influence alkene stability:

1. **Degree of substitution:** More highly alkylated alkenes are more stable, so stability of alkenes decreases in the following order:

tetra > tri > di > mono-substituted.

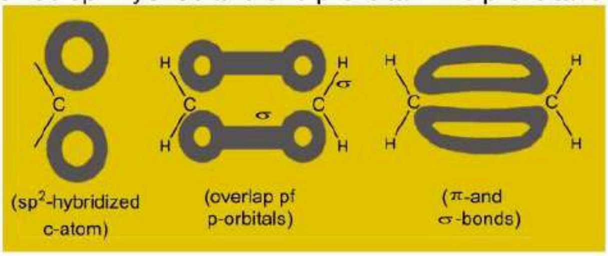
2. Stereochemistry: Trans alkenes are more stable than cis alkenes due to reduced stearic interactions when R groups are on opposite sides of the double bond.

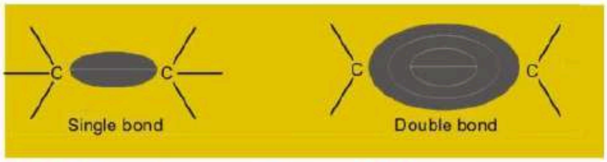
3. Conjugated alkenes are more stable than isolated alkenes.

1,3-Butadiene is more stable than 1,4-butadiene

16.5.3 Structure

The carbon atoms linked through π-bond are sp^2 hybridized. Therefore, each atom carries three sp^2-hybrids and one p-orbital. The p-orbital overlap to form π-bond and hybrid orbitals form σ-bonds due to linear overlap.





The carbon-carbon distance in ethene is shorter (1.34A) than the C-C bond distance of ethane (1.54A). It is due to increased electron density between carbon atoms.

Carbon atoms are coplanar, and the rotation of one C-atom with respect to other is restricted which results in cis-trans isomerism in alkene.

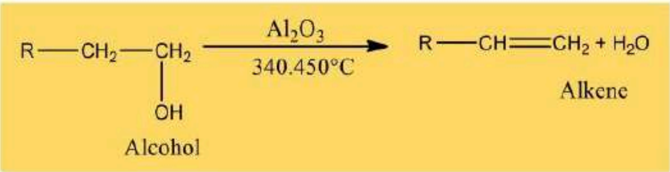
16.5.4. Preparation of Alkenes

1. Dehydration of Alcohols

Removal of water molecule is called dehydration.

Example

When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.

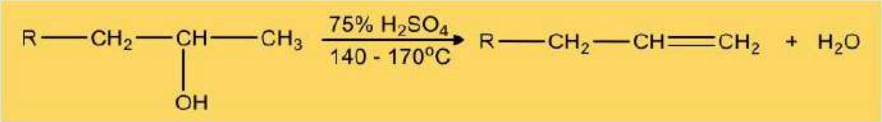


$$\underset{\text{Alcohol}}{R-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}} \xrightarrow[340.450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

P_4O_{10}, H_2SO_4, H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order.

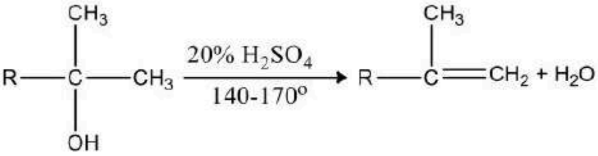
Ter.alcohol > sec.alcohol > pri.alcohol

For secondary alcohol



$$R-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[140-170^\circ C]{75\%\ H_2SO_4} R-CH_2-CH=CH_2 + H_2O$$

For tertiary alcohold



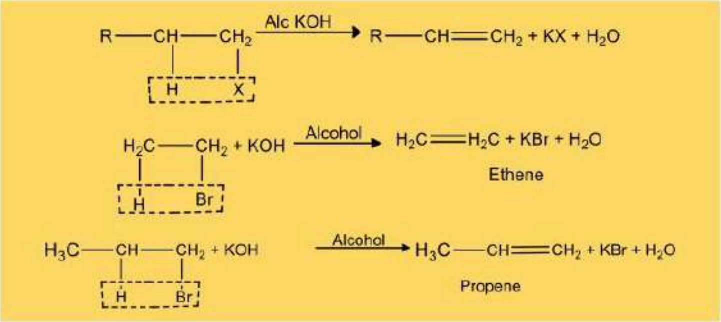
$$R-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3 \xrightarrow[140-170^\circ]{20\%\ H_2SO_4} R-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + H_2O$$

2. Dehydrohalogenation of Alkyl Halides

Removal of hydrogen halide (HX) from alky halides is called Dehydrohalogenation"

Example

Alkyl halides on heating with alcoholic potassium hydroxide undergo Dehydrohalogenation to form alkenes.



16.5.5 Reactivity

There is a relatively diffuse region of high electron density in alkenes as compared to alkanes. This is due to π-bonds in alkenes. Since an ethene π-bond is weaker than σ-bond, it requires less energy to break a π-bonds. Hence the reactions of alkenes involve weaker π-bond and electrophillic addition occurs. It involves the change of a π-bond to sigma bond through addition reactions.

16.5.6 Reactions

Hydrogenation

A process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5atm) to give a saturated compound is known as catalytic hydrogenation.

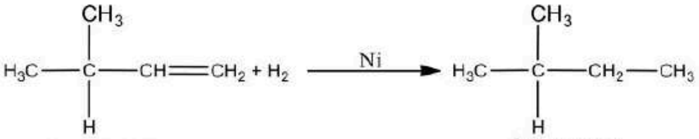
Explanation:

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 alkene is about 120kJ mole^{-1} for each double bond present in a molecule. The catalysts employed are Pt, Pd and Raney Nickel.

Raney Nickel:

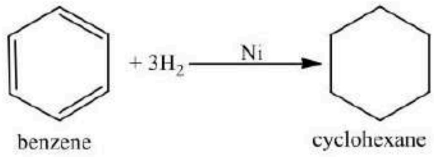
It is prepared by treating a Ni – Al alloy with caustic soda.

$$Ni{-}Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + {}^{3}/_{2}H_2$$



3-methyl-1-butene

iso-pentane

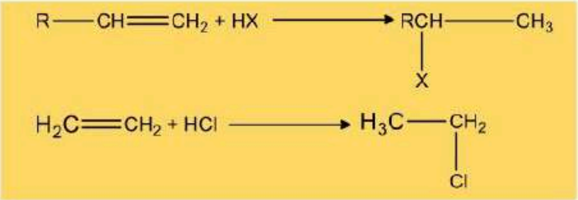


Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of vegetable ghee from vegetable oils. In the laboratory, it is used as a synthetic as well as an analytical tool.

Hydrohalogenation

Alkenes react with aqueous solution of halogen acid to form alkyl halides.

The order of reactivity of halogen acids is HI>HBr>HCl

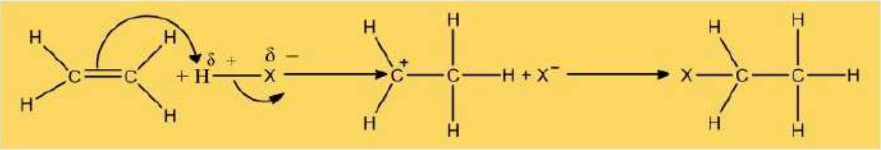


$$R-CH=CH_2 + HX \longrightarrow RCH(X)-CH_3$$

$$H_2C=CH_2 + HCl \longrightarrow H_3C-CH_2Cl$$

Mechanism of Reaction:

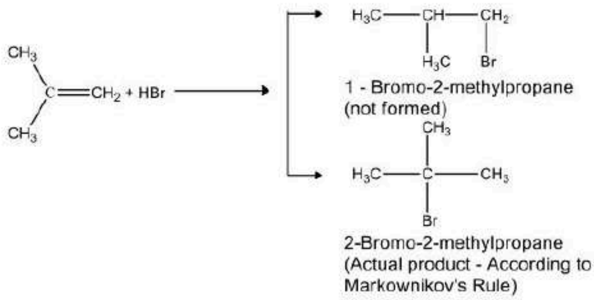
The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a corbocation. The carbocation then reacts with the halide ion.



Markownikov's Rule:

The addition of hydrogen halide over an unsymmetrical alkene is according to Markownikov's Rule. Which states that; in the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms.

Example:



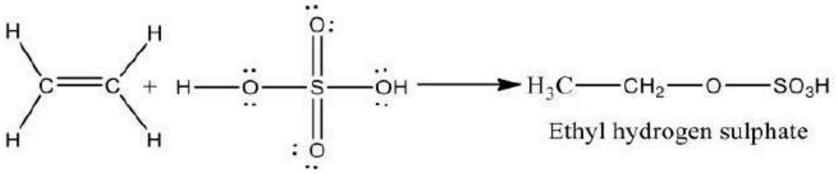
1 - Bromo-2-methylpropane
(not formed)

2-Bromo-2-methylpropane
(Actual product - According to
Markownikov's Rule)

Hydration

Addition of water is called hydration. Some reactive alkenes react with water in the presence of suitable substances as acid etc. to form alcohol. It is possible as alkenes are soluble in cold concentrated sulfuric acid. They react by addition to form alkyl hydrogen sulphate.

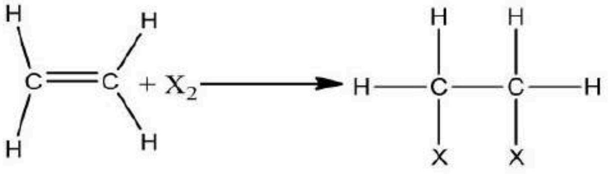
These alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.



$$H_2C-CH_2-O-SO_3H + H_2O \xrightarrow{100^\circ C} H_3C-CH_2-OH + H_2SO_4$$

Halogenation

The alkenes react with halogen in an inert solvent like carbon tetrachloride at room temperature to give vicinaldihalides or 1,2 dihalogenatd products.


Vicinal dihalide

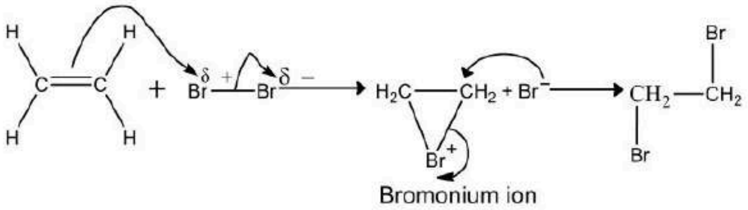
Br_2 and Cl_2 are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

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 ions to form vic. dibromide and the color of bromine is discharged.

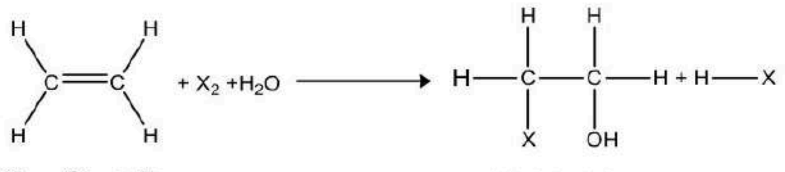
This test is applied for the detection of double bond in a molecule.



Halohydration

Addition of hypohalous acid (HOX) is called halohydration.

Alkenes react with hypohalous acid to give halohydrin. In this reaction, molecules of the solvent become reactants too.

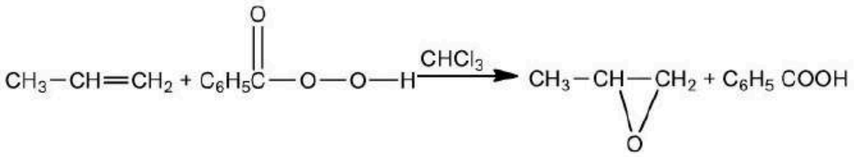


$X_2 = Cl_2$ or Br_2

Halohydrin

Epoxidation

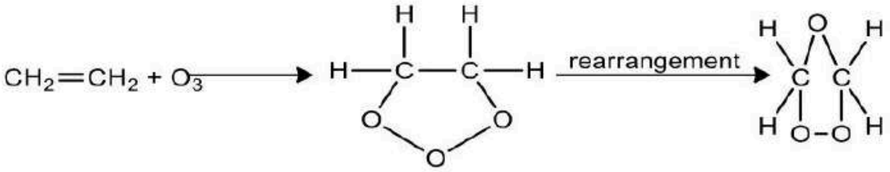
It is the formation of epoxides. Peracids such as per oxyacetic acid or peroxy benzoic acid react with alkenes to form epoxides.



(Epoxy propane) Benzoic acid

Ozonolysis

Ozone (O_3) reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.



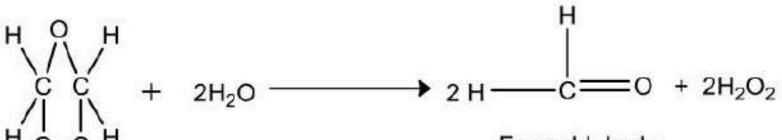
Molozonide (unstable)

Ozonide

Reduction Ozonide

Ozonides are unstable compounds and are reduced directly on treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).

Ozonolysis is used to locate the position of double bond in an alkene. The C-atom of double bond is changed to carbonyl group.

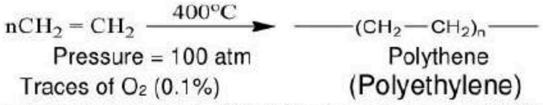


Formaldehyde

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Polymerization

Polymerization is a process in which a small organic molecules which are called monomers combine together to form a larger molecule. The substances so produced are called polymers.



$$nCH_2=CH_2 \xrightarrow[\text{Pressure = 100 atm, Traces of } O_2 \text{ (0.1\%)}]{400^\circ C} -(CH_2-CH_2)_n-$$

Polythene
(Polyethylene)

Ethene polymerizes to polythene at 400 °C at a pressure of 100 atm.

A good quality polythene is obtained when ethane is polymerized in the presence of aluminium triethyl $Al(C_2H_5)_3$ and titanium tetrachloride ($TiCl_4$).

Interesting Information

Examples of natural and synthetic polymers

	Polyhmer	Monomer	Where your find it
		Amino acids	Wool, silk, muscle, etc
Natural	Protein	Glucose	Potato, wheat, etc
	Starch	Glucose	Paper, wood, dietary fibre chromosomes,
	Cellulose	Nucleotides	genes
	DNA		Bags, washing-up bowls, etc
	Poly (ethane)	Ethane	Fabric coatings, electrical insulation, toys,
Synthetic	Poly (chloroethene)	Chloroethene	expanded polystyrene
	(PVC)	Phenylethene	Skirts, shirts, trousers
	Poly (phenylethene)		
	(polystyrene)	Ethane-, 2-diol and	
	polyester	benzene- 1, 2-	
		dicarboxylic acid	

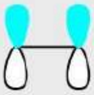
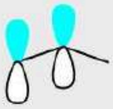
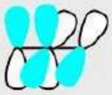
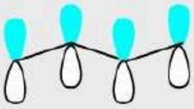
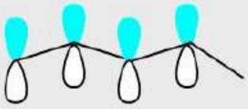
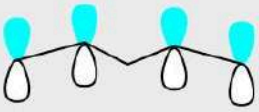
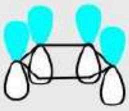
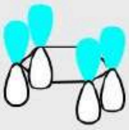
16.5.7 Conjugation

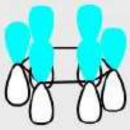
The word "***conjugation***" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when p systems are "linked together".

- An "***isolated***" p system exists only between a single pair of adjacent atoms (*e.g.* **C=C**)
- An "***extended***" p system exists over a longer series of atoms (*e.g.* **C=C-C=C** or **C=C-C=O** *etc.*).
- An extended p system results in a extension of the chemical reactivity.

The fundamental requirement for the existence of a conjugated system is revealed if one considers the orbital involved in the bonding within the system.

- A conjugated system requires that there is a continuous array of "p" orbitals that can align to produce a bonding overlap along the whole system.
- If a position in the chain does not provide a "p" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point. You can investigate these differences by studying the following examples, pay particular attention to the "p" orbitals:

System	p system	Type
ethene		isolated
propene		isolated
1,2-propadiene (allene)		cumulated
1,3-butadiene		conjugated
1,3-pentadiene		conjugated
1,4-pentadiene		isolated
1,3-cyclopentadiene		conjugated
1,3-cyclohexadiene		conjugated
1,4-cyclohexadiene		isolated

benzene		conjugated

The result of conjugation is that there are extra p bonding interactions between the adjacent p systems that results in an overall stabilisation of the system.

Quick Quiz

1. What is conjugations?
2. What are conjugated alkenes?
3. What is pi bond?
4. What are s and p orbitals?
5. What is dehydration?
6. What id dehydrohalogenation?
7. What is hydrogenation?
8. What is ozonolysis?
9. What is Markownikov's rule?
10. What is electrophilic reagent?
11. What is nucleophilice reagent?
12. What is halohydration?
13. What is polymerization?

16.6 ISOMERISM

Compounds that have the same molecular formula but different chemical structures are called *isomers* and the phenomenon is called *isomerism.*

Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. There are two main types of isomerism:

(1) Structural Isomerism (2) Stereoisomerism

Structural Isomerism: When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called Structural Isomerism. In other words, structural isomers are compounds that have the same molecular formula but different structural formulas. Structural isomerism is of five types:

(a) Chain isomerism (b) Position isomerism (c) Functional group isomerism (d) Metamerism (e) Tautomerism

Stereoisomerism: When isomerism is caused by the different arrangements / orientation of atoms or groups in space, the phenomenon is called Stereoisomerism. The stereoisomers have the same structural formulas but differ in arrangement of atoms in space. In other words stereoisomer is exhibited by such compounds which have the same structural formula but differ in configuration, (The term configuration refers to the three-dimensional arrangement of atoms that characterizes a particular compound). Stereoisomerism is of two types:

(a) Geometrical or Cis-Trans Isomerism (b) Optical Isomerism

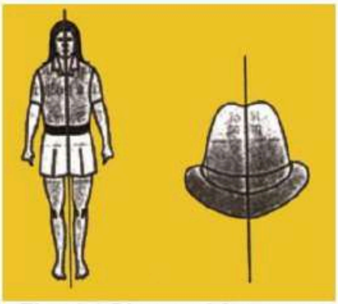


Fig.16.6 Planes of Symmetry

16.6.1 Chiral Center

First, we will discuss plane of symmetry which help us to understand this topic.

Plane of Symmetry

A plane which divides an object into two symmetrical halves, is said to be plane of symmetry. For example, a person or a hat has a plane of symmetry (Fig. 16.8). A person's hand or gloves lack plane of symmetry.

An object lacking a plane of symmetry is called dissymmetric or Chiral (pronounced as Ki-ral). A symmetric object is referred to as Achiral.

Fig.16.7 The mirror image relationship of the left hands, Notice that right hand is the mirror image of the left hand.

A dissymmetric object cannot be superimposed on its mirror image. A left hand for example does not possess a plane of symmetry, and its mirror image is not another left hand but a right hand (Fig. 16.7). The two are not identical because they cannot be superimposed. If we were to lay one hand on top- of the other, the fingers and the thumb would clash.

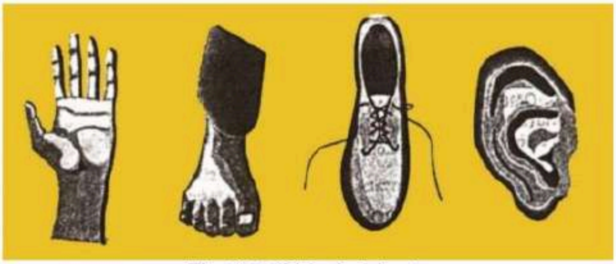


Fig 16.8 Chiral objects

Achiral molecule has at least one asymmetric center and does not have a plane of symmetry.

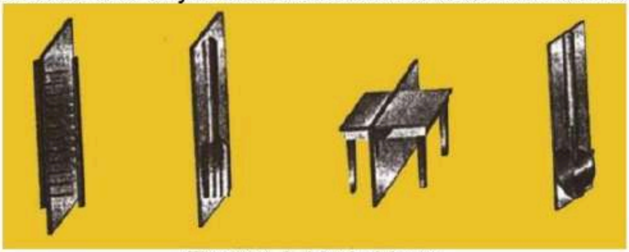
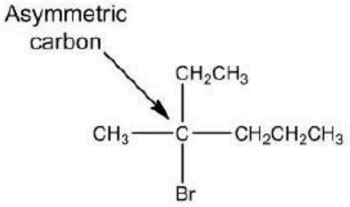


Fig 16.9 Achiral objects

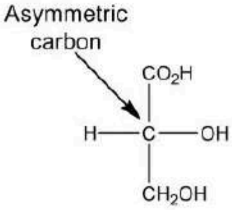
An achiral molecule has a plane of symmetry

16.6.2 Carbon-Based Chiral Centers:

A carbon atom which is bonded to four different groups is called an Asymmetric Carbon Atom. Examples are:



$$\begin{array}{ccc} & CH_2CH_3 & \\ & | & \\ CH_3- & C & -CH_2CH_2CH_3 \\ & | & \\ & Br & \end{array}$$



$$\begin{array}{ccc} & CO_2H & \\ & | & \\ H- & C & -OH \\ & | & \\ & CH_2OH & \end{array}$$

The term asymmetric carbon atom is rather misleading. It only means that a carbon atom is bonded to four different groups and that a molecule of this type lacks plane of symmetry. Such a molecule is called asymmetric (Latin a = without), that is, without symmetry. Presently the term Dissymmetric or Chiral Molecules is often for asymmetric molecules.

16.6.3. Optical Activity

Light from ordinary electric lamp is composed of waves vibrating in many different planes. When it is passed through Nicol prism (made of calcite, $CaCO_3$) or polaroid lens, light is found to vibrate in only one plane, and is said to be plane-polarized or simply polarized. The diagrams illustrate the vibrations of ordinary and polarized light from a beam propagated perpendicularly to the plane or paper. Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be Optically Active. This property of a compound is called Optical Activity.

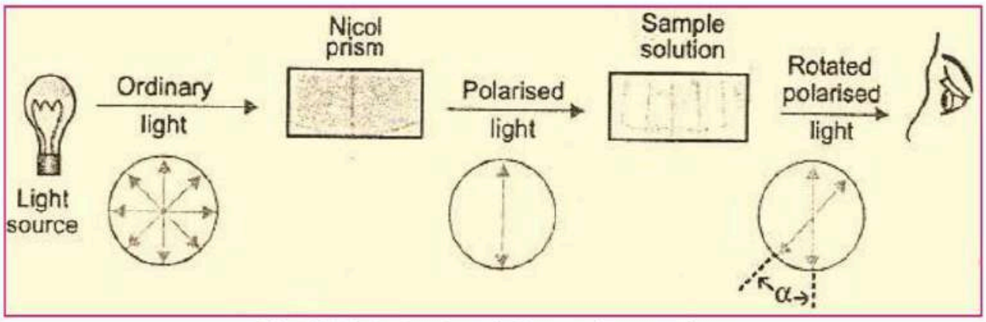


Fig.16.10 A simple polarimeter in operation

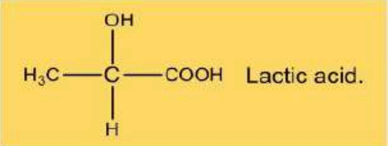
Optical activity in a compound is detected and measured by means of a Polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarized light is rotated through a certain number of degrees, either to the right (clockwise) or to the left (antic-clockwise). The compound which rotates the plane of polarized light to the right (clockwise) is said to be Dextrorotatory. It is indicated by the sign (+). The compound which rotates the plane of polarized light to the left (anticlockwise) is said to Laevorotatory. It is indicated by the sign (-). The magnitude of rotation in degrees is referred to as observed rotation, alpha, Fig 16.10 shows the part of polarimeter.

16.6.4. Optical isomerism

An optically active compound can exist in two isomeric forms which rotate the plane of polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical Isomerism.

The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory Isomer** or (+) isomer. The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Laevorotatory Isomer** or (-) isomer.

Optical Isomerism of Lactic Acid

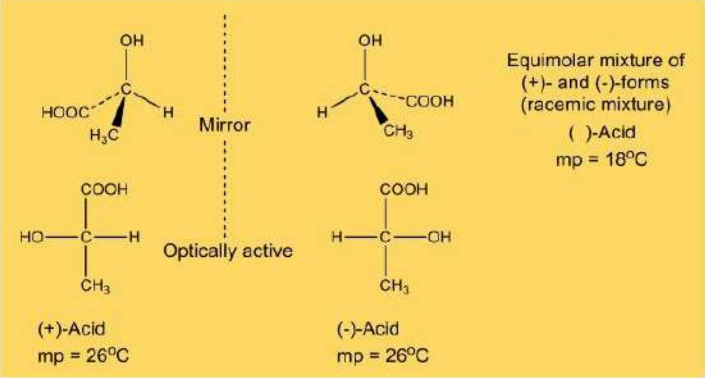


$$\begin{array}{c} \text{OH} \\ | \\ H_3C-C-COOH \\ | \\ H \end{array}$$

Lactic acid.

Lactic acid (2-Hydroxypropanoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom. Two three dimensional structures are possible for Lactic acid. These structures are not identical because they cannot be superimposed on each other. On the mirror image of the other, such non superimposable mirror image forms are optical isomers and called *enantiomers*. Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive.

(+) Lactic Acid: it rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.



(-) Lactic Acid: it rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (-) Lactic acid is the mirror image of (+) lactic acid and vice versa.

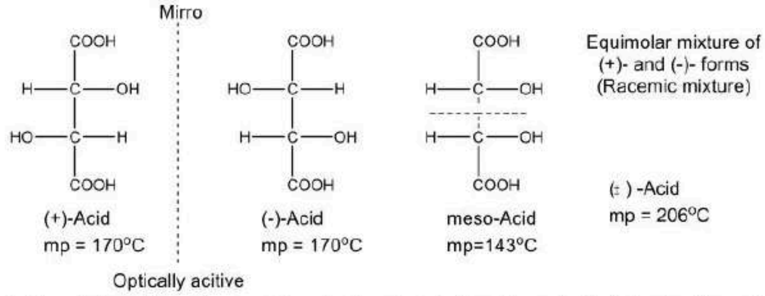
(±) Lactic Acid: it does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms.

Four forms of tartaric acid are known. Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image. That is, they are enantiomers.

Isomers of Tartaric Acid



(+)Tartaric Acid: It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory. (-) Lactic acid is the mirror image of (+) lactic acid and vice versa.

(-) Tartaric Acid: It rotates the plane of polarized light to the left (anticlockwise direction) is called levorotatory.

(±)Tartaric Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

16.6.5. Sterioisomerism - Geometric isomerism

It is of two types:

1. Optical isomerism (already discussed in sections 16.6.3 and 16.6.4)
2. Geometric or Cis-trans Isomerism.

Its explanation is given below

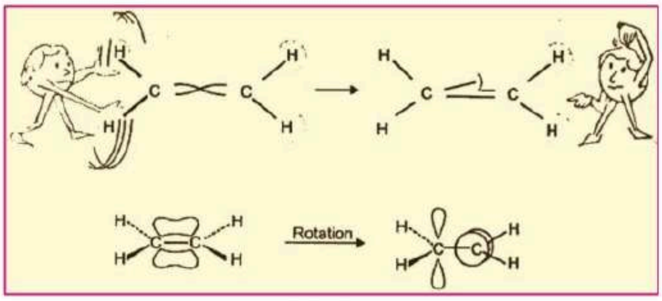


Fig. 16.11

Geometrical Isomerism

Geometrical isomerism (also called cis-trans isomerism) results from a restriction in rotation about double bonds, or about single bonds in cyclic compounds.

(I) Geometrical Isomerism in Alkenes

The carbon atoms of the carbon-carbon double bond are sp^2 hybridized. The carbon-carbon double bond consists of a sigma bond and a pi bond. The sigma bond is formed by the overlap of sp^2 hybrid orbitals. The pi bond is formed by the overlap of p orbitals. The presence of the pi bond locks each molecule in one position. The two carbon atoms of the C=C bond and the four atoms that are attached to them lie in one plane and their position in space are fixed. Rotation around the C=C bond is not possible because rotation would break the pi bond.

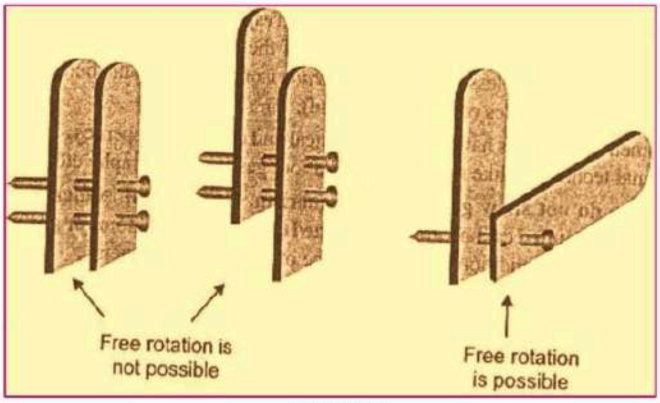


Fig. 16.12

Rotation about pi bond is not possible because it would break the pi bond

This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes. A popular analogy for this situation is based upon two bonds and two nail. Driving one nail through two boards will not prevent free rotation of the two bonds. But once a second nail used, the boards cannot be freely rotated.

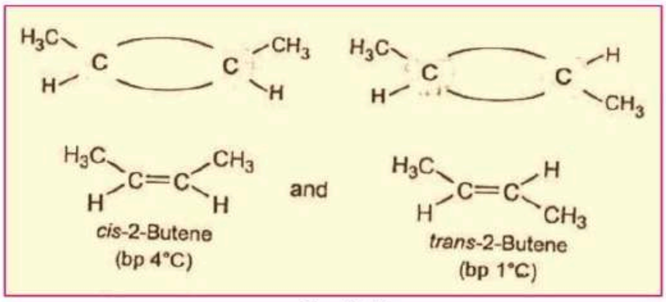


Fig. 16.13

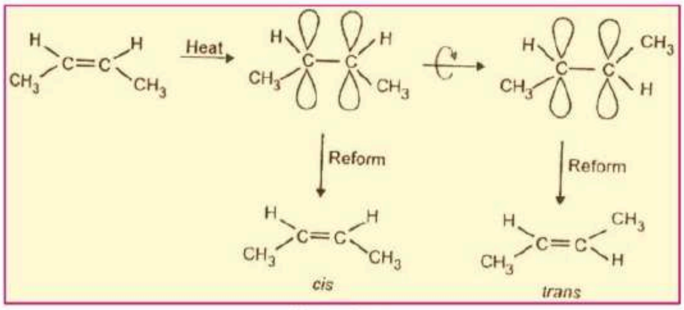


Fig. 16.14

Consider the case of 2-butene. It exists in two special arrangements:

These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms cis and Trans. **The cis isomer is one in which two similar groups are on the same side of the double bond. The Trans isomer is that in which two similar groups are on the opposite sides of double bond**. Consequently, this type of isomerism is often called cis-trans isomers. Geometrical isomers are stereoisomer, because they have the same structural formula but different special arrangement of atoms.

The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62 Kcal/mole) to break the pi bond so that rotation about sigma bond becomes possible. Upon cooling, the reformation of the pi bond can take place in two way giving mixture of trans-2-butene plus cis-2-butene.

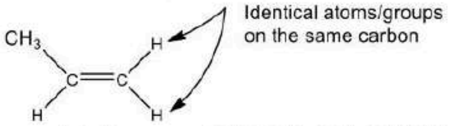
The trans isomers are more stable than the corresponding cis isomers. This is because, in cis isomer, the bulky groups are on the same side of the double bond. The stearic repulsion of groups makes the cis isomers less stable than the trans isomer in which the bulky groups are far (they are on the opposite sides of the double bond).

The geometrical isomers have different physical and chemical properties. They can be separated by conventional physical techniques like fractional distillation, gas chromatography etc.

All alkenes do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded carbon atoms is attached to two different atoms or groups. The following examples illustrate this condition for the existence of geometrical isomers.

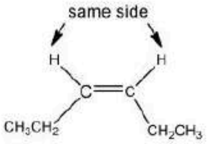
Example 1. Consider the case of Propene

No geometrical isomers are possible for propene ($CH_3CH=CH_2$). This is because one of double bonded carbons has two identical groups (H atoms) attached to it.

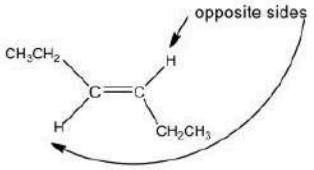


Example 2. Consider the case of 3-Hexene ($CH_3CH_2CH=CHCH_2CH_3$)

This is because each double bonded carbon atom is attached to two different groups (CHCH and H). the cis and trans isomers of 3-hexene are shown below:



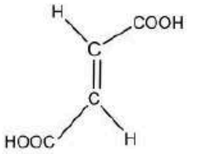
cis-3-Hexene



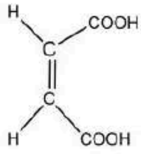
trans-3-Hexene

Example 3. Consider the case of Butenedioic acid. (HOOC-CH=CH-COOH)

Geometrical isomers are possible has this because each double bonded carbon atoms has two different groups attached to it (H and COOH).



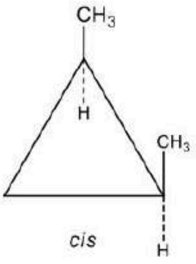
trans-butenedioic acid
(Fumaric acid)
mp 130°C



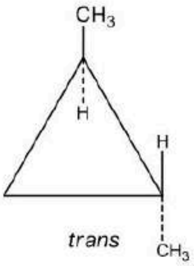
cis-butenedioic acid
(Maleic acid)
mp 288°C

(2) Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break ring. For example 1,2-dimethylcyclopropane exists in two isomeric forms.

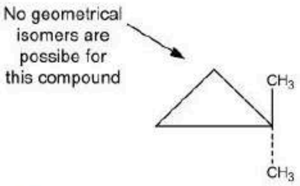


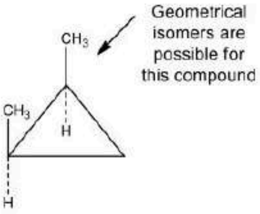
cis



trans

In cis-1,2-dimethylcyclopropane the two methyl groups are on the same side of ring. In trans 1, 2-dimethylcyclopropane, they are on opposite sides. A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups beside hydrogen on the ring and these must be on different ring carbon atoms. For example, no geometrical isomers are possible for 1,1-dimethylcyclopropane.





16.6.6 Structural Isomerism

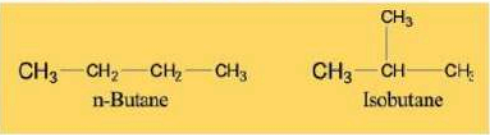
In structural isomerism the isomers have the same molecular formula but differ in structural formula Structural isomerism is of five types:

1). Chain Isomerism:

Chain isomers have the same molecular formula but differ in order in which the carbon atoms are bonded to each other. For example.

Example 1. n-Butane and Isobutane

Example 2. 2-Methylbutane and 2,2-Dimethylpropane

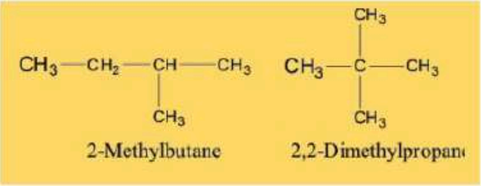


$CH_3-CH_2-CH_2-CH_3$

n-Butane

$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$

Isobutane



$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-Methylbutane

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

2,2-Dimethylpropane

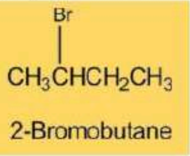
2). Position Isomerism

Position isomers have the same molecular formula but different in the position of a functional group on the carbon chain such as.

1-Bromobutane and 2-Bromobutane
n-Propyl alcohol and Isopropyl alcohol

$CH_3CH_2CH_2CH_2Br$

1-Bromobutane

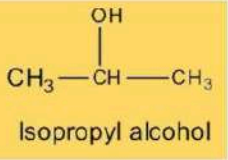


$CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3$

2-Bromobutane

$CH_3-CH_2-CH_2OH$

n-Propyl alcohol



$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$

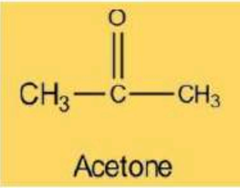
Isopropyl alcohol

3) Functional group Isomerism

Functional isomers have the same molecular formula but different functional groups. For example

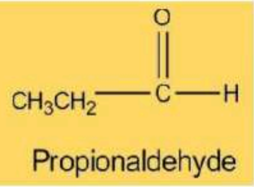
Acetone and Propionaldehyde

Acetic acid and Methyl formate



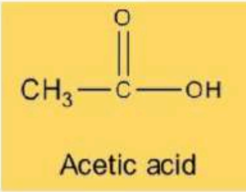
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Acetone



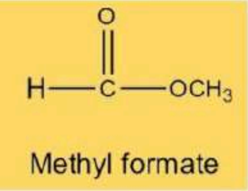
$CH_3CH_2-\overset{\overset{O}{\|}}{C}-H$

Propionaldehyde



$CH_3-\overset{\overset{O}{\|}}{C}-OH$

Acetic acid

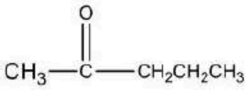


$H-\overset{\overset{O}{\|}}{C}-OCH_3$

Methyl formate

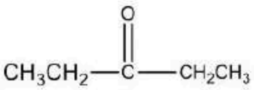
1) Metamerism

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Members belong to the same homologous series. For example:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3$$

2-Pentanone



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$$

3-Pentanone

$CH_3CH_2-NH-CH_2CH_3$ $CH_3-CH_2CH_2-NH-CH_3$

Diethylamine Methylpropylamine

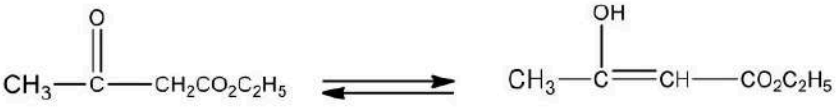
1. 2-pentane and 3-pentane
2. Diethyl ether and methyl propyl ether

$CH_3CH_2-O-CH_2CH_3$ $CH_3-O-CH_2CH_2CH_3$

Diethyl ether Methyl propyl ether

2) Tautomerism

A type of isomerism in which a compound exists simultaneously in two forms in equilibrium with one another. It involves the shifting of position of proton. This type of hydrogen atom is known as “mobile” hydrogen.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CO_2C_2H_5 \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH-CO_2C_2H_5$$

Keto-Form Enol-Form

Quick Quiz

1. Define or explain the following terms
   (a) Structural isomerism (b) Stereoisomerisms
   (c) Geometrical isomerism (d) Optical isomerism
   (e) Asymmetric carbon (f) Chiral molecule
2. State the necessary condition for a compound to show geometrical isomerism. Illustrate your answer with examples.
3. Which of the following compounds shows geometrical isomerism?

(a) 2-Butene
(b) 2-Methyl-Butene
(c) 2-Pentene
(d) 1,2-Dichloropropane

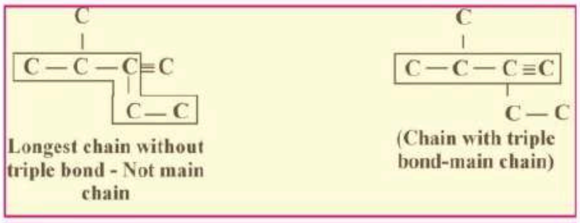
4. Which of the following compounds show isomerism

(a) $CH_3-CH=CH_2$

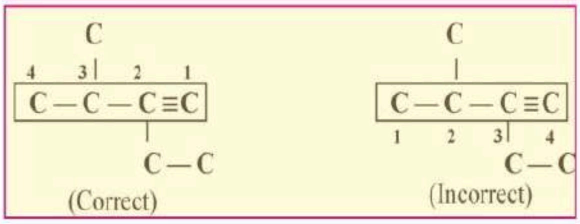
(b) $CH_3CH_2CH_2CH{=}CHCH_3$

5. What is optical activity: how is it measured?
6. Write a note on Optical Isomerism of Lactic acid
7. Write a note on Optical isomerism of tartaric acid
8. An acid of formula $C_5H_{10}O_2$ is optically active. What is its structure?
9. How does Cis-isomer convert into trans-isomer?
10. The trans-isomer is more stable. Why?

16.7 ALKYNES


Longest chain without triple bond - Not main chain

(Chain with triple bond-main chain)


(Correct)

(Incorrect)

16.7.1 Nomenclature:

IUPAC System:

1) The parent hydrocarbon is the continuous chain containing triple bond.

2) The ending 'ane' of the alkane is charged by- yne.

3) The main chain is numbered starting from the terminal carbon nearer to the triple bond.

4) Triple bond is given the number of the lower carbon atom attached to triple bond separated by hyphen.

5) If two or more triple bonds are there in the molecule, use the prefixes di-, tri-, etc.

6) Alkyl groups are indicated by the methods described while naming alkanes.

Naming of Molecules Containing Both the Double and Triple Bonds

1) The suffix 'ene' is used to denote the presence of Double bond the suffix –yne to denote the presence of triple bond.
2) The suffix –'ene' always precedes –'yne' in the name of compound, even when the double bond is assigned the large number.
3) The position number for the double bond is placed before the name of parent hydrocarbon.

$$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH_2}{-}\overset{4}{C}{\equiv}\overset{5}{CH}$$

1-Pentene-4-yne

4) The position number of triple bond is placed between –'ene' and –'yne'.

5) If same number would result from each terminal, the double bond is given the lower possible number. e.g,

Activity

Give the IUPAC name of the following:

(a) $CH_3CH_2C{\equiv}CH$

(b) $HC\equiv C-C\equiv CH$

(c) $CH_2=CH-C\equiv CH$

(d) $CH\equiv C-C\equiv C-CH=CH-CH_3$

(e) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

16.7.2. Relative Stability

Alkynes are more stable as compared to alkenes due to the presence of extra pi-bond. That is why alkynes are less reactive than alkenes. This can be supported if we compare thermodynamic data of alkynes and alkenes, i.e.

ΔH of 1-Hexyne = 290 kj/mol while

ΔH of 1Hexene = 126 kj/mol.

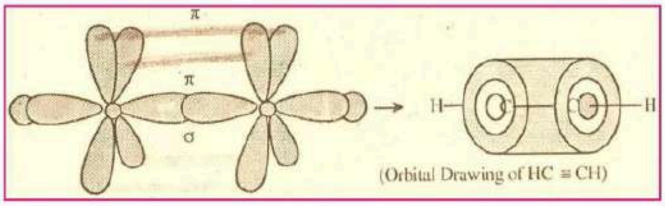
16.7.3. Structure:

The two carbons of acetylene (alkyne) are sp-hybridized. They are linked by a sigma-bond due to sp-sp orbitals overlap. The unhybridized two p-orbitals on one carbon overlap with two p-orbitals on other carbon to form two pi-bonds. The cloud of pi-electrons is present cylindrically symmetrical about the carbon-carbon sigma-bond.

Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is a linear molecule, and hence geometrical isomer is not observed in it.

16.7.4. Physical Properties

1. In general, alkynes are non-polar and are insoluble in water but soluble in non-polar organic solvents.
2. They are colourless, odourless except acetylene which has a garlic like odour.
3. The melting points, boiling points and densities increases gradually with the increase in molecular masses.
4. The first three members carbon alkynes (C2-C4) are gases. The next eight members (C5-C12) are liquids and higher members are solids at room temperature.



(Orbital Drawing of $HC\equiv CH$)

Fig. 16.15

Preparation of Alkynes by Elimination Reactions

Alkynes can be prepared by the following methods:

(i) Elimination reaction

(ii) Alkylation of sodium acetylide.

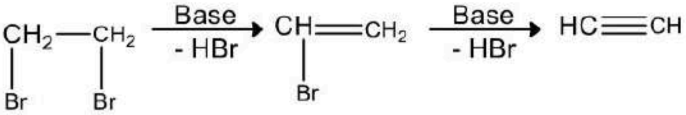
But we discuss here only elimination reactions

(i) Elimination of Hydrogen Halide:

Alkynes can be prepared by dehydrohalogenation of vicinal and germinal dihalides in the presence of some alkaline reagents.

(a) A vicinal dihalide contains two halogen atoms on adjacent carbon atoms. On elimination of two molecules of hydrogen halides from two adjacent carbons to give an alkyne.

Higher alkynes are also formed in the presence of alcoholic KOH, e.g.

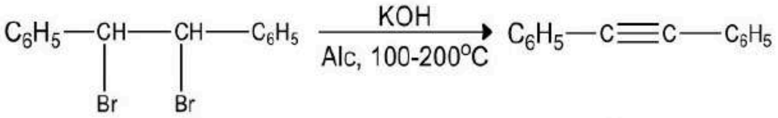


$$\underset{\mathrm{Br}}{\mathrm{CH_2}}-\underset{\mathrm{Br}}{\mathrm{CH_2}} \xrightarrow[\mathrm{-\,HBr}]{\mathrm{Base}} \underset{\mathrm{Br}}{\mathrm{CH}}=\mathrm{CH_2} \xrightarrow[\mathrm{-\,HBr}]{\mathrm{Base}} \mathrm{HC\equiv CH}$$

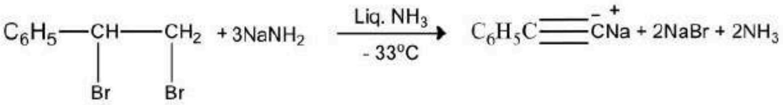
In the presence of strong base such as KOH and at high temperature triple bond at terminal C-atom migrates to give more disubtitutued alkyne.

Therefore, alcoholic KOH is useful when rearrangement is not possible,

1-alkynes can be prepared from vic-dihalides with sodium amide in liquid ammonia



$$\mathrm{C_6H_5}-\underset{\mathrm{Br}}{\mathrm{CH}}-\underset{\mathrm{Br}}{\mathrm{CH}}-\mathrm{C_6H_5} \xrightarrow[\mathrm{Alc,\ 100\text{-}200^oC}]{\mathrm{KOH}} \mathrm{C_6H_5-C\equiv C-C_6H_5}$$

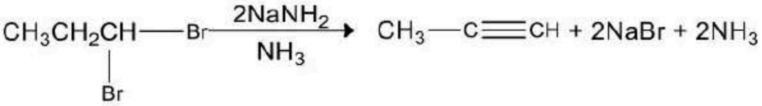


$$\mathrm{C_6H_5}-\underset{\mathrm{Br}}{\mathrm{CH}}-\underset{\mathrm{Br}}{\mathrm{CH_2}} + 3\mathrm{NaNH_2} \xrightarrow[\mathrm{-\,33^oC}]{\mathrm{Liq.\ NH_3}} \mathrm{C_6H_5C\equiv \overset{-\ +}{C}Na} + 2\mathrm{NaBr} + 2\mathrm{NH_3}$$

$$\mathrm{C_6H_5C\equiv \overset{-\ +}{C}Na} \xrightarrow{\mathrm{H_2O}} \mathrm{C_6H_5C\equiv CH}$$

(b) Geminal Dihalide:

A dihalide containing two halogen atoms linked with the same carbon atom) on treatment with strong base gives alkyne, e.g.,



$$\mathrm{CH_3CH_2}\underset{\mathrm{Br}}{\mathrm{CH}}-\mathrm{Br} \xrightarrow[\mathrm{NH_3}]{\mathrm{2NaNH_2}} \mathrm{CH_3-C\equiv CH} + 2\mathrm{NaBr} + 2\mathrm{NH_3}$$

16.7.5. Reactivity

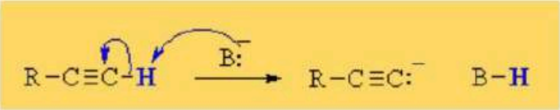
Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions. It also undergoes substitute reactions due to easy cleavage of C-H bond. The pi-electrons are present cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon –carbon boding. Therefore electrophile substitute reactions are possible in 1-alkyens.

16.7.6. Acidity of Terminal Alkynes

$$\mathrm{R{-}C{\equiv}C{-}\mathbf{H}} \xrightarrow{\mathrm{B\colon^-}} \mathrm{R{-}C{\equiv}C\colon^-}\quad \mathrm{B{-}\mathbf{H}}$$

$$\mathrm{H-C\equiv C\overset{\delta\,-}{-}H^{\delta\,+}}$$

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atoms with sp-s overlap. As sp hybrid orbital has 50% S-character in it and renders the carbon atoms more electronegative. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.



This $H^{\delta+}$ can be substituted with metal. Thus substitution reaction occurs due to $H^{\delta+}$

Examples:

(i) When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.

$$R—C\equiv CH + 2NaNH_2 \xrightarrow{\text{liq } NH_3} R—C\equiv \overset{-}{C}\overset{+}{Na} + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow Na\,C\equiv \overset{-}{C}\overset{+}{Na} + NH_3$$

Disodium acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

Silver and copper acetylides react with acids to regenerate alkynes.

These alkynides are used for the preparation, purification separation, and identification of alkynes.

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC\equiv CAg + 2NH_4NO_3 + 2H_2O$$

Disilver acetylide or silver ethynide, (white ppt.)

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC\equiv CCu + 2NH_4Cl + 2H_2O$$

Dicopper acetylide or copper ethynide (Reddish brown)

$$AgC\equiv CAg + \text{dil. } H_2SO_4 \longrightarrow CH\equiv CH + Ag_2SO_4$$

$$AgC\equiv CAg + \text{dil. } HNO_3 \longrightarrow HC\equiv CH + 2AgNO_3$$

16.7.7 Addition Reactions of Alkynes

- Alkynes undergo addition reactions in an analogous fashion to those of alkenes.
- The high electron density of the pi bonds makes them nucleophilic.
- Two factors influence the relative reactivity of alkynes compared to alkenes:

1. increased nucleophilicity of the starting pi system, and
2. stability of any intermediates (for example carbocations)

Hydrogenation

Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or Pd. In the first step alkenes are formed which them take up another molecule of hydrogen to form an alkaline.

$$\underset{\text{Ethyne}}{HC\equiv CH} + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} \underset{\text{Ethene}}{H_2C=CH_2}$$

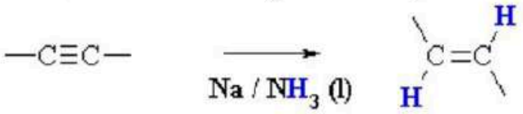
$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} \underset{\text{Ethane}}{H_3C-CH_3}$$

Dissolving Metal reduction

Reaction Type: Addition

Elaboration

Alkynes can be reduced to ***trans***-alkenes using Na in NH_3 (liq.)
This reaction is **stereospecific** giving only the ***trans***-alkene via an ***anti*** addition.
Note that the stereochemistry of this reaction complements that of catalytic hydrogenation.
The reaction proceeds via single electron transfer from the Na with H coming from the NH_3
These reaction conditions do not reduce alkenes, hence the product is the alkene.



Hydrohalogenation

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes. The reaction occurs in accordance with Markownikov's rule.
Second addition is according to Markownikov's Rule.

$$CH\equiv CH + H-Br \longrightarrow \underset{\text{Vinyl bromide}}{H_2C=CHBr}$$

1,1- dibromoethane

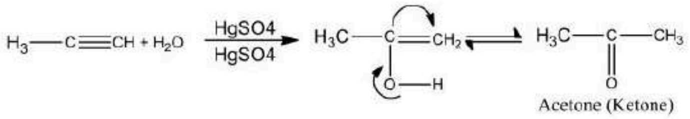
Hydration Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C.

$$HC\equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Vinyl alcohol}}{H_2C=CHOH}$$

Rearrangement of Alcohol

Vinyl alcohol is an unstable. It has the hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde. Eccept acetylene all others alkynes give ketones.

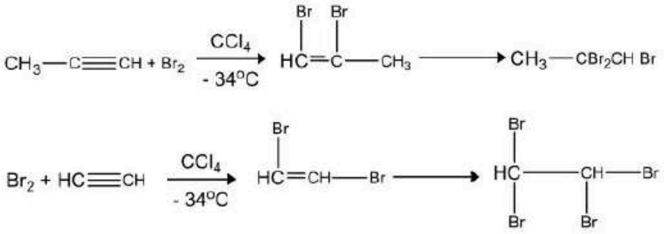
This reaction is industrially important because aldehydes can be prepared by this method.



Bromination

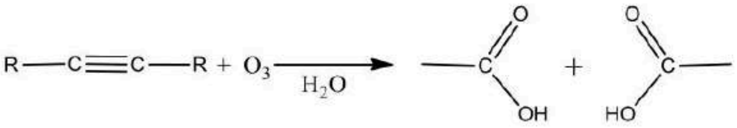
Chlorine and bromine add to the acetylenic triple bond in the presence of lewis acid as catalyst

The Halogenation may be stopped at the dihaloalkene stage because the double bond of dihaloalkene is less nucleophilic than even triple bond itself.



Ozonolysis

When ozone reacts with alkyne followed by aqueous work up we get 2RCO_2H.



Quick Quiz

What are reducing agent would you use to convert an alkyne to a (i) Cis-alkene (ii) Trans-alkene?

16.8 BENZENE AND SUBSTITUTED BENZENES

Discovered by = Michael Faraday
Isolated by = Hoffmann
Molecular formula = C_6H_6
Molecular weight = 78
Special Feature = (i) Resonance
(ii) Electrophilic substitution reactions

Michael Faraday discovered benzene in 1825, during the destructive distillation of vegetable oil. Hoffmann isolated it form coal tar.

As a functional group, benzene and substituted benzenes are called arenes.

16.8.1 Nomenclature

Mono Substituted Benzenes:

Common system of naming:

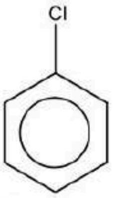
The following procedures are adopted for naming mono substituted benzenes:

(1) Parent name is benzene and the substituent is indicated by a prefix, e.g., methyl. Ethyl, chloro, Nitro etc.

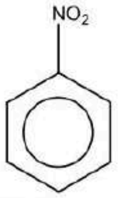
(2) The substituent and the benzene ring taken together may form s new parent name. The largest parent name is preferred e.g., $C_6H_5CH_3$ may be named as: (i) Methyl benzene (ii) Phenyl methane. According to "the largest rule" methyl benzene is preferred. The common name of some compunds are:

IUPAC System of Naming:

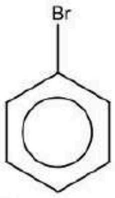
Mono substituted derivatives of benzene are named by prefixing the name of substituted to the word 'benzene'. e.g.,



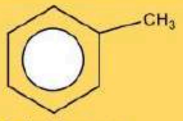
Chlorobenzene



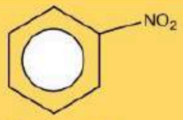
Nitrobenzene



Bromobenzene

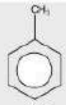
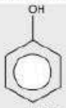
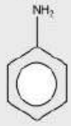
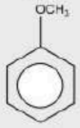
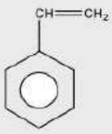
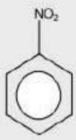
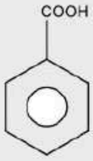
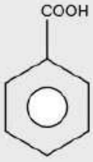


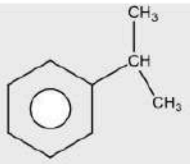
Methyl benzene



Nitrobenzene

Many aromatic compounds have been known by their common or trivial names, which are still in use. IUPAC system retains these names: A few are given below:

Structure	Names	Structure	Names
	Toluene		Phenol
	Aniline		Anisole
	Styrene		Nitrobenzene
	Benzoic acid		Bromobenzene



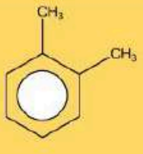
Cumene

Disubstituted Benzene:

1) When there are two substituents on benzene ring their relative positions are indicated by prefixes ortho(o), meta(m) and para(p) in common system of naming and by numerals while naming according to IUPAC system.

2) If the substituents are different and one of them is an alkyl group the numbering is started from the ring carbon which is linked to the alkyl group and the second substituent gets the lowest possible number.

3) When a common name is used, the substituent which is responsible for name, e.g., CH_3 in toluene, and –OH in phenol, is considered to be on carbon -1, i.e., numbering is started from the carbon of ring bearing that group such a disubstituted compound.

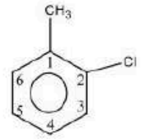


o-dimethylbenzene

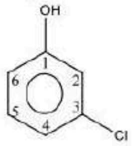
m-dimethylbenzene

p-dimethylbenzene

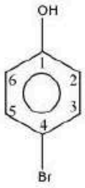
4) When two substituents are different, they are usually put in alphabetical order.



o - chlorototoulene
2 - chlorotoulene
(IUPAC)

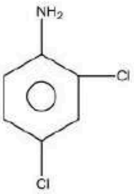


m - chlorophenol
3 - chlorophenol
(IUPAC)

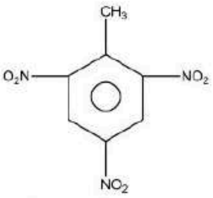


p - bromonitrobenzene
4 - bromonitrobenzene
(IUPAC)

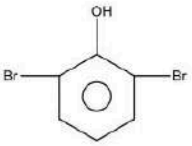
5) Poly substituted benzenes are named by numbering the substituent to ring so as to give the substituents lowest possible numbers. The last named substituent is assumed to be at position number 1. This number is not indicated in the name.



2, 4 - Dichloroaniline

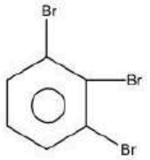


2, 4, 6 - Trinitrotoluene
(TNT)

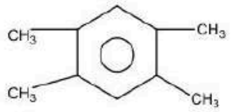


2, 6 - Dibromophenol

6) If the substituents are all alike their positions are indicated by numbering the substituents in a manner so as to give the lowest number to the substituents.

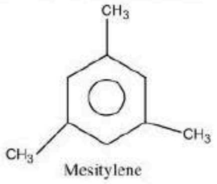


1, 2, 3 - Tribromoibenzene

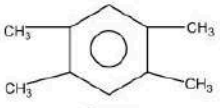


1, 2, 4, 5 - Tetramethylbenzene

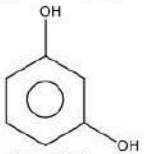
7) Some poly substituted benzenes are still known by their common name.



Mesitylene



Durene

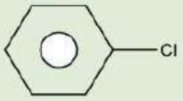


Resorcinol

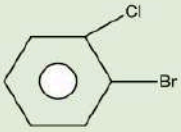
Activity

1- Give the suitable name to each of following:

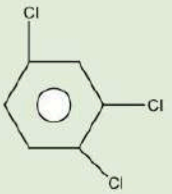
(a)



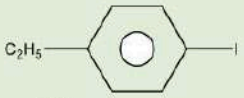
(d)



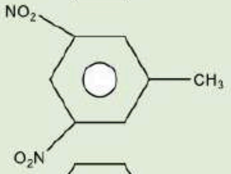
(b)



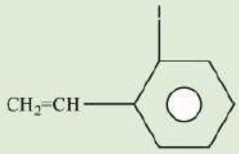
(e)



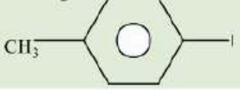
(f)



(c)



(g)



16.8.2. Physical Properties

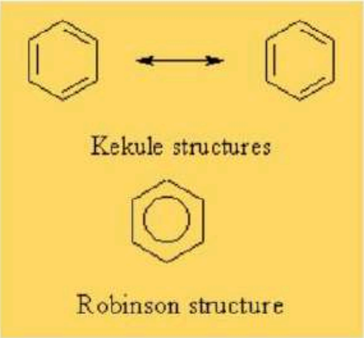
In the absence of polar substituents, arenes are typical of hydrocarbons: low melting and boiling points, low solubility in polar solvents.

16.8.3 Structure (Molecular Orbital Aspects)

All 12 atoms in benzene, C_6H_6, lie in the same plane.

Benzene has a planar, cyclic, conjugated structure.

If one draws benzene as alternating C=C and C-C then the two different Kekule structures are obtained.



Kekule structures

Robinson structure

These are two equally valid resonance contributors.

Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.

Note that all of the C-C bonds are 1.4 Å (between typical C=C and C-C distances).

Which representation structure of benzene the best?

In benzene all the C-C bonds are known to be of equal length (above) so there are no C=C and C-C. This is best represented by the resonance hybrid in the Robinson form. However, since the key to organic chemistry is being able to understansd mechanisms and drawing curved arrows to account for the positions of the electrons, the Kekule structures give a more precise description of the electron positions that can avoid confusion. **Therefore, it is a good idea to use a Kekule representation.**

MOLECULAR ORBITAL TREATMENT OF BENZENE

Remember

Kekule's structure failed to explain as to why

1. Benzene is less reactive
2. It shows dual character, i.e., it shows addition as well as substitute reaction.
3. It has less heat of formation, and
4. It has equal C-C bonds.

Spectroscopic studies and X-rays analysis have shown that benzene is a regular, flat planar hexagon. All six hydrogen atoms are co-planar with six carbon atoms. The bond angles are:

(i) $C\text{-}\hat{C}\text{-}C=120$, and (ii) $C\text{-}\hat{C}\text{-}H=120^\circ$

Thus each C-atom is in a state of sp^2-hybridization because each C-atom is attached to three atoms.

Combination of such six structures and overlap of six hydrogen atoms (1s1) produces the following sigma framework of benzene.

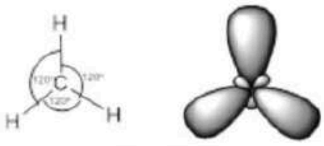


Fig. 16.16

Six atomic p-orbitals one on each c-atom, are present perpendicular to this sigma bonding. Each p-orbital is in a position to overlap in parallel manners with neighbouring p-orbitals to give a continuous sheath of negative charges as shown in the figure above.

It results in extensive delocalized pi-bonding which spreads over all the carbon nuclei of benzene. Delocalization of p-orbitals over the entire ring produces sandwhich like structure of benzene and decreases the energy of molecule. Consequently, the molecule becomes more stable and less reactive.

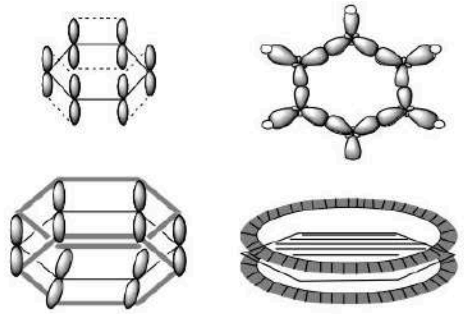


Fig. 16.17

According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full sigma-bond and half a pi-bond. Because of this reason, the carbon-carbon bond length is equal and benzene shows substitution as well as addition reactions.

Quick Quiz

Criticize the following statement:
"Benzene is a mixture of molecules most of which have the structure."

or

Modern Representation of Benzene

With the help of molecular orbital behaviour we conclude that benzene has a regular hexagonal structure with an inscribed circle.

A hexagon with alternate double and single bonds.

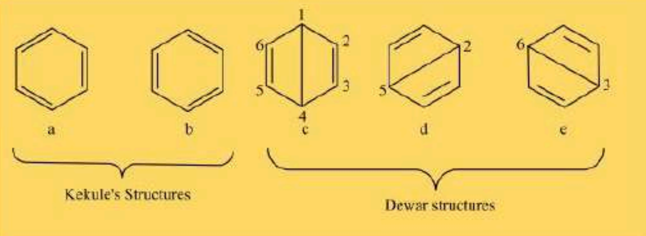
16.7.4. Resonance, Resonance Energy and Stabilization

I- Resonance:

"The possibility of different pairing schemes of valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures".

Explanation:

The resonance is represented by a double-headed arrow e.g. the following different pairing schemes of the fourth valence (the p-electrons) of carbon atoms are possible in benzene. This gives the following resonating structures of 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 fact the structure of benzene is a resonance hybrid of all five structures, (a), (b), (c), (d), and (e) in which the Kekule's structure (a) and (b) have the larger contribution and Dewar's structures contribute a little. Therefore, benzene molecule can be represented by either of the two Kekule's structure.

The three alternate single and double bonds in the above structure are called conjugate bonds of 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. It is intermediate between those in alkanes and alkenes.

II- Resonance Energy:

The ***resonance energy*** of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds. This can be calculated from experimental measurements.

The diagram shows the experimental heats of hydrogenation, ΔH_h, for three molecules, benzene, 1,3-cyclohexadiene and cyclohexene. These are related in that under appropriate conditions they can all be reduced to the same product, cyclohexane.

The ΔH_h for "cyclohexatriene", a hypothetical molecule in which the double bonds are assumed to be isolated from each other, is calculated to be 3 times the value for cyclohexene. This value reflects the energy we could expect to be released from 3 isolated C=C.

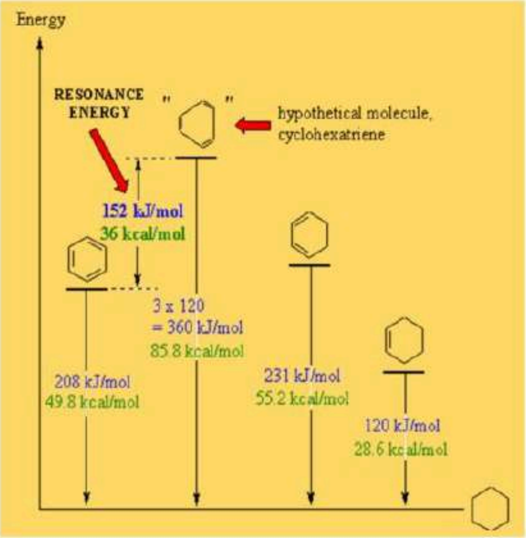


Fig. 16.18

By comparing this value with the experimental value for benzene, we can conclude that benzene is 152 kJ or 36 kcal / mol ***more stable*** than the hypothetical system. This is the resonance energy for benzene.

16.8 .5. Reactivity and Reactions

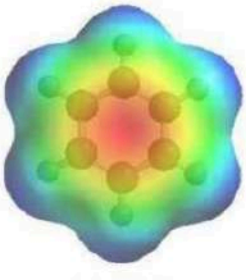


Fig. 16.19

The image shows the electrostatic potential for benzene. The more red an area is, the higher the electron density and the more blue an area is, the lower the electron density. Note the nucleophilic character of the aromatic p system.

The reactivity issues can be separated into two types of reactions: reactions of electrophiles directly on the aromatic ring, and reactions of the substituents (since the neighboring aromatic group influences its reactivity).

For reactions directly on the aromatic ring:

The cyclic array of p-bonds is a region of high electron density so arenes are typically nucleophiles (like alkenes and alkynes).

Unlike alkenes and alkynes (which undergo addition reactions), arenes typically undergo substitution reactions in which a group (usually -H) is replaced and the aromatic system is retained.

The stability of the aromatic system favours substitution over addition which would destroy the aromatic system.

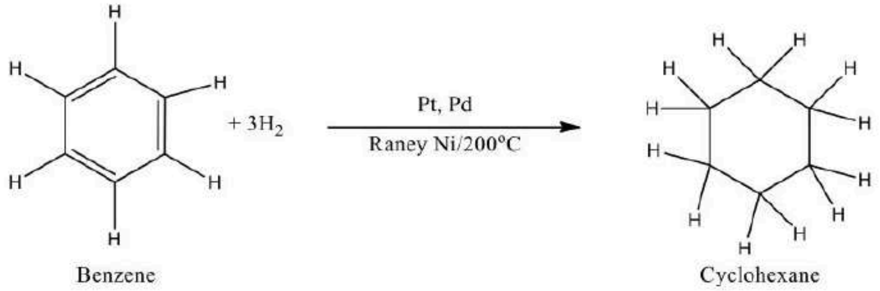
Addition Reactions

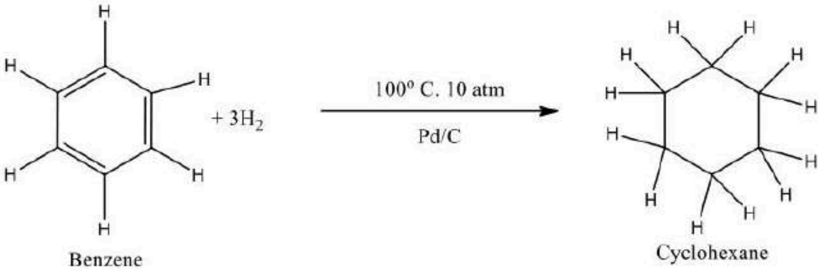
Benzene is highly unsaturated compound. It has three double bonds in it. But it does not undergo addition reaction happily. The reason is that it shows resonance. The delocalization of six pi-electrons makes it extra stable.

So for addition reaction benzene requires more vigorous condition than that of alkenes and alkynes.

(a) Catalytic Hydrogenation

Benzene can be hydrogenated in the presence of a catalyst as Pt, Pd, or Raney Ni only at higher temperature and pressures.

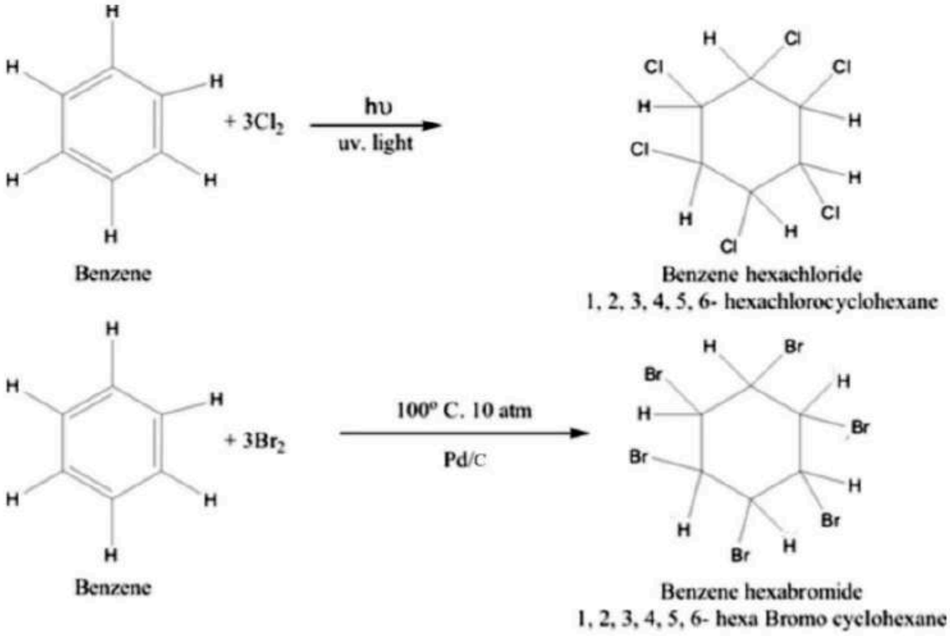




If we use the metals like Ru, Rh, supported at carbon then hydrogenation becomes easier

(c) Addition of Halogens

Benzene can add three molecules of chlorine or bromine under the influence of light. The benzene ring becomes saturated, and we get benzene hexachloride and benzene hexabromide. This reaction shows that benzene has three double bonds in the ring.



Reaction of F_2 and I_2:

The reaction of F_2 with benzene is very vigorous, while with I_2 it is very slow.

Conclusion:

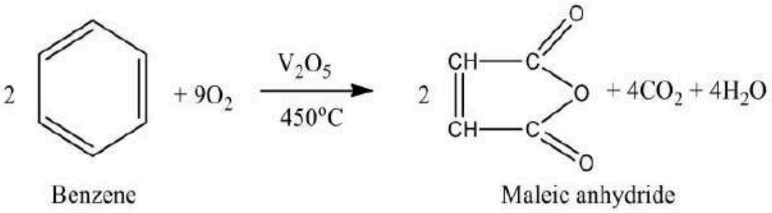
The addition reactions of hydrogen and chlorine with benzene show that benzene is unsaturated hydrocarbon and has three double bonds in it.

(c) Oxidation Reactions

Benzene is stable towards general oxidizing agents. However, it can be oxidized under certain conditions:

(i) Catalytic Oxidation

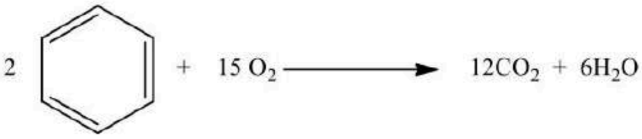
When benzene is oxidized with air in the presence of V_2O_5 at 450^0C, then we get maleic anhydride



This is commercial method for the preparation of maleic anhydride. Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$.

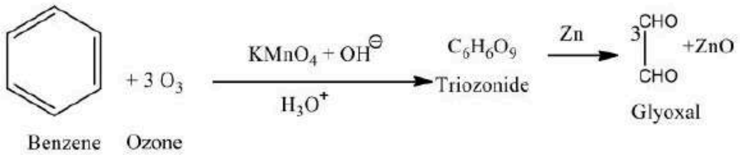
(ii) Combustion:

When benzene is burnt in the presence of air or oxygen, CO_2 and H_2O are produced, just like other aliphatic hydrocarbons

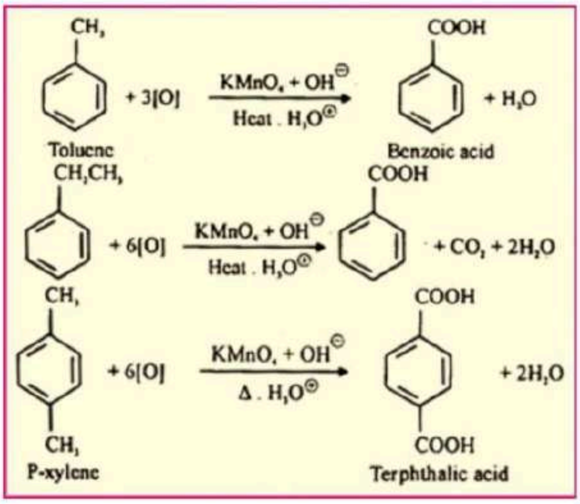


(iii) Ozonolysis:

Benzene reacts with ozone and gives glyoxal. First of all triozonide is produced as an intermediate



(iv) Oxidation of side chain:



Alkyl groups present in the benzene ring are oxidized into carboxylic groups. The oxidizing agents are:

1. $KMnO_4 + H_2SO_4$
2. $K_2Cr_2O_7 + H_2SO_4$
3. Dil. HNO_3

Conclusion:

When both methyl groups are oxidized and benzene ring remains unaffected, then it means that benzene ring is stable towards oxidizing agents.

Electrophilic Aromatic Substitution Reactions

General Introduction

The pi-electrons of benzene are highly stabilized due to resonance. They are not readily available for the electrophilic attack like the electros of alkenes. They do not assist in the attack of weak electrophiles. Hence more powerful electrophiles are required for a successful attack to penetrate and break the continuous sheath of electron cloud in benzene.

Explanation and Example:

Substitution of halogen in benzene requires iron or corresponding ferric halide as catalyst. It reacts with halogen molecule to produce a powerful electrophile:

1. **Formation of a strong electrophile (X^+)**

$2Fe + 3X_2 \rightarrow 2FeX_3$

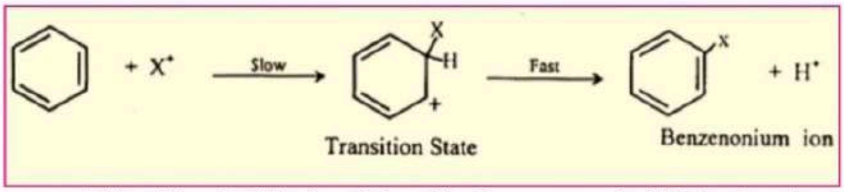
$FeX_3 + X_2 \rightarrow FeX^-_4 + X^+$

Tetra haloferrate ion (III) Halogenoium ion

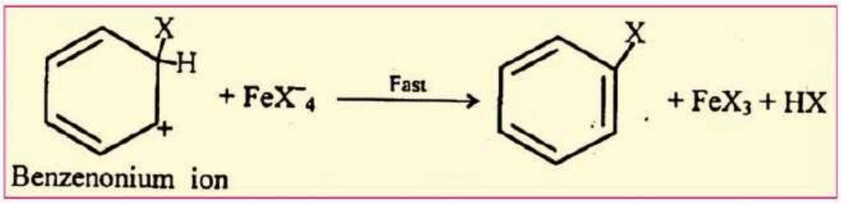
2. **Attack of electrophile at pi-bond:**

The halogenation ion thus produced attacks as a powerful electrophile on the electrons of benzene ring.

$$X_2 + FeX_3 \longrightarrow X^+ + FeX^{-4}$$

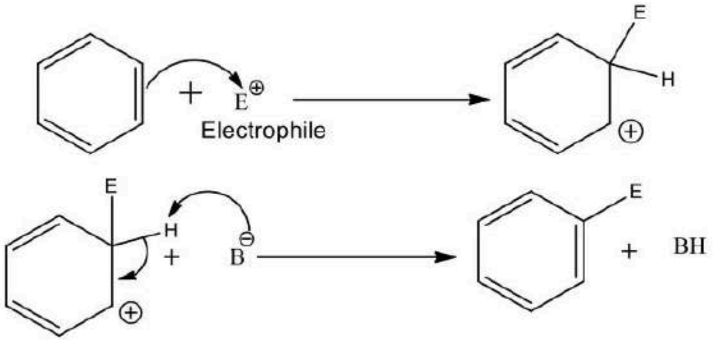


It had benzene unstable. The stability is retained by the removal of H^+ ion to give substitution product.

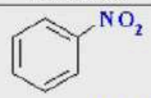
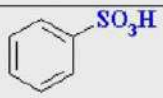
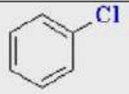
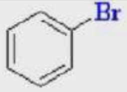
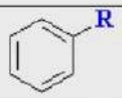
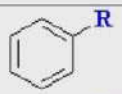
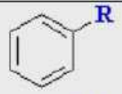
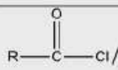
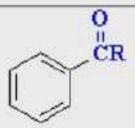


General Pattern of Substitution

The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.

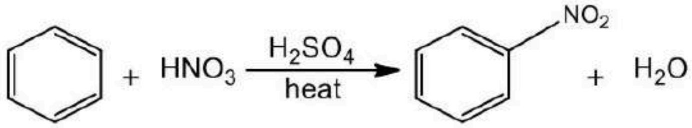


Substitution is preferred over addition in order to preserve the stable aromatic character

Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO_3 / H_2SO_4	NO_2^+		E^+ formed by loss of water from nitric acid
<u>Sulfonation</u>	H_2SO_4 or SO_3 / H_2SO_4	SO_3		Reversible
Halogenation	Cl_2 / Fe or $FeCl_3$	Cl^+		E^+ formed by Lewis acid removing Cl^-
	Br_2 / Fe or $FeBr_3$	Br^+		E^+ formed by Lewis acid removing Br^-
Alkylation	R-Cl / $AlCl_3$	R^+		E^+ formed by Lewis acid removing Cl^-
	R-OH / H^+	R^+		E^+ formed by loss of water from alcohol
	RC=CR / H^+	R^+		E^+ formed by protonation of alkene
Acylation	 $R-\overset{O}{\overset{\Vert}{C}}-Cl$ / $AlCl_3$	RCO^+		E^+ formed by Lewis acid removing Cl^-
	 $R-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-R$ /$AlCl_3$	RCO^+		E^+ formed by Lewis acid removing RCO_2^-

Nitration

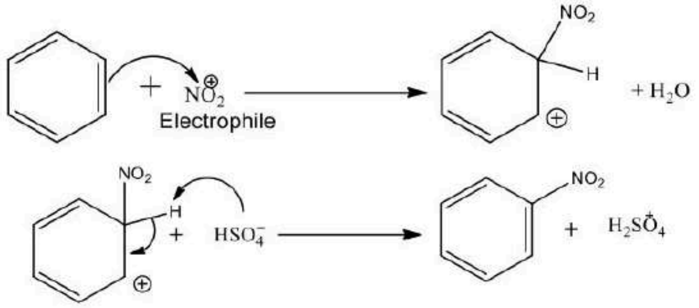
The introduction of – NO_2 group in benzene by substituting hydrogen of benzene ring is called Nitration



Mechanism

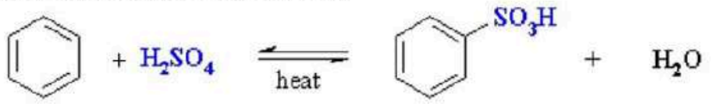
Sulphuric acid reacts with nitric acid to generate nitronium ion.

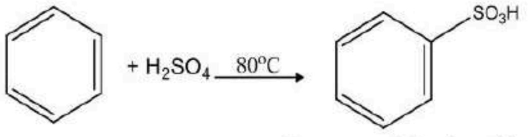
$$HONO_2 + H_2SO_4 \xrightleftharpoons{50^oC} NO_2^+ + HSO_4^- + H_2O$$



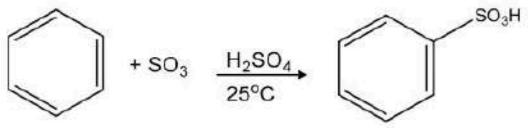
Sulfonation

The introduction of sulphonic acid group in benzene by substituting hydrogen of benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or concentrated H_2SO_4 it yields benzene sulphonic acid. Fuming H_2SO_4has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.





Benzenesulphonic acid

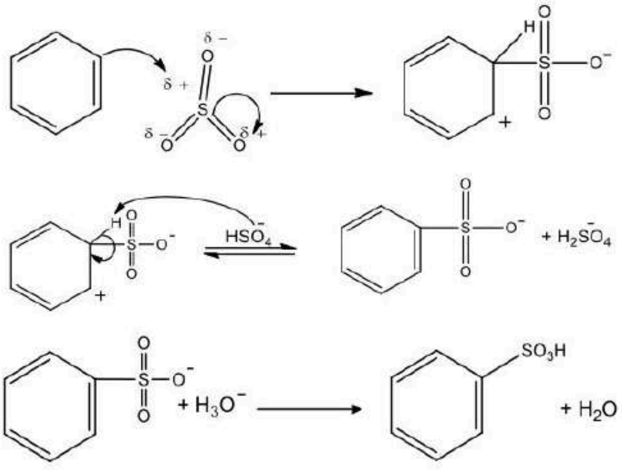


Benzenesulphonic acid

Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3

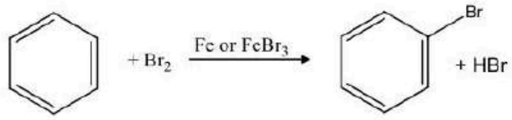
$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO_4^-$$



Halogenation

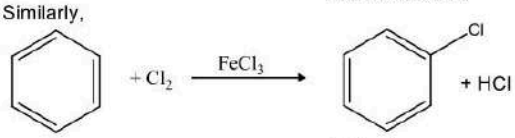
The introduction of halogen in benzene by substituting hydrogen of benzene ring is called halogenation.

Explanation and Examples:

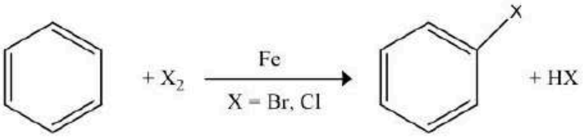


Bromobenzene

Similarly,



Chlorobenzene



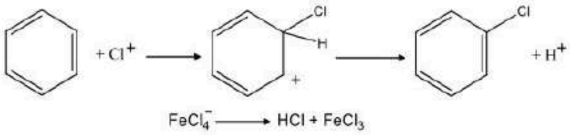
Halogenation of benzene occurs with halogens (X_2) in the presence of a catalyst FeX_3. Chlorination and bromination are normal reaction but fluorination is too vigorous to control. Iodination gives poor yield.

Mechanism:

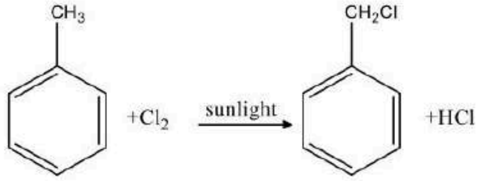
$$X_2 + FeX_3 \longrightarrow X^+ + FeX_4^-$$

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

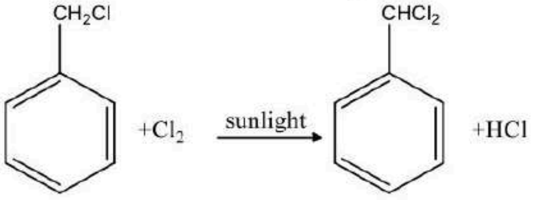
The actual halogenation agent is X^+ that is formed by the following mechanism Cl^+ being a strong electrophile is ready for successful attack on benzene.



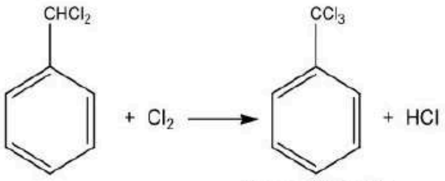
When alkyl benzenes are treated with chlorine or bromination in the presence of sunlight, only the alkyl groups are substituted.



Benzyl chloride



Benzal chloride

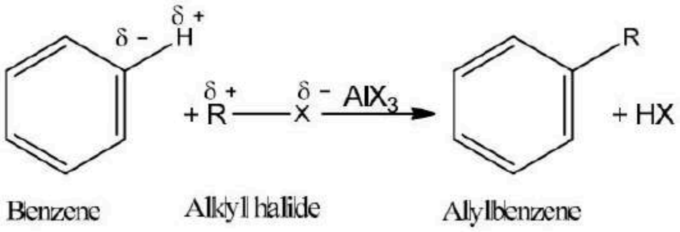


Benzotrichloride

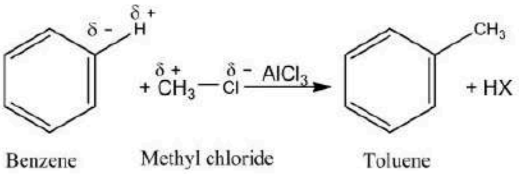
Friedel-Crafts Alkylation

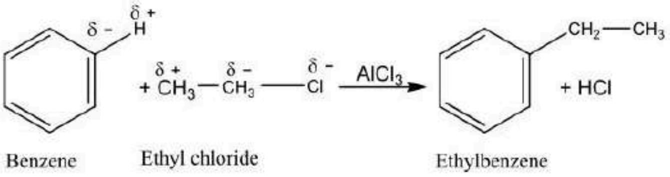
The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst $AlCl_3$ is called Friedel Crafts alkylation or Alkylation.

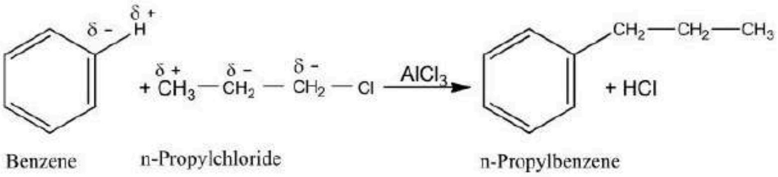
Overall reaction:



Examples:

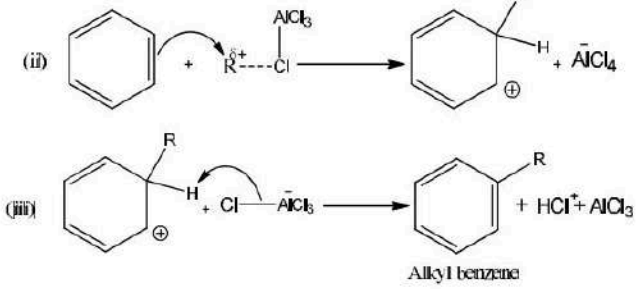




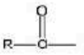


Mechanism:

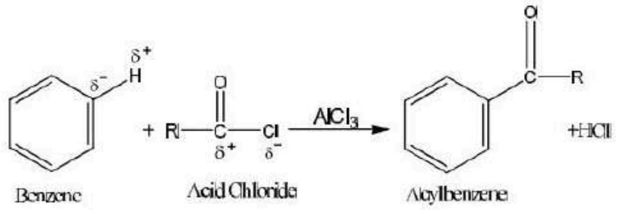
$$\text{(i)}\quad R—Cl + AlCl_3 \longrightarrow \overset{+}{R} + AlCl_4^-$$



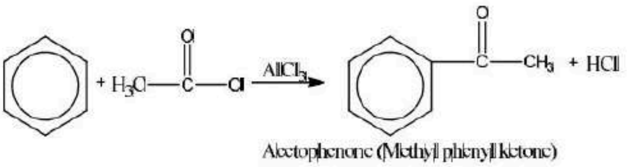
Friedel-Crafts Acylation

The introduction of an acyl group  $R-\overset{O}{\overset{\|}{C}}-$ in the benzene by substituting hydrogen of benzene ring in the presence of an acyl halide and a catalyst $AlCl_3$ is called Friedel Crafts Acylation or Acylation.

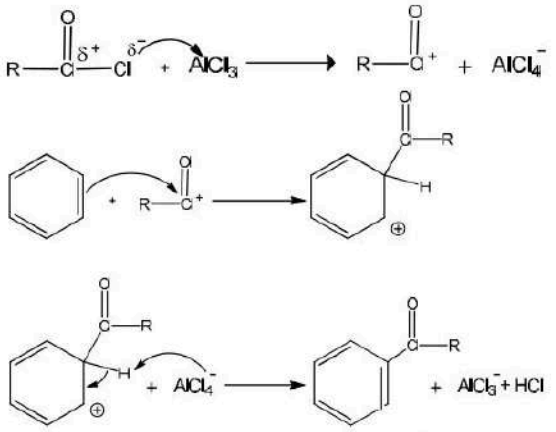
Overall reaction:



Example:



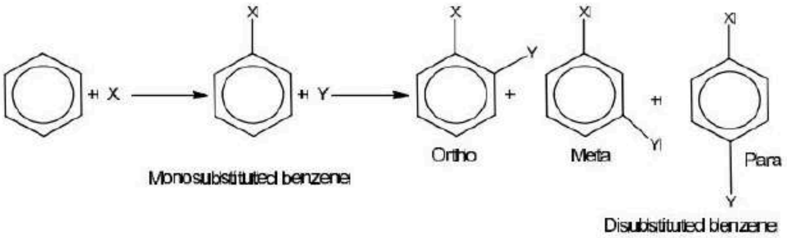
Mechanism:



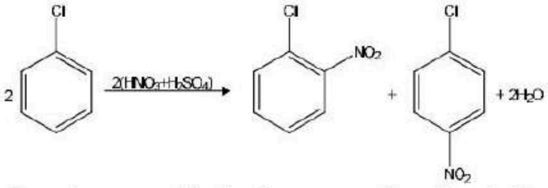
Substituent Effects - (Table of Substituent Effects) and Making Poly-substituted Benzenes

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 position of a second group into the ring depends on the nature of the first group. The second substituted may enter at ortho, para or meta position.

On chance basis 40% ortho, 40% meta and 20% para disubstituted products are expected. However, the results do not agree with chance substitution ratio, e.g. m-nitrochlorobenzene is the main product of the following halogenation reaction.



On the other hand, a mixture of o-nitrochloro-benzene and p-nitrochloro-benzene is obtained from the nitration of chlorobenzene.



It means that the groups already present in the benzene ring directs the second entrant and thus determines the position, which may be taken up by it. There are two types of groups:

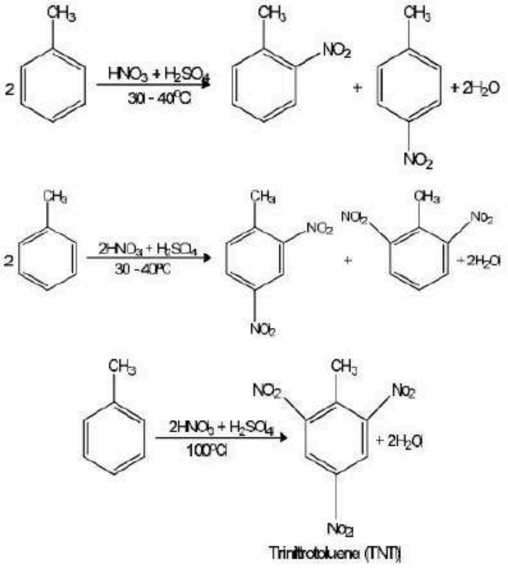
a. Ortho- and para- directing groups
b. Meta- directing groups

1. Ortho and para directing groups

These groups release electrons towards the benzene ring, at ortho and para positions. Because these position are richer in electron for attack of an electrophile. The second group is substituted at ortho and para positions. They also enhance the reactivity of benzene ring.

Example:

The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.

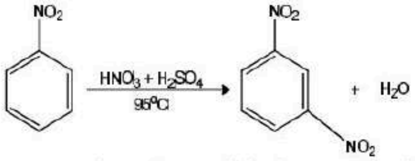


Other examples of ortho and para directing groups are:-

$-N(CH_3)_2$, $-HNH_2$, -OH, $-OCH_3$, -Cl, -Br, -I

2. Meta-Directing Groups

These groups withdraw the electrons of the benzene ring from ortho and para positions. Due to the electro withdrawing effect of such substituents, the ortho and para position are more electrons 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. These groups decrease the chemical reactivity of benzene.



The substitution of third nitro groups is not possible because nitro group has deactivated the ring, other examples of meta directing groups are $-C\equiv N$, NO_2, $-COOH$, $-CHO$

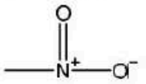
Rule:

If the electronegativity of the atom of the group attached to the benzene ring is greater than any atom of the group, the whole group will act as electron repelling, will increase the reactivity of benzene all direct the new entrant to ortho, para positions. On the other hand

If the electronegativity of such atom is less, it will be under constraint and it turn withdraw electron form the ring making it less reactive and directing the new entrant to meta position

e.g. (i) $-NH_2$ Nitrogen with greater electronegativity from hydrogen.

(ii) –Cl has no other atom hence will have no danger of pulling electrons. Thus it is electron repelling and o, p- directing group. Hence o, p-, directing

i.  $-\overset{\overset{\displaystyle O}{\|}}{N^{+}}-O^{-}$ Nitrogen with less E.N from O. Hence meta directing.

ii. In $-SO_3H$ E.N of oxygen is greater then that of S. hence oxygen disturbs sulphur, which in turn withdraws electrons from benzene ring hence m-directing.

Making Polysubstituted Benzenes

Since the position of electrophilic attack on a substituted benzene ring is controlled by the substituent already present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted benzenes need careful planning to ensure success.

Quick Quiz

1. (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.

2. Predict the major products of bromination of the following compounds

(a) Toluene (b) Nitrobenzene (c) Bromobenzene (d) Benzoic acid (e) Benzaldehyde (f) Phenol

SOCIETY, TECHNOLOGY AND SCIENCE

HYDROCARBONS IMPORTANT AS FUEL FOR FUTURE ENERGY NEEDS OF PAKISTAN

Ethanol,
Natural Gas,
Propane,
Biodiesel - an alternative fuel based on vegetable oils or animal fats,
Methanol - also known as wood alcohol,
P-Series fuels - a blend of ethanol, natural gas liquids and methyltetrahydrofuran (MeTHF). P-Series fuels can be used alone or mixed with gasoline in any ratio by simply adding it to the tank.

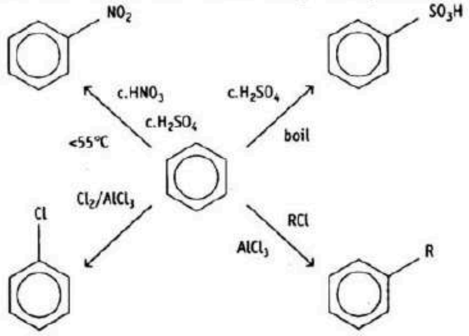
Uses of Hydrocarbons

1. Butane is used as a fuel in lighter.
2. Butane is also used in same camping stoves
3. Coal is used for the manufacturing of synthetic petrol
4. Ethylene is the hormone that causes tomatoes and apples to ripen
5. Oxyacetylene torch is used for cutting of metals
6. Methane is used to manufacture urea fertilizer

Key Points

- Compared to other functional groups, alkanes tend to have low melting and boiling points and very low solubility in polar solvents such as water.
- Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by sigma bonds. They have a general formula of C_nH_{2n+2}.
- Branched alkanes are more stable than linear alkanes, *e.g.* 2-methylpropane is more stable than n-butane.
- Alkanes react with halogens by a radical mechanism to give haloalkanes. The mechanism consists of three steps, initiation, propagation and termination.
- 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.
- Alkenes are very reactive compounds. They undergo electrophilic reactions very easily.
- Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's Rule.
- Compounds that have the same molecular formula but different chemical structures are called *isomers*.
- **Constitutional** (or structural) isomers differ in the order in which the atoms are connected so they contain different functional groups and / or bonding patterns:
- *Example:* 1-propanol, 2-propanol and ethyl methyl ether (C_3H_8O) **Stereoisomers** contain the same functional groups and differ only in the arrangement of atoms in space.
- **Conformational** isomers (or conformers or rotamers) are stereoisomers produced by rotation about sigma bonds.

- **Configurational** isomers are stereoisomers that do not readily interconvert at room temperature and can (in principle at least) be separated.
- **Geometric** isomers are configurational isomers that differ in the spatial position around a bond with restricted rotation (e.g. a double bond).
- **Optical** isomers are configurational isomers that differ in the 3D relationship of the substituents about one or more atoms.
- **Enantiomers** are optical isomers that are non-superimposable mirror images.
- **Diastereomers** are optical isomers that are not enantiomers.
- Hydrocarbons containing a triple bond are known as alkynes or acetylenes.
- Alkynes undergo addition reactions and two molecules of a reagent are added in it.
- The decreasing reactivity order of alkanes, alkenes and alkynes are as follows: Alkenes > Alkynes > Alkanes
- Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.
- Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons.
- Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
- 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.
- Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitution are the main reaction of benzene.
- Resonance energy of benzene is 152kJ/mole.
- Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures.
- The C_6H_5- group is called phenyl
- The characteristic reaction type of benzene is electrophilic substitution. Some important substitution reactions are shown on the following diargram



- 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.
- Groups like CN,-CHO, NH_3, NR_3, CCl_3, which decrease the reactivity of Benzene nucleus and direct the incoming group at m- position

Exercise

1. The molecule of ethane posses which hybridization;

a. sp^3 b. sp^2 c. sp d. sp^2d

2. The sp^2 hybrid orbitals are oriented in space at one angle;

a. 109.5^0 b. 180^0 c. 100^0 d. 120^0

3. The geometry of acetylene is,

a. angular b. bent c. trigonal d. linear

4. Which reaction is used as test for the presence of alkene;

a. reaction of cold diluted alkaline $KMnO_4$ b. Combustion

c. Polymerization d. Catalytic hydrogenation

5. The general formula of alkane is;

a. C_nH_{2n+2} b. C_nH_n c. C_nH_{2n} d. C_nH_{2n-2}

6. Sodalime is;

a. NaOH b. KOH c. Mixture of Na and Ca hydroxide d. CaO and NaOH

7. The marsh gas is

a. Ethane b. Methane c. Propane d. Butane

8. Acidic hydrogen is present in

a. Acetylene b. Ethane c. Benzene d. Ethene

9. The benzene molecule contains:

a. Three double bonds b. Two double bonds

c. One double bond d. none of these

10. The electrophile in aromatic sulphonation is;

a. H_2SO_4 b. HSO^-_4 c. SO_3 d. SO^-_4

11..The conversion of n-hexane into benzene by heating in the presence of Pt is called;

a. Isomerization b. Aromatization c. Dealkylation d. Rearrangement

12. Catalyst used for Friedal Craft's reaction is;

a. HNO_3 b. $AlCl_3$ c. $BeCl_3$ d. $FeCl_3$

13. Benzene can not undergo

a. Elimination b. Substitution c. Oxidation d. Addition

14. Shape of benzene molecule is

a. Pyramidal b. Liner planar c. Trigonal d. Hexagonal planar

15. In which one of the following compounds the benzene ring is isolated;

a. Naphthalene b. Anthracene c. Phenthrene d. Diphenyl ethane

16. Two compounds have the same composition and also have the same atoms attached to the same atoms, although with different orientations in space. These compounds are

(a) identical (b) Position isomers c) structural isomers (d) stereoisomerism

17. the isomers of a substance must have

(a) same chemical properties (b) same molecular weight

(c) same structural formula (d) same functional groups

18. Ethanol and dimethyl ether are best considered:
    (a) structural isomers (b) stereosierms (c) enantiomers (d) diasteromers
19. Alkenes show geometrical isomers due to
    (a) asymmetry (b) rotation around a single bond
    (c) resonance (d) restricted rotation around a double bond
19. Geometrical isomerism is shown by
    (a) lactic acid (b) maleic acid (c) 1-butene (d) 1,1-dichloroethylene
20. A molecule is said to be chiral
    (a) if it contains plane of symmetry
    (b) it it contains center of symmetry
    (c) if it cannot be superimposed o its mirror image
    (d) if it can be superimposed on its mirror image
21. Which of the statements is false regarding chiral compounds
    (a) rotate the plane of polarized light (b) have cis and tans isomers
    (c) exist as enantiomers (d) can be detected with a polarimeter
22. An optically active compound
    (a) must contain at least four carbons
    (b) when in solution rotate the plane of polarized light
    (c) must always contain an asymmetric carbon atom
    (d) in solution always give a negative reading in polarimeter
23. Plane polarized light is affected by
    (a) identical molecules (b) all polymers
    (c) chiral molecules (d) all biomolecules
24. It is possible to distinguish between optical isomers
    (a) by using chemical tests (b) by mass spectrometry
    (c) by IR spectroscopy (d) by polarimetry

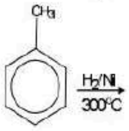
2. Give brief answers to the following questions

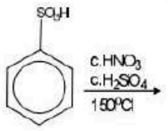
1. Why carbon is SP^3 hybridized in the compounds?
2. How is pi-bond formed in alkenes and alkynes?
3. What is cis-trans isomerism?
4. Why alkanes are relatively chemically inert?
5. Alkenes usually undergo addition reactions while alkanes do not why?
6. What is stereoisomerism?
7. How optical isomers arise?
8. What are conjugated bonds formed?
9. Why alkenes are more reactive than alkynes?
10. Justify the given order of reactivity? Alkenes > Alkynes > Alkanes
11. What is meant by dehydration of alcohols?
12. What are polymerization reactions?
13. How will you convert acetylene into benzene?
14. What is resonance?
15. What is resonance energy?

3. Give detailed answers for the following questions

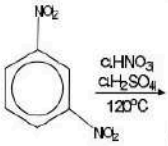
1. What is isomerism? Explain different types of isomerism?

2. How will you prepare 1-butene from?
   (i) an alkyl halide (ii) Alcohols (iii) Electrolysis of salt (iv) Vic-dihalides.
   (b). What products is formed when n-propane undergo following reactions?
   (i) Combustion (ii) Nitration
3. (a). When ethane reacts with Cl_2 in UV light the mixture of products is formed. Give the detail of reaction with mechanism and all types of products.
   (b) A compound when treated with Zn in methanol, the alkene is formed. When alkene is ozonolysed the acetaldehyde is formed as the major product. Explain reactions, give name and structure of the compound.
4. (a). How will you prove that benzene has cyclic structure?
   (b). Explain the structure of benzene according to atomic orbital structure.
5. Explain Friedal Craft acylation and alkylation with complete mechanism.
6. Explain the following electrophilic substitution reactions of benzene with mechanism. (i) Halogenation (ii) Nitration (iii) Sulphonation.
7. Write the structural formulas for the following benzene derivatives:
   a) 2,4,6-trinitrophenol
   b) 1,4-dichlorobenzene
   c) 4-nitrophenylamine
   d) 2-methlbenznesulphonic acid
   e) 2-hydroxybenzoic acid
   f) 2-chlorophenylamine
8. Predict the major products of the following reactions.

(a)


(b)


(c)


(d)


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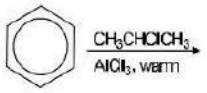

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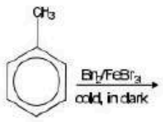
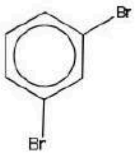
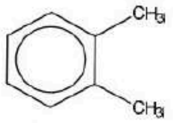
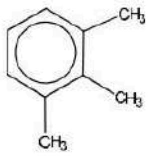
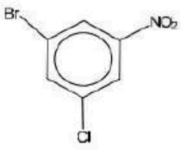


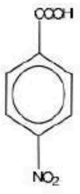
9. Name the following benzene derivatives:

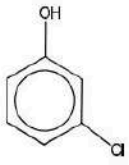
(a)


(b)


(c)


(d)


(e)


(f)


17

ALKYL HALIDES AND AMINES

After completing this lesson, you will be able to:

This is 12 days lesson (period including homework)

- Name alkyl halides using IUPAC system.
- Discuss the structure and reactivity of RX.
- Describe the preparation of RX by the reaction of alcohols with HX, $SOCl_2$ and PX_3 and by radical halogenations of alkanes.
- Describe the mechanism and types of nucleophilic substitution reaction. (Understanding)
- Describe the mechanism and types of elimination reactions.
- Describe the preparation and reactivity of Grignard's' Reagents.
- Discuss chemistry of Grignard's reagent by the addition of aldhydes, ketons, esters and carbon dioxide..
- Discuss nomenclature, structure and basicity of amines. Describe the preparation of amines by alkylation of ammonia to RX and reduction of nitriles, nitro and amide functional groups.
- Discuss reactivity of amines.
- Describe chemistry of amines by alkylation of amines wit RX, reaction with aldeydes, ketons preparations of amides and diazonium salts.
- Describe isomerism in alkyl halides and amines.

Reading

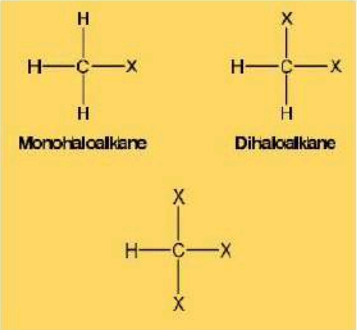
17.1 ALKYL HALIDE

Introduction

"Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by one halogen atom. They are also known as halogen derivatives of alkanes."

Types:

They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides having general formula R-X.



Classification of Alkyl Halides:

Alkyl halides are classified into primary, secondary and tertiary alkyls halides.

(i) Primary Alkyl Halides:

"Alkyl halide in which halogen atom is attached with primary carbon are called primary alkyl halide". **(Carbon atom attached to one or no carbon atom is called primary C-atom.)**

$\overset{*}{C}H_3-Cl$

Methyl chloride
Chloromethane

$CH_3-\overset{*}{C}H_2-Cl$

Ehyl chloride
Chloroethane

$CH_3-CH_2-\overset{*}{C}H_2-Cl$

n-Propyl chloride
Chloropropane.

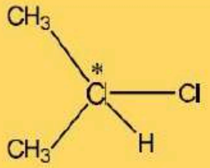
($\overset{*}{C}$ is primary carbon atom)

(ii) Secondary Alkyl Halides:

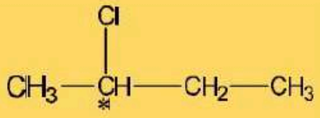
"Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide."

Secondary C-atom:

"C-atom, attached to two C-atoms simultaneously is called secondary C-atom."



Iso-Propyl chloride
2-Chloro propane

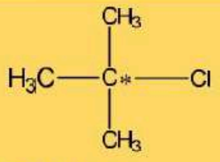


$CH_3-\underset{*}{\overset{Cl}{\overset{|}{C}}}H-CH_2-CH_3$

Sec- Butyl chloride
2-Chlorobutane.

($\overset{*}{C}$ is secondary carbon atom)

(iii) Tertiary Alkyl Halides:



$H_3C-\underset{CH_3}{\overset{CH_3}{C^*}}-Cl$

t- Butyl chloride
2-Methyl-2-chloropropane.

($\overset{*}{C}$ is tertiary C-atom)

"Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halide".

Tertiary C-atom

"C-atom, attached to three C-atoms simultaneously is called tertiary C-atom".

17.1.1. Nomenclature

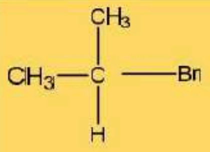
Alkyl halides are named according to the following systems:

(i) Common System of naming.
(ii) IUPAC System of naming.

(i) Common System of Naming:

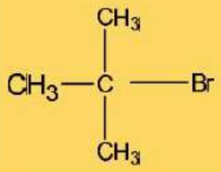
This method consists in first writing the name of alkyl group to which halogen atom is attached and then writing the name of halide ion, e.g.,

CH_3-CH_2-Cl Ethyl Chloride



$CH_3-\underset{H}{\overset{CH_3}{C}}-Br$

Sec or Isopropyl bromide



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

Ter-butyl bromide

For secondary alkyl halides, the prefix sec _ and for tertiary alkyl halides, the prefix ter_ or t_ is added before the name of alkyl halides, e.g,.

When all the carbons of alkyl group of primary alkyl halides are in a straight chain, the prefix n- is used before the name which indicates 'normal'. e.g,

$CH_3-CH_2-CH_2-CH_2-Br$

n_butyl bromide

(ii) IUPAC System of naming.

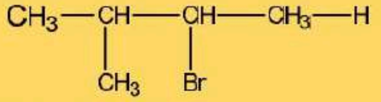
According to this system alkyl halides are named as derivatives of alkanes. The following rules are observed for this purpose:

(i) The longest chain bearing halogen is selected as parent hydrocarbon.

(ii) Prefix 'halo' i.e., Chloro for Cl, Bromo for Br, etc, is used before the name of hydrocarbon.

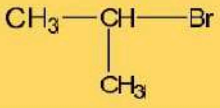
(iii) Positional numbers are used to indicate halogen and other substituent by the usual methods, e.g,.

$CH_3-CH_2-CH_2-CH_2-Br$ Bromo butane



$CH_3-\underset{CH_3}{CH}-\underset{Br}{CH}-CH_3-H$

2-Bromo-3-methyl butane

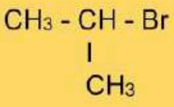


$CH_3-\underset{CH_3}{CH}-Br$

2-Bromo propane

The names given below are also accepted by the IUPAC

CH_3-CH_2-Cl Ethyl Chloride



$CH_3-\underset{CH_3}{CH}-Br$

Iso_propyl Bromide

$(CH_3)_3CBr$ ter-butyl bromide

17.1.2. Physical Properties:

The polar bond creates a molecular dipole that raises the melting points and boiling points compared to alkanes.

17.1.3. Structure:

- The alkyl halide functional group consists of an sp^3 hybridized C atom bonded to a halogen, (X), via δ bond.
- The carbon halogen bonds are typically quite polar due to the electronegativity and polarizability of the halogen.

Preparations of Alkyl Halides

17.1.4.1 Reaction of Alcohols with Hydrogen Halides

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.

$$CH_3CH_2-OH+HX \xrightarrow{ZnCl_2} CH_3CH_2-X+H_2O$$

Ethyl halide

Reaction of Alcohols with other Halogenating agents ($SOCl_2$, PX_3, PX_5)

(a) Alcohols react with thioyl chloride in pyridine as a solvent to give alkyl chlorides. This is the best method because HCl, and SO_2 escape leaving behind the pure product.

$$ROH+SOCl_2 \longrightarrow R-Cl+SO_2+HCl$$

(b) Phosphorous trihalides or phosphorous pentahalides react with alcohols to from alky halides.

$$3CH_3-CH_2-OH+PBr_3 \longrightarrow 3CH_3-CH_2-Br+H_3PO_3$$

$$CH_3-CH_2-OH+PCl_5 \longrightarrow CH_3-CH_2-Cl+POCl_3+HCl$$

Halogenation of Alkanes

By the action of chlorine or bromine, alkanes are converted into alky halides. This reaction takes place in the presence of diffused sunlight or ultraviolet light.

$$CH_3-CH_3+Cl_2 \xrightarrow{h\upsilon} CH_3.CH_2Cl+HCl$$

This method does not give pure alkyl halides. Halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

The detail mechanism of this reaction has already been discussed in section 16.3.2.

17.1.5 Reactivity

There are two main factors which control the reactivity of alkyl halides:

(i) Bond polarity of C-X bond

(ii) Bond energy of C-X bond

1. Bond Polarity

The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C.

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

Hence carbon acquires partial positive whereas halogens acquires partial negative charge.

Halogen becomes nucleophilic in character, which can be replaced by another nucleophile on the basis of bond polarity reactivity of alkylhalides decreases in the following order.

$$R—F > R—Cl > R—Br > R—I$$

2. Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alky halides, and not the polarity of the molecule.

A study of bond energies of C-X bond shows that C-F bond is the strongest. So the overall order of reactivity of alkyl halides is:

R-iodide > R-bromide > R-chloride > R-fluoride

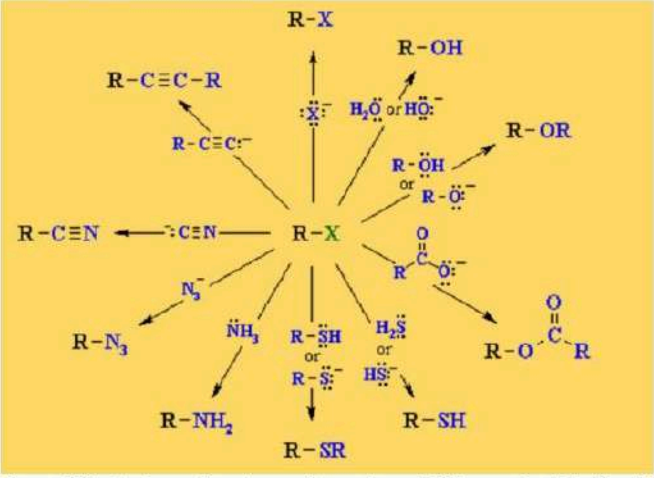
In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

17. 1.6 Nucleophilic Substitution Reactions of Alkyl Halides

- Alkyl chlorides, bromides and iodides are good substrates for nucleophilic substitution reactions.
- A variety of nucleophiles can be used to generate a range of new functional groups.
- The following diagram reflects some of the more important reactions you may encounter.

Reactions

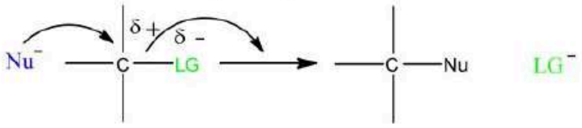
Nucleophilic Substitution Reactions



General Introduction What does the term "***nucleophilic substitution***" imply?

- A **nucleophile** is electron rich species that will react with an electron poor species
- A **substitution** implies that one group replaces another.

Nucleophilic substitution reactions occur when an electron rich species, the **nucleophile**, reacts at an electrophilic **C** atom attached to an electronegative group (important), the **leaving group**, that can be displaced as shown by the general scheme:



The electrophilic C can be recognized by looking for the polar sigma bond due to the presence of an electronegative substituent (esp. **C-Cl**, **C-Br**, **C-I** and **C-O**)

Nucleophilic substitution reactions are an important class of reactions that allow the interconversion of functional groups.

There are two fundamental events in a nucleophilic substitution reaction:

1. formation of the new δ bond to the nucleophile
2. breaking of the δ bond to the leaving group

Depending on the relative timing of these events, two different mechanisms are possible:

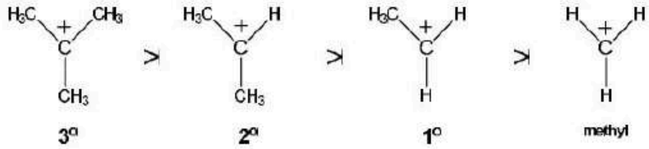
- Bond breaking to form a carbocation preceeds the formation of the new bond : SN_1 reaction
- Simultaneous bond formation and bond breaking : SN_2 reaction

Important Concepts

Carbocations and their Stability

Stability:

The general stability order of simple alkyl carbocations is: (most stable) 3° > 2° > 1° > methyl (least stable)



This is because alkyl groups are weakly electron donating due to hyperconjugation and inductive effects. Resonance effects can further stabilize carbocations when present.

Reactions involving carbocations:

1. Substitutions via the SN_1
2. Eliminations via the E_1
3. Additions to alkenes and alkynes

Nucleophiles and Base

It is species rich in electron and has an unshared pair of electrons available for bonding. In most cases it is basic. It may be negatively charged or neutral.

Examples of Nucleophiles:

HO^-	Hydroxide ion	NH_2^-	Amino group
$C_2H_5O^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thio cyanate ion	$\ddot{N}H_3$	Ammonia
$H_2\ddot{O}:$	Water		

Substrate and Leaving Group

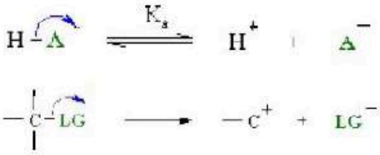
Substrate Molecule:

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Leaving Group (LG):

Leaving group is also a nucleophile. It departs with an unshared pair of electrons. The incoming nucleophile must be stronger than the departing one, Cl^-, Br^-, I^- HSO_4^- are good leaving groups. Poor leaving groups are OH^-, OR and NH^{2-}, Iodide ion is a good nucleophile as well as a good leaving group.

What do we mean by this? First we should write the chemical equations for the two processes:



These two equations represent Bronsted acid dissociation and loss of a leaving group in a SN_1 type reaction.

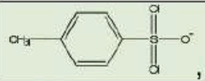
Note the similarity of the two equations: both show heterolytic cleavage of a sigma bond to create an anion and a cation.

For acidity, the more stable A^- is, then the more the equilibrium will favor dissociation, and release of protons meaning that HA is more acidic.

For the leaving group, the more stable **LG**$^-$ is, the more it favors "leaving".

Hence factors that stabilize A^- also apply to the stablization of a **LG**$^-$.

Here is a table classifying some common leaving groups that we will eventually meet......

Excellent	 , NH_3
Very Good	I^-, H_2O
Good	Br^-
Fair	Cl^-
Poor	F^-
Very Poor	HO^-, NH_2^-, RO^-

But water itself, is a good leaving group, since it is the conjugate base of H_3O^+.

SN_1 Mechanism

"It is substitution nucleophilic unimolecular two step reaction."

Explanation:

$$R-X \underset{}{\overset{\text{Slow}}{\rightleftharpoons}} \overset{+}{R} + X^-$$

$$\overset{+}{R}\,Nu^- \xrightarrow{\text{Fast}} R-Nu$$

The substrate R-X first ionizes reversibly into R^+ and X^- ions.

Then the carbonium ion combines with the attacking nucleophile to form product.

Mechanism:

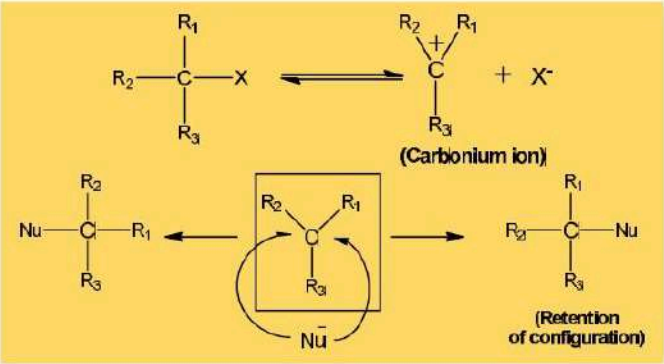
Since only one molecule is undergoing a change in covalency in rate determining step, this two step nucleophilic substitution reaction is unimolecular and is called SN_1 reaction. The brief mechanistic picture of SN_1 reaction base upon the following evidences:

1) Kinetic Evidence:

The rate of an SN1 reaction depends upon the concentration of alky halide only. The change in concentration of attacking nucleophile has no effect on the rate

$$\text{Rate} = k[R\text{-}X]$$

It is because the nucleophile combines with the carbonium ion in the second step. for the same reason, the rate of an SN_1 reaction does not depend on the nature of attacking nucleophile.

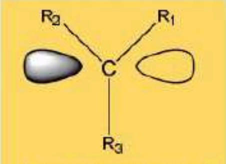


2) Stereo Chemical Evidence:

Experiments have shown that SN_1 reaction occur with partial racemization. The extent of partial racemization depends upon several factors including stability of carbonium ion.

The carbon atom of carbonium ion is sp^2 hybridized and carries one empty p-orbital.The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. The expected product is a recemic mixture. However, the partial recemization suggests a different way of attachment, e.g., in case of unstable carbonium ion, the attack of nucleophile is greater from the side opposite to that of leaving group. Thus the side of carbon atom to which the leaving group is attached is some what shielded from the attack of nucleophile. The attack of nucleophile occurs more often on the side opposite to the side to which leaving group is attached, leading to partial inversion of configuration

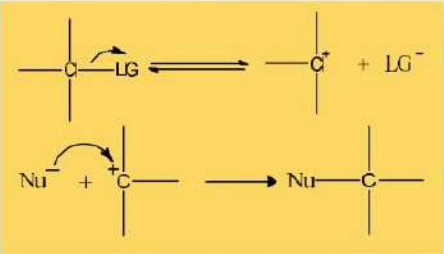
Therefore, the product has some optical activity.



(Planar Carbonium ion)

Step 1: Slow loss of the leaving group, **LG**, to generate a carbocation intermediate, then

Step 2: Rapid attack of a nucleophile on the electrophilic carbocation to form a new δ bond



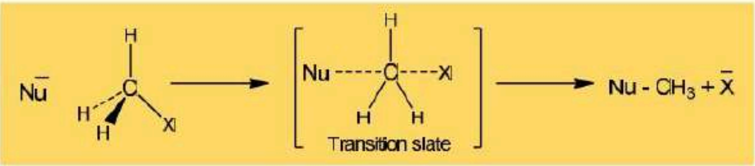
SN_2 Mechanism

"It is substitution nucleophilic bimolecular reaction. It occurs in one step".

$$\underset{\text{(Nucleophile)}}{\overline{Nu}} + CH_3 - X \longrightarrow Nu - CH_3 + \overline{X}$$

Mechanism:

The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step.



This is rate-determining step because the bond breaking and bond making processes occur simultaneously. Since two molecules are undergoing change in covalency in rate determining step. It is a bimolecular nucleophilic substitution reaction which is taking place in one step. This mechanistic picture is based upon the following evidences.

1) Kinetic Evidence:

The rate of an SN_2 reaction depends upon the concentration of nucleophile as well as the concentration of alky halide. The rate expression for the reaction can be written as

$$\bar{Nu} + R - X \longrightarrow Nu - R + \bar{X}$$

Rate = [Nu][R-X]

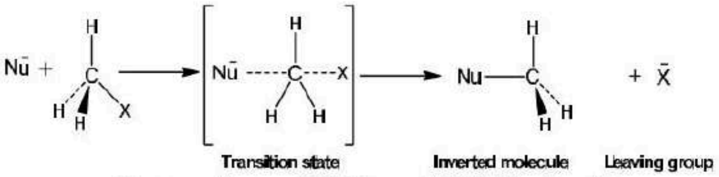
Where k = specific rate constant.

This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of increases when Cone of either $\bar{O}H$ or CH_3-Br is increased.

$$CH_3—Br + OH^- \longrightarrow CH_3 - Br + \bar{Br}$$

2) Stereo Chemical Evidence:

A bimolecular nucleophilic substitution always occurs with inversion of configuration. The carbon atom in transition state is sp^2-hybridized and is planar. The attacking nucleophile ad the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



Comparison of SN1 and SN2 Mechanism

Sr. No.	SN_1	Sr. No.	SN_2
(1)	It is a two step mechanism.	(1)	It is a single step mechanism.
(2)	First step is slow one and second is fast.	(2)	It has only one step and that is slow.
(3)	It is a unimolecular reaction.	(3)	It is a bimolecular reaction.
(4)	It is favoured in polar solvents.	(4)	It is favoured in non-polar solvents.

(5)	Mostly tertiary alkyl halides give this reaction.	(5)	Mostly primary alkyl halides give this reaction.
(6)	50 % is inversion and 50% retension of configuration takes place.	(6)	100% inversion of configuration takes place.
(7)	Rate = K[R-X)	(7)	Rate = [Nu][R-X]

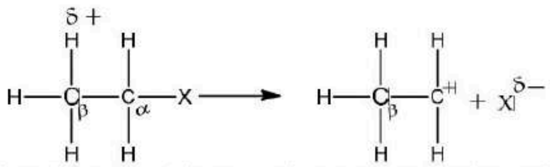
17.1.7 1,2 Elimination Reactions

Definition of Elimination Reaction:

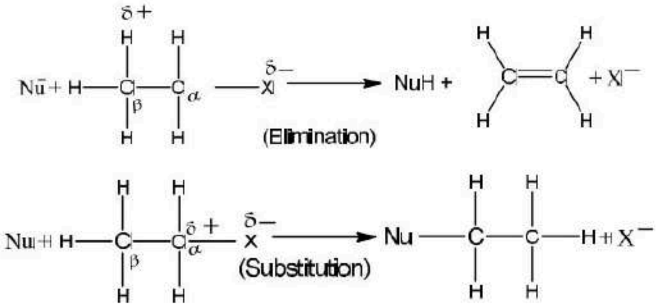
"The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction". Since β-hydrogen is necessary for eliminations, it is also called β-elimination.

Explanation:

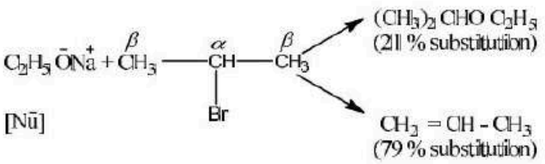
β-hydrogen atom in alkyl halides is slightly acidic due to electron with drawing effect of halogen.



The attacking nucleophile can either attack α-carbon to give substitution product or β-hydrogen to give elimination reaction.



Strong bases such as $\overset{-}{OH}$ OR, NH_2 cause elimination in preferences to substitution. Highly polarizable nucleophile and weak bases such as I^-, RS^- etc. give substitution reactions.

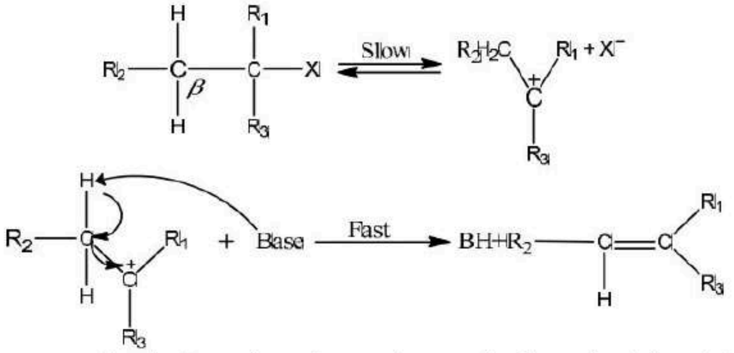


E_1 mechanism

"It is unimolecular two step elimination reactions."

Explanation:

The substrate undergoes slow ionization in the first step to form carbonium ion, in the second step the solvent or base pulls off a β-hydrogen

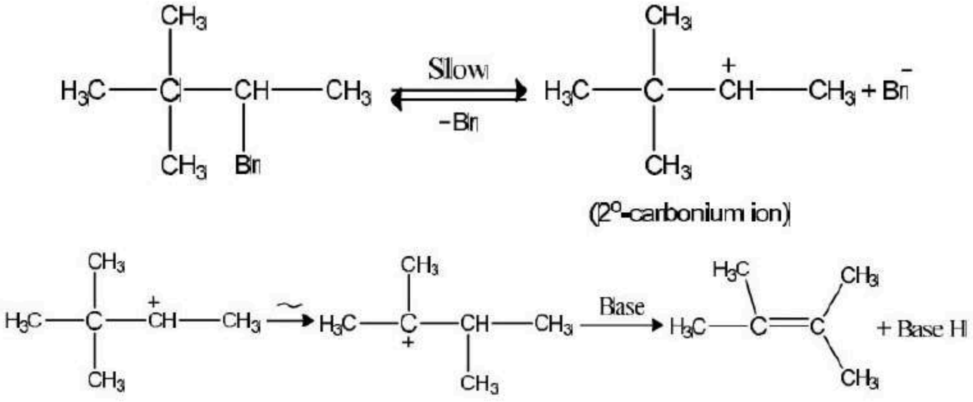


Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

The E_1-mechanism has been supported by the study of the reaction. It follows first order kinetics, in which rate of reaction depends only on the concentration of substrate.

$$\text{Rate} = k[R\text{-}X]$$

The presence of carbonium ion as an intermediate has been indicated by the presence of more than one kind of elimination products. A relatively less stable carbonium ion rearranges to give stabler carbonium before giving elimination product.

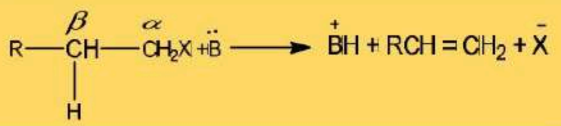


E_2 mechanism

"It is bimolecular one step elimination reaction".

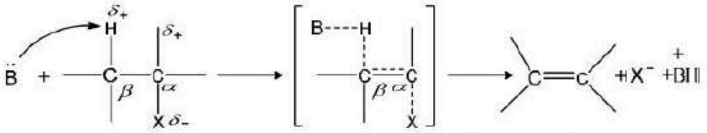
Explanation:

Consider the reaction,



$$R-\underset{\underset{H}{|}}{\overset{\beta}{C}H}-\overset{\alpha}{C}H_2X+\ddot{B} \longrightarrow \overset{+}{B}H + RCH=CH_2 + \overset{-}{X}$$

The attacking base removes a proton from the β-carbon simultaneously with the formation of double bond between C_α and C_β and the loss of halide ions.

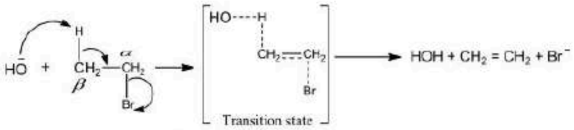


This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

Since two molecules are undergoing a change in transition state, it is a bimolecular one step elimination reaction. Thus E_2 is a one step process in which both the substrate and the base participate. The observed rate law for E_2-reaction is

$$\text{Rate} = K[R - X][\ddot{B}]$$

The rate of E_2-reaction depends upon the concentration of substrate and the base e.g., for the reaction



The rate of reaction follows second order kinetics

$$\text{Rate} = K[CH_3CH_2Br][\bar{O}H]$$

17.1.8 Substitution versus Elimination Reactions

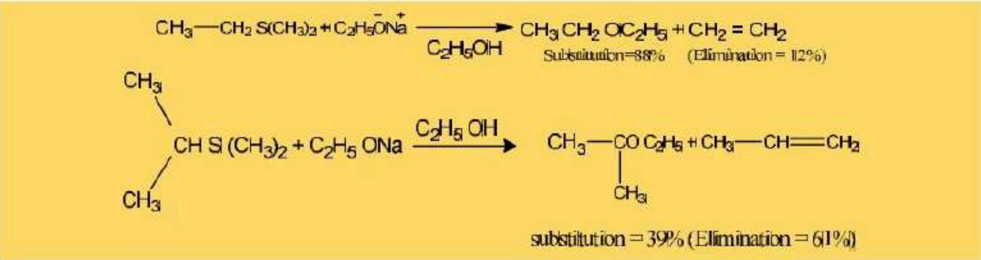
Though substitution and elimination reaction lead to different products, there is always a competition between them because of close resemblance in their mechanism. Since substitution is more favorable energetically it is the dominant reaction in the substitution-elimination reaction.

Elimination occurs only in the presence of β- Hydrogen where substitution reactions do not require this condition to be satisfied.

The following factors help to compare these two path ways:

(i) Structure of Substrate:

Crowding within the substrate favors elimination over substitution because the approach of the nucleophile to α-carbon is difficult for substitution. However, the elimination is favorable because the removal of β-H atom by base from tertiary planar carbonium ion is easy, e.g.,



$$CH_3-CH_2S(CH_3)_2 + C_2H_5\bar{O}\overset{+}{Na} \xrightarrow[C_2H_5OH]{} CH_3CH_2OC_2H_5 + CH_2=CH_2$$

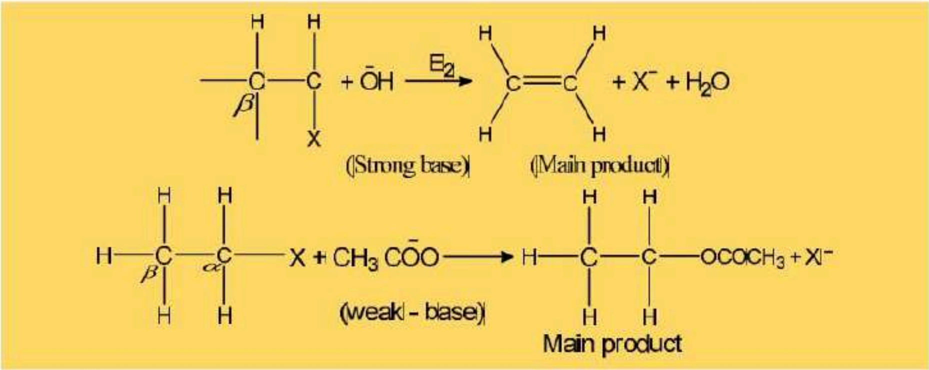
Substitution=88% (Elimination = 12%)

$$(CH_3)_2CHS(CH_3)_2 + C_2H_5ONa \xrightarrow{C_2H_5OH} CH_3-\underset{CH_3}{\underset{|}{C}}O C_2H_5 + CH_3-CH=CH_2$$

substitution = 39% (Elimination = 61%)

(ii) Nature of Base:

When the electron pair donor is a strong base, e.g., $\bar{O}H$, $\bar{O}R$ etc., the dominant reaction is E_2 and SN_2 reaction is a side reaction. However, when the nucleophile is a weak base like X-, RS-, etc,. The main reaction will be substitution and E2 will be minor side reaction.



(iii) The Nature of Leaving Group:

The role of leaving groups in Elimination reactions is similar to that in substitution reactions. In unimolecular reactions it does not affect the mechanism because both the elimination and substitution products are decided with carbonium ion. However, in the bimolecular reactions the nature of product greatly depends upon the nature of leaving group, e.g.,

$$n—C_{18}H_{37}—X + (CH_3)_3COK \xrightarrow{(CH_3)_3COH} n\,C_{16}H_{33}CH=CH_2 + n-C_{18}H_{37}OC(CH_3)_3$$

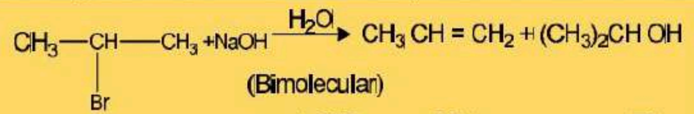
X = Br	85%	15%
X = OTS	1%	99%

(iv) Nature of Solvent

Elimination is favored more than substitution by decreasing the solvent polarity. Thus, alcoholic KOH affects elimination while more polar aqueous KOH is used for substitution. E1 is favored by polar solvents like SN_1 reaction. In non-polar solvents, the reaction will follow E2-mechansim.

(v) Effect of Temperature

An increase in temperature will favor elimination more than substitution, because substitution reaction involve less reorganization of bonds as compared to eliminations, e.g.,



$$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 + NaOH \xrightarrow[\text{(Bimolecular)}]{H_2O} CH_3CH=CH_2 + (CH_3)_2CHOH$$

at 45°C	53%	47%
at 100°C	64%	36%

Quick Quiz

1. What are monohaloalkanes?
2. What are primary, secondary and tertiary carbons atoms?
3. What is carbonium ion?
4. What is leaving group?
5. What is sp3 hybridization?
6. Define bond polariy.
7. Define bond energy.
8. What is nuleophile?
9. What is electrophile?
10. Define inductive effect.
11. Define resonating effect.
12. What is racemization?
13. Define transition state.

17.2 ORGANOMETALLIC COMPOUNDS (GRIGNARD'S REAGENTS)

17.2.1. Preparation of Grignard's Reagents

$$R—X + Mg \xrightarrow[\text{Ether}]{\Delta} R\,Mg\,X$$

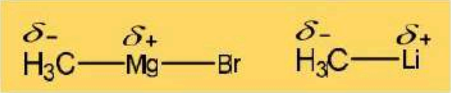
Magnesium metal cut into small pieces is added to a solution of an alkyl halide or aryl halide in only dry ether. The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.

Alky bromide are generally used in the preparation of Grignard's reagent because of its intermediate reactivity, when alkyl halides are used, the solvent is either the high boiling solvent such as tetrahydrofuran is employed when less reactive aryl halides are used . Alkyl magnesium halides are not isolated but are used as ethereal layers.

17.2.2. Reactivity

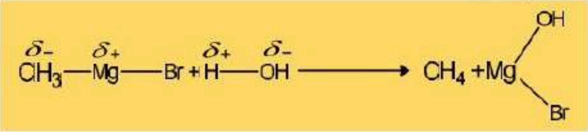
$$\overset{\delta-}{R}—\overset{\delta+}{Li}, \qquad \overset{\delta-}{R}—\overset{\delta+}{Mg}—X$$

Organo metallic compounds are nucleophile because of partial negative charge on the carbon of alkyl group



$$\overset{\delta-}{H_3C}—\overset{\delta+}{Mg}—Br \qquad \overset{\delta-}{H_3C}—\overset{\delta+}{Li}$$

Carbon atom being more electronegative the metals such as Mg, Li etc. The alkyl group as a whole bears partial negative charge and organo metallic compounds act as source of nucleophile, e.g.,

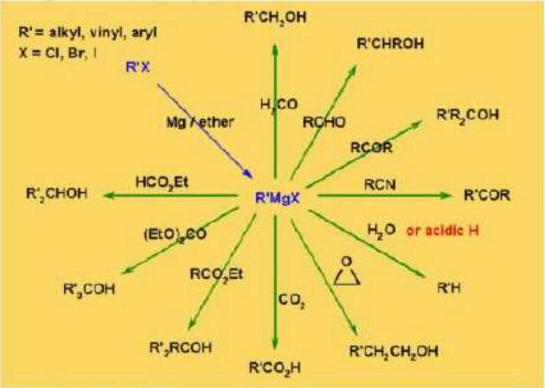


The following reaction supports the electrophilic character of organic metallic compounds;

17.2.3. Reactions of Grignard's Reagents

With Aldehydes and Ketones

This is done in following three steps to produce primary, secondary and tertiary alcohols. These reactions are carried in the presence of ether followed by H_3O^+. First two reaction are with aldehydes while third belongs to ketones.



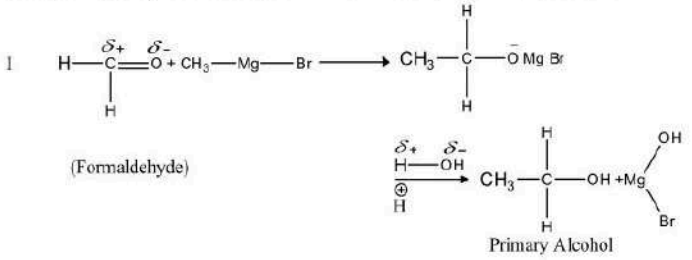
Classification of Monohydric Alcohols:

Monohydric alcohols are classified into the following three families:

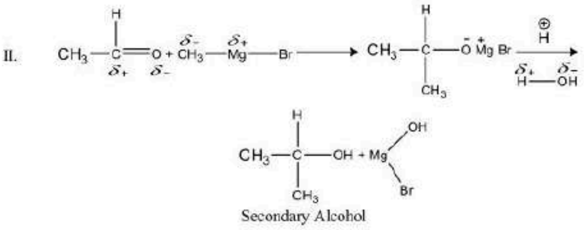
(i) Primary alcohols
(ii) Secondary alcohols
(iii) Tertiary alcohols

(i) Reaction with Methanal (Aldehyde) to form primary alcohol
(ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol
(iii) Reaction with Propanone (Ketone) to form tertiary alcohol.

Reaction type: Nucleophilic acyl substitution then nucleophilic addition

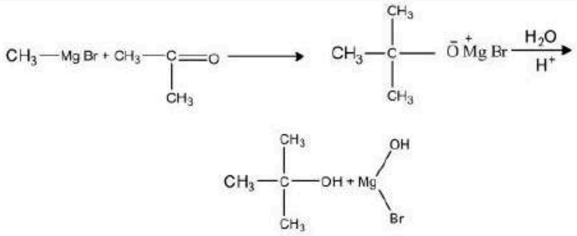


Primary Alcohol



Secondary Alcohol

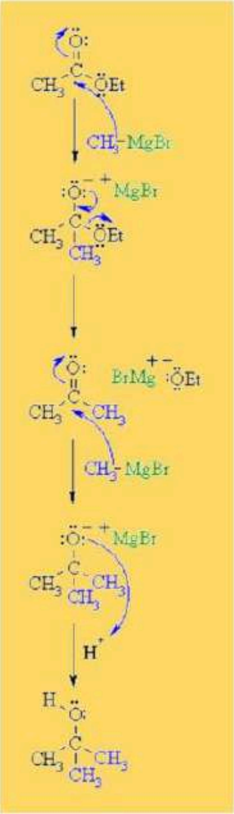
III.



(Ter-butyl alcohol)

1. Carboxylic esters, R'CO₂R", react with 2 equivalent of organolithium or Grignard reagents to give tertiary alcohols.
2. The tertiary alcohol contains 2 identical alkyl groups.
3. The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent.
4. Since the ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones.

REACTION OF RLi or RMgX WITH AN ESTER



Step 1:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 2:

The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group, this produces a ketone as an intermediate.

Step 3:

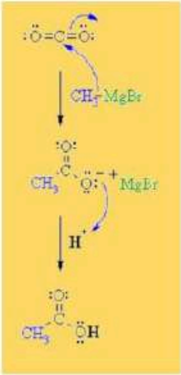
The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 4:

This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

With CO_2 (Carbonation of Grignard Reagents, RMgX)

NUCLEOPHILIC ADDITION OF RMg X TO CARBON DIOXIDE



Step 1:

The nucleophilic C in the Grignard reagent adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate magnesium carboxylate complex.

Step 2:

This is the work-up step, a simple acid/base reaction. Protonation of the carboxylate oxygen creates the carboxylic acid product from the intermediate complex.

Quick Quiz

1. What are organometallic compounds?
2. Define protonation.
3. What is formula of organolithium?
4. How does RMgX reacts with CO_2?
5. Write the formula of Grignard Reagent.

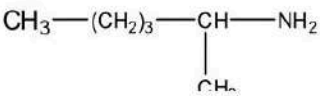
17.3 AMINES

17.3.1 Nomenclature:

1. Common System of Naming

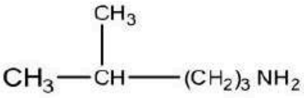
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals.

$CH_3\,CH_2\,NH_2$ Ethyl amine



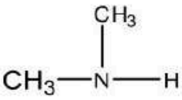
$$CH_3-(CH_2)_3-\underset{\underset{CH}{|}}{CH}-NH_2$$

Sec-hexyl an



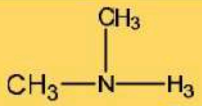
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-(CH_2)_3\,NH_2$$

Iso-hexyl amine
(a primary amine)



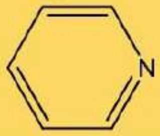
$$CH_3-\overset{\overset{CH_3}{|}}{N}-H$$

Dimethyl amine (a sec-amine



$CH_3-\overset{\overset{CH_3}{|}}{N}-H_3$

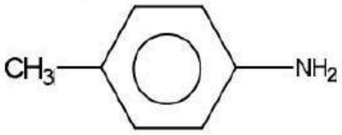
Trimethly amine (a ter-amine)



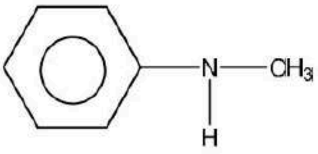
Pyridine (a ter-amine)

Aniline, $C_6H_5NH_2$ containing methyl group on the ring is called Toluidine. If there is some alkyl group substituted in $-NH_2$ its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring. It there are two substituent on N, it is repeated twice,

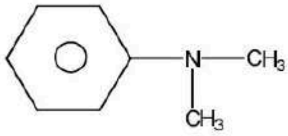
2. IUPAC System of Naming



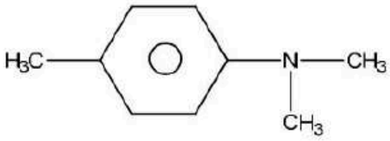
p-Toluidine



N-methyl aniline



N, N-dimethyl aniline



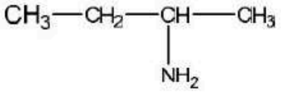
N, N-dimethyl
p-toluidine

In this system amino group is indicated by a prefix-amino followed by name of hydrocarbons, the position of amino group is indicated by a number obtained by numbering the chain of hydrocarbon.

Secondary and tertiary amines are named by using a compound prefix that includes the names of all but the largest alkyl group.

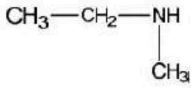
CH_3NH_2

Amino methane



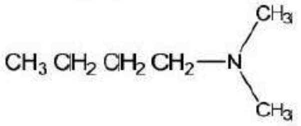
$CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$

2-Aminobutane



$CH_3-CH_2-NH(CH_3)$

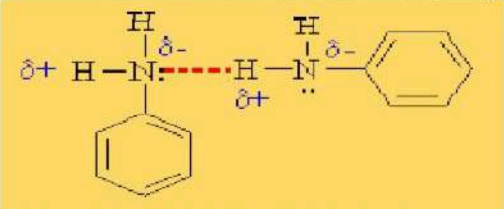
Methyl amino ethane



(Dimethyl amino butane)

17.3.2. Physical Properties:

- The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules, see below, or other H-bonding systems (*e.g.* water). The applications of this are:
  - high melting and boiling points compared to analogous alkanes
  - high solubility in aqueous media



intermolecular H-bonding in amines

(Such tertiary amine is optically active)

17.3.3 Structure:

In amines, nitrogen atom is sp^3-hybridized and has nearly tetrahedral structure. It forms three sigma bonds with its three sp^3-hybrid orbitals while the fourth non-bonding sp^3-hybrid carries a pair electron

The non-bonding electron pair is extremely important in explaining the chemical behavior of amines because it is responsible for the basic and nucleophilic properties of these compounds. An amine with three different groups is optically active.

17.3.4. Basicity:

Amines may act as bases towards acids and as Nucleophiles towards electrophile. They are more basic than alcohols and ethers and they are also more nucleophilic, e.g., ether does not react where as at the same temperature amines gives addition product with CH_3-I,

$$C_2H_5OC_2H_5 + CH_3 - 1 \longrightarrow \text{No reaction}$$

$$(C_2H_5)_3N + CH_3I \longrightarrow [(C_2H_5)_3\overset{+}{N}CH_3]I^-$$

17.3.5 Preparation of Amines

Alkylation of Ammonia by Alkyl Halides

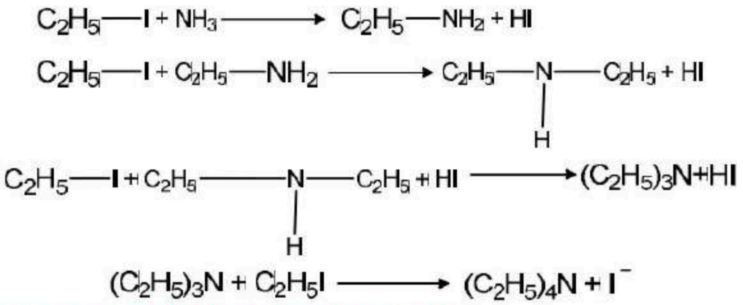
$$R—X + 2NH_3 \longrightarrow R—NH_2 + \overset{+}{N}H_4X^-$$

When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of prim-, sec-, ter- amines and a quaternary ammonium salt is obtained. The reaction occurs with nucleophilic displacement of halide by ammonia of amines,

$$NH_3 + R—X \longrightarrow (R—NH_3)^+\bar{X} \rightleftharpoons R—NH_2 + HX$$

This reaction is further alkylated, e.g., accompanies by the following reactions

At the end of the reaction, addition of strong alkali such as KOH liberates free amines from heir salts but the quaternary salt is unaffected. The three amines are separated by fractional distillation. Over alkylation can be avoided by using excess of ammonia but the yield is low.



$$C_2H_5-I + NH_3 \longrightarrow C_2H_5-NH_2 + HI$$

$$C_2H_5-I + C_2H_5-NH_2 \longrightarrow C_2H_5-\underset{\displaystyle H}{\underset{|}{N}}-C_2H_5 + HI$$

$$C_2H_5-I + C_2H_5-\underset{\displaystyle H}{\underset{|}{N}}-C_2H_5 + HI \longrightarrow (C_2H_5)_3N{+}HI$$

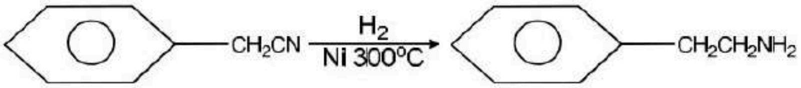
$$(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4N + I^-$$

Reductions of nitrogen containing functional groups:

Reduction of Nitriles

Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by $LiAlH_4$, or sodium in ethanol. Catalytic hydrogen with Rh-Al_2O_3, Pt or Raney nickel may also be employed to get primary amines

$$CH_3\,CN + 2H_2 \xrightarrow{Rh.\ Al_2O_3} CH_3\,CH_2NH_2$$



Reduction of Nitro Compounds

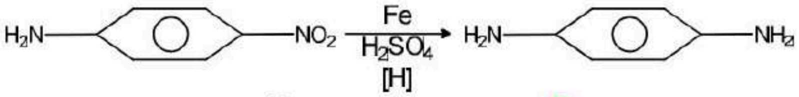
Nitro compounds on catalytic or chemical reduction produce primary amines

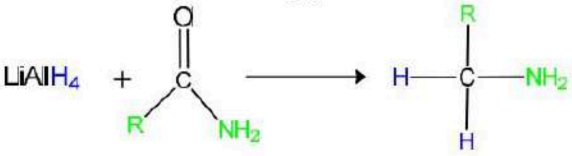
- Nitroarenes can be reduced to primary aryl amines.
- Typical reducing agents include, Fe / H^+, Sn / H^+ or catalytic hydrogenation (*e.g.* H_2 / Pd)

$$Ar-NO_2 \xrightarrow{[R]} Ar-\ddot{N}H_2$$

Nitroarene
primary aryl amine

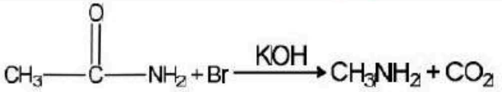
$$C_6H_5NO_2 \xrightarrow[{[H]}]{Sn + HCl} C_6H_5NH_2$$



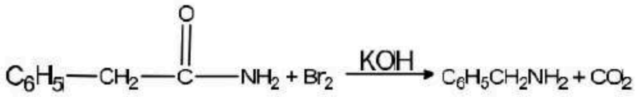


Reduction of Amides

An amide on treatment with Bromine in the presence of KOH yields primary amines. The reaction occurs through rearrangement.



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br \xrightarrow{KOH} CH_3NH_2 + CO_2$$



$$C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 \xrightarrow{KOH} C_6H_5CH_2NH_2 + CO_2$$

17.3.6 Reactivity:

Amines are basic and nucleophiles because of non-bonding pair of electrons on nitrogen. The relative availability of this pair of electron and the relative stability of corresponding ammonium ion is responsible of basicity of different amines. Consider the following reactions.

The strength of a base is expressed in terms of pkb, i.e., $pk_b = -logk_b$

For ammonia and methyl amine, the pk_b values are $PK_{NH3} = 4.76$; $PK_{CH3NH2} = 3.38$

$$\ddot{N}H_3 + H^+ \underset{}{\overset{KNH_3}{\rightleftharpoons}} NH_4$$

$$CH_3-NH_2 + H^+ \underset{KCH_3NH_2}{\overset{KNH_3}{\rightleftharpoons}} CH_3-\overset{+}{N}H_3$$

Since $PK_{NH3} < PK_{CH3NH2}$ methyl amine is a stronger base than ammonia. It can be explained as under:

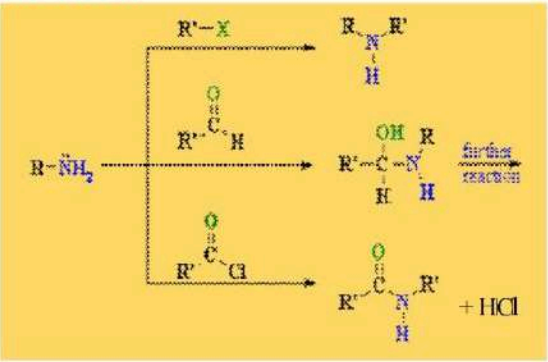
In ammonia, the pair of electron attracted by s-orbitals of hydrogen atoms where as in $CH^-_3\,NH_2$, sp^3— orbital of carbon pushes electrons towards nitrogen.

Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia. The methyl ammonium ion, $CH^-_3\,NH^+_3$ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms. Both these factors favor methylamine to a stronger base than ammonia.

Higher members show deviation to these arguments. It is because the stabilization of a positive ion also depends upon the extent of salvation, hydrogen bonding and resonance stabilization. Moreover, the availability of non-bonding pair of electrons is also affected by steric factor in addition to these aspects

17.3.7 Reactions of Amines

Overview



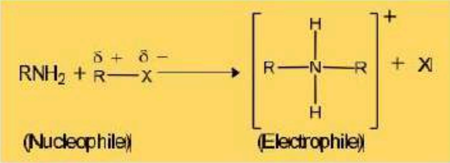
The important organic reactions of amines (nucleophiles) are with the common electrophiles:

- Alkyl halides via nucleophilic substitution
- Aldehydes or ketones via nucleophilic addition
- Carboxylic acid derivatives, especially acid chlorides or anhydrides, via nucleophilic acyl substitution.

Alkylation of Amine by Alkyl Halides

"The alkylation of amine is called alkylation". It produces sec- or tertiary amine,"

$R_2NH_2^+$ loses a proton with a base to give a free amine.



Reactions of Primary Amines with Aldehydes and Ketones

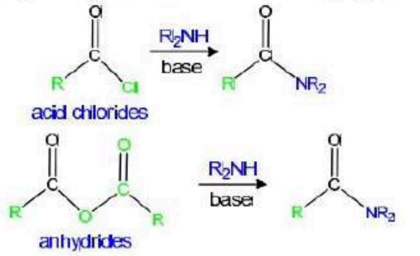
Aldehydes and ketones react with primary amines to form Schiff's base

Preparation of Amides

Preparation of Diazonium Salts

When amines react with nitrous acid, diazonium compounds are formed.

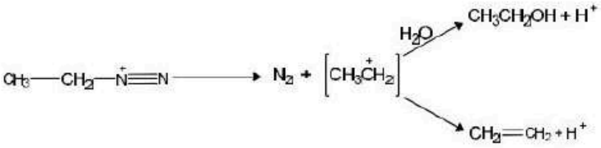
$$CH_3CH_2\text{-}NH_2 + CH_3CHO \longrightarrow C_2H_5\text{-}N = CH\text{-}CH_3$$



$$RNH_2 + HNO_2 \longrightarrow \underset{\text{diazonium ion}}{R-\overset{+}{N}\equiv N} + \overset{-}{O}H + H_2O$$

The diazonium group, is rather unstable. In case of ethyldiazonim ion, it decomposes at once:

When the diazonium group is attached to a benzene ring, through, the ion is stabilized to some extent by the delocalized electron of the ring. The benzenediazonium ion is therefore much more stable than its aliphatic counterparts. Nevertheless, it decomposes readily above 10°C.



Quick Quiz

1. Define hydration
2. What is the difference between alicyclic and aromatic compounds?
3. Define IUPAC.
4. Write the equation for the preparation of mustard gas.
5. Define polymers
6. What is polymerization?
7. What is Markownikov's rule?
8. What are amines?
9. Why halogen of vinyl chloride is inert?

Society, Technology and Science

ORGANOMETALLIC COMPOUNDS IN MEDICINES

- Cisplatin $(C_5H_5)_2TiCl_2$ displays anti-cancer activity in chemotherapy.
- Arene- and cyclopentadienyl complexes are kinetically inert platforms for **the design** of new radiopharmaceuticals.
- Mercurochrome (Merbromin) is an over-the-counter topical antiseptic.
- Merthiolate (Thiomersal) has applications as an antifungal and antiseptic agent. This compound is also used as a vaccine preservative, in immunoglobulin preparations and nasal products.
- Salvarsan (arsphenamine in the States) is an anti-syphilis medication.
- Titanocene dichloride, Cp_2TiCl_2 has shown significant anticancer attributes.
- Tamoxifen is an anticancer compound.
- Ferrocenyl derivative chloroquine is an antimalarial compound.
- Titanocene dichloride, $(Cp)_2V(NCSe)_2$ 1, and carboplatin are anticancer drugs.
- Ferroquine, a combination of ferrocene and chloroquinine, is antimalarial drug.
- Vanadocene acetylacetonate has potential in preventing HIV transmission.
- Ru $(\eta_6\text{-}C_6H_6)Cl_2$(DMSO) has been shown to inhibit topoisomerase II, an important target in chemotherapy.

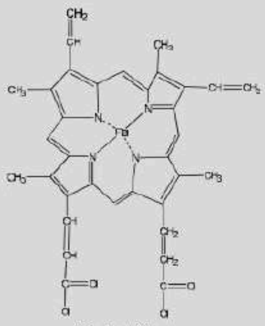
Do You Know?

1. CD's are made from vinyl chloride
2. Ethyl chloride is used as a typical anesthetic
3. Erupting volcanoes emit large quantities of halogens and halides

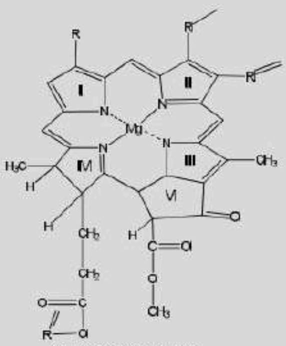
Comparison between hemoglobin and chlorophyll

Hemoglobin and chlorophyll both are natural organo-metallic compounds. Both consist of a substituted porphyrin ring coordinated with a metal ion.

1. Hemoglobin is a porphyrin ring with iron while chlorophyll is a porphyrin ring with magnesium while chlorophyll is a porphyirn ring with magnesium.
2. Hemoglobin is the red pigment in the blood while chlorophyll is the green pigments in green plants, algae, and certain organism.
3. Hemoglobin is involved in oxygen transport while chlorophyll functions as a receptor of light energy during photosynthesis.



Structure of Heme



Structure of Chlorophyll

Key Points

- Monohalo derivates of alkanes are called alkyl halides.
- The general formula of alkyl halides in $C_nH_{2n+1}X$.
- 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.
- Alkyl halides are very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reaction in the presence of nucleophile or a base.
- Nucleophilic substitution reactions can take place in two distinct ways. A one step mechanism is called SN_2 while a two step mechanism is called SN_1. SN_1 reaction show first order kinetics whereas SN_2 reaction show 2nd order kinetic.
- Nucleophilic substitution reactions take place simultaneously with elimination reaction and often compete with them.
- Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophile substitution, β-elimination reactions also take place in two distinct ways E_2 and D_1.
- A nucleophile is an the electron rich species that will react with an electron poor species
- A substitution implies that one group replaces another.
- Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
- Grignard reagent ahs a reactive nucleophilic carbon atom which can react with electrophilic centered to give the products in high yields. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.
- The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules.
- Primary amines, **R-NH_2** or **ArNH_2**, undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines.**
- **Primary alkyl or aryl amines** yield diazonium salts.

Exercise

1. Choices given with each question.

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. SN_2 reactions can be best carried out with:

a. Primary alkyl halides b. Secondary Alkyl halides

c. Tertiary alkyl halides d. All the three

iii. For which mechanisms, the first step involved is the same;

a. E_1 and E_2 b. E_2 and SN_2 c. E_1 and SN_2 d. E_1 and SN_1

iv. The rate of E_1 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.

v. 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

vi. Which one of the following is not a nucleophile:

a. H_2O b. H_2S c. BF_3 d. NH_3

vii. Double bond is formed as a result of;

a. Substitution reactions b. Elimination reactions

c. Addition reactions d. Rearrangement reactions

viii. Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen

a. RBr b. RCl c. RF d. RI

ix. CH_3CH_2Br on treatment with alc.KOH gives:

a. Propanal b. Propene c. Propane d. None

x. Grignard's reagent gives alkane with;

a. Water b. Ethylamine c. Ethanol d. All of these

xi. Action of alkyl halides with Na metal yield;

a. Alkanes b. Alcohols c. Alkenes d. Phenols

xii. Alkyl halides react with excess of ammonia to give;

a. 1^0-amine b. 2^0-amine c. 3^0-amine d. all

xiii. Among the alkyl halides the primary alkyl halides always follow the mechanism;

a. SN_1 b. SN_2 c. SN_3 d. SN_4

xiv. Grignard's regent on treatment with chloramines gives;

a. Acetamide b. Primary amine c. Secondary amine d. urea

xv. Nucleophilic addition of a primary amine giving;

a. Imine b. urea c. ammonia d. Nitrobenzene

2. Give brief answers for the following questions.

i. What are primary, secondary and tertiary alkyl halides?

ii. Why alkyl iodides cannot be prepared by directly heating iodine with alkene?

iii. What are Nucleophilic substation reactions or SN reaction?

iv. Tertiary alkyl halides show SN_1 reactions mostly, why?
v. What are elimination reactions?
vi. Which factor decides the reactivity of alkyl halides?
vii. What are the diazonium salt?
viii. How can nucleophilic addition of a primary amine giving an imine?
ix. Amines are more basic than analogous alcohols why?
x. How tertiary alcohols are obtained from R-Mg-X?

3. Give detailed answers for the following questions.

i. Discuss the reactivity of alkyl halides.
ii. Give three methods for the preparation of alkyl halides.
iii. Explain in detail SN_1 and SN_2 reactions with mechanism.
iv. What are β-elimination reactions? Explain them with detail.
v. How will you convert ethyl chloride to the (i) ethyl cyanide (ii) ethanol (iii) propane (iv) n-butane (v) tetraethyl lead.
vi. Discuss the preparation and reactivity of Grignard's reagent.
vii. What are the amines? Give its nomenclature.
viii. What are the main features which increase the basicity of amine?
ix. Amides are reduced by $LiAlH_4$. Give mechanism.
x. What are the diazonium salts? How they can be prepared? Give their reactions?

18

ALCOHOL, PHENOLS AND ETHERS

This is 10 days lesson (period including homework)

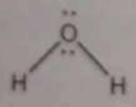
After completing this lesson, you will be able to:

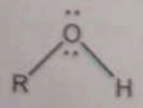
- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol.
- Describe the preparation of alcohols by reduction of aldehydes.
- Explain reactivity of alcohols.
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1,2 –diols.
- Discuss thiols RSH.
- Explain the nomenclature, structure and acidity of phenols.
- Describe the preparation of phenols from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diamzonium salts.
- Discuss the reactivity of phenol and their chemistry by electrophonic aromatic substitution, reaction with Na metal and oxidation.
- Differentiate between alcohols and phenol
- Describe isomerism in alcohols and phenols.
- Identify ethers from their formula.

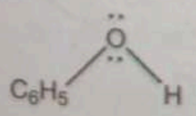
Reading

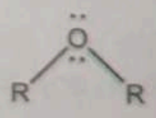
The structure of alcohols, phenols and ethers are much closer to water.

Alcohols and phenols both contain hydroxyl (--OH) group attached to alkyl and phenyl groups, respectively. In ether both hydrogen atoms of water are replaced by alkyl or phenyl groups.


Water


Alcohol


Phenol

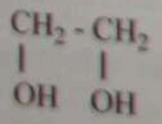

Ether

18.1 ALCOHOLS

The aliphatic organic compounds containing hydroxyl group –OH, as functional group are called alcohols. Alcohols containing one –OH group are called monohydric alcohols and those containing two or more hydroxyl groups are known as polyhydric alcohol e.g.

CH_3-CH_2-OH

Monohydric alcohol



$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

Dihydric alcohol

Classification of Monohydric Alcohols:

Monohydric alcohols are classified into the following three families:

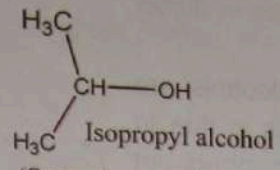
(i) Primary alcohols (ii) Secondary alcohols and (iii) Tertiary alcohols

Examples:

$CH_3—CH_2—OH$

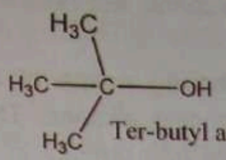
Ethyl alcohol

(Primary alcohol)



Isopropyl alcohol

(Secondary alcohol)



Ter-butyl alcohol

(Tertiary alcohol)

18.1.1 Nomenclature:

1. Common System of Naming

In common system, alcohols are named by adding the word alcohol after the name of the alkyl group to which the –OH group is attached e.g.

C_2H_5OH	$C_6H_5CH_2OH$
Ethyl alcohol	Benzyl alcohol

2. IUPAC System

According to this system

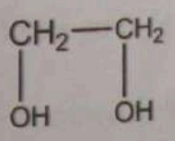
(i) The longest chain of carbon atoms containing the hydroxyl group is selected as the parent hydrocarbon.

(ii) The ending **'e'** of the parent hydrocarbon (alkane) is replaced by **'ol'**

(iii) The position of –OH group is indicated by placing the number of carbon to which –OH is attached before the name of alcohol.

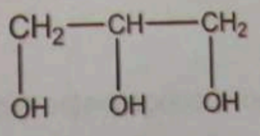
(iv) The carbon chain bearing –OH group is numbered, beginning from that end which would assign the lowest possible number to carbon atom linked to the –OH group.

(i) The presence of more than one -OH groups is indicated by suffixes –diol, -triol, etc. and repeating the number of carbon atoms one which –OH groups are attached e.g.



$$\underset{OH}{CH_2}—\underset{OH}{CH_2}$$

1, 2-ethanediol or
Ethane-1, 2-diol
(glycol)



$$\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2}$$

1, 2, 3-propane triol
(glycerol)

(Common names are given in brackets)

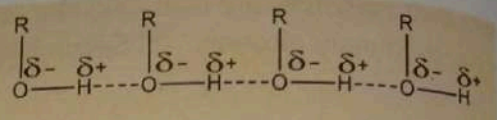
(vi) In unsaturated alcohol, the hydroxyl group gets the lower number rather than unsaturation, e.g.,

$CH_3—CH{=}CH—CH_2—OH$ 2-butene-1-ol

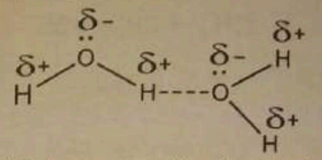
18.1.2 Physical Properties:

Alcohol upto butanol are generally colorless liquids with characteristic sweet smell and burning taste. They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but deceases in higher alcohol.

Melting and boiling points of alcohols are higher than corresponding alkanes. This is due to hydrogen bonding which is present in alcohols but absent in alkanes.



(Hydrogen bonding in alcohol)



(Hydrogen bonding in water)

18.1.3 Structure:

- The alcohol functional group consists of an O atom bonded to a C atom and an H atom via s bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.

18.1.4 Acidity:

- Due to the electronegativity of the O atoms, alcohols are slightly acidic
- The anion derived by the deprotonation of an alcohol is the **alkoxide**.

$$2\,R{-}O{-}H + 2\,Na \longrightarrow 2\,NaOR + H_2$$

$$2\,H{-}O{-}H + 2\,Na \longrightarrow 2\,NaOH + H_2$$

- Alkoxides are important bases in organic chemistry.
- Alcohols react with Na (or K) like water to give the alkoxide:

18.1.5 Preparations of Alcohols

1. Hydration of Alkenes

Hydration of alkenes is carried out in the following two steps:

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3{-}CH_2OSO_3H}$$

(a) Preparation of alkyl hydrogen sulphate

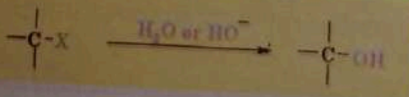
(b) Hydrolysis of alkyl hydrogen sulphate

(a) Alkenes are dissolved in concentrated H_2SO_4 to form alkyl hydrogen sulphate

(b) On dilution with water followed by heating alkyl hydrogen sulphates are hydrolyzed to alcohols.

(c) $CH_3CH_2OSO_3H + H\text{-}OH \longrightarrow CH_3CH_2OH + H_2SO_4$

2. Hydrolysis of Alkyl halides



$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{H_2O \text{ or } HO^-} -\overset{|}{\underset{|}{C}}-OH$$

Elaboration

- Alkyl halides can be converted to alcohols using water or hydroxide as the nucleophile.

- Mechanism is a simple nucleophilic substitution

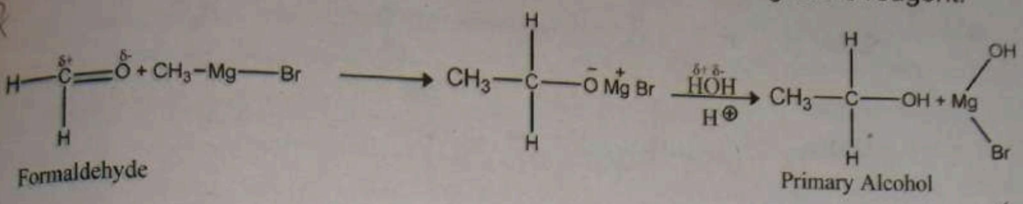
3. Reactions of RMgX with Aldehydes and Ketones

Primary, secondary and tertiary alcohols can be prepared by the use of Grignard's reagent. The Grignard reagent adds to a carbonyl molecule and the resulting compounds forms alcohol on hydrolysis.

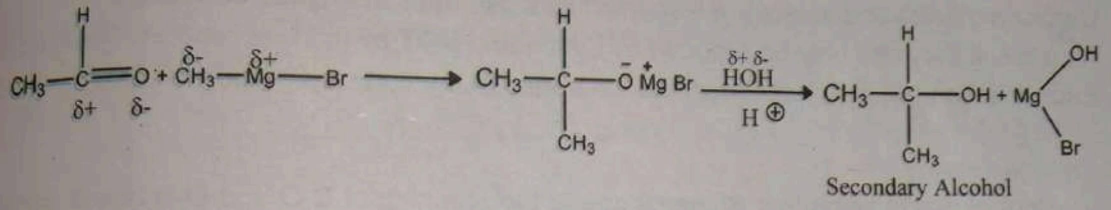
Imp

(a) **Primary alcohol:** Formaldehyde gives primary alcohol with Grignard's reagent:

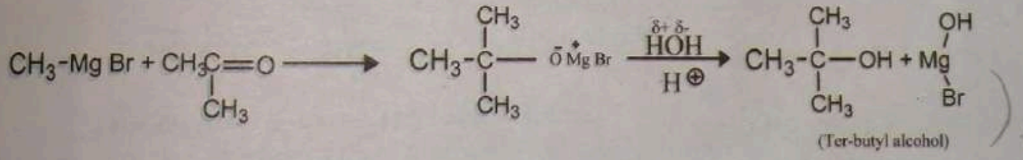
Imp



(b) **Secondary Alcohols:** All other aldehydes give secondary alcohols, e.g.,

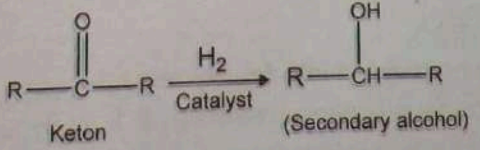


(c) **Tertiary Alcohols:** Ketones form tertiary alcohols with Grignard's reagent under similar conditions, e.g.



4. Reduction of Aldehydes and Ketones

Reduction of aldehydes, ketones and carboxylic acid (esters in the presence of Ni, Pd or Pt) gives alcohols, e.g.,



$LiAlH_4$ besides reducing aldehydes, ketones and ester, also reduces carboxylic acids, e.g.,

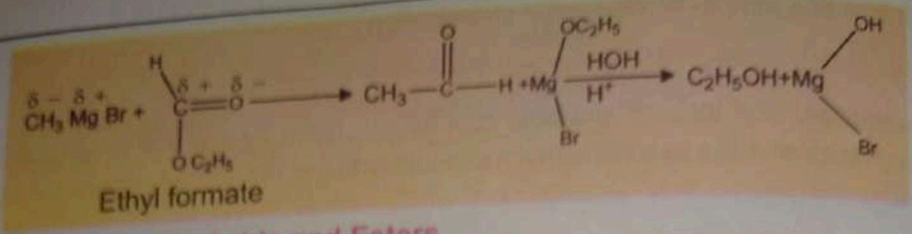
$$RCOOH + LiAlH_4 \rightarrow RCH_2OH$$

5. Reaction of RMgX with Esters

Esters react with Grignard reagents to form aldehyde.

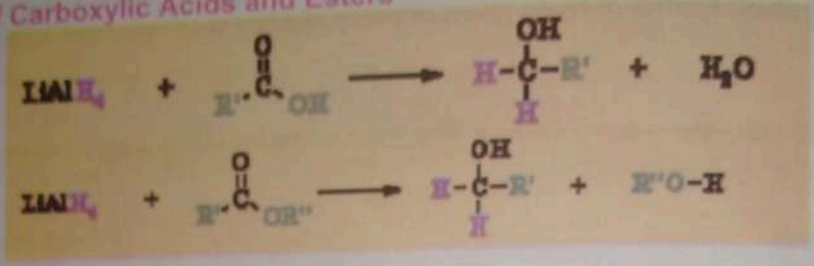
The aldehyde so formed reacts with another molecule of Grignard's reagent to give alcohol.

Similarly other esters give secondary and tertiary alcohols with Grignard's Reagents,



Ethyl formate

6. Reduction of Carboxylic Acids and Esters



Elaboration

- Carboxylic acids and esters are less reactive to **Nu** than aldehydes or ketones
- As a result they can only be reduced by $LiAlH_4$ and **NOT** by the less reactive $NaBH_4$
- Each reaction requires that 2 hydrides be added to the carbonyl carbon of acids or esters

18.1.6 Reactivity

Alcohol reacts with other reagents due to the breaking of C-O and O-H bonds. Breaking of bonds depends upon the nature of the attacking reagent. If a nucleophile attacks, the C-O bonds breaks and if an electrophile attacks the O-H bond breaks i.e.

$$CH_3—\overset{\delta+\ \delta-}{CH_2OH} \xrightarrow{\text{Nucleophile}} CH_3—CH_2—\overset{+}{C}H_2 + \overset{-}{O}H$$

$$CH_3—CH_2\overset{\delta-}{O}—\overset{\delta+}{H} \xrightarrow{\text{Electrophile}} CH_3—CH_2—CH_2\overset{-}{O} + \overset{+}{H}$$

The order of reactivity of alcohols with respect to cleavage of C-O bond is
Tertiary alcohol > Secondary alcohol > Primary alcohol
The order of reactivity of alcohol with respect to O-H bonds cleavage:
CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol
(Stable)

18.1.7 Reactions of Alcohols

The reactions of alcohols may be divided into four types:

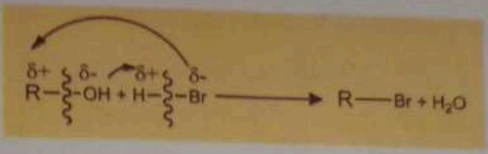
a) Reactions in which C – O bond is broken **(reaction # 1, 2, 3)**
b) Reactions in which O – H bond is broken **(reaction # 4)**
c) Reactions in which oxygen of an alcohol act as a base **(reaction # 4)**
d) Oxidation of alcohols. **(reaction # 5)**

1. Reaction with HX to give Alkyl Halides

Due to the presence of unshared electron pairs on the oxygen atom of alcohols, they act as bases and react with halogen acids to form their respective alkyl halides.

$$R—O—H + H—Br \longrightarrow R—Br + H_2O$$

The C-O bond in an alcohol is very slightly polarized. Therefore the following reaction mechanism is not possible.

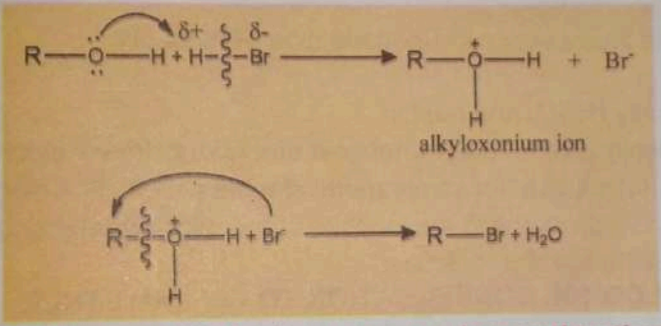


In fact, the alcohol acting as a base first forms an alkyl oxonium ion. Now the C-O bond becomes highly polarized. This electrophilic carbon is easily attached by a nucleophile.

The orders of reactivity of halogen acids and alcohols are HI > HBr > HCl and ter-alcohol>sec-alcohol>prim-alcohol. HCl and prim-alcohol are the least reactive amongst halogen acids and alcohols respectively. Therefore they react only in the presence of a catalyst. A solution of $ZnCl_2$ in concentrated HCl is used as a catalyst.

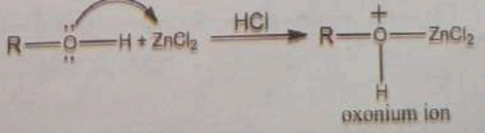
$$CH_3OH + HCl \xrightarrow{ZnCl_2/HCl} CH_3Cl + H_2O$$

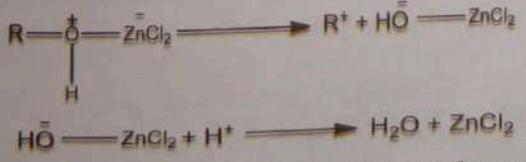
The reaction mechanism is:



Lucas Test: (Test for identification of primary, secondary and tertiary alcohols)

The difference of chemical reactivity of alcohols with halogen acids is used for their identification. For this purpose alcohol is treated with a solution of $ZnCl_2$ in concentrated HCl.





(i) Tertiary alcohol immediately forms an insoluble layer of a ter-alkyl chloride.

(ii) Secondary alcohol forms an insoluble sec-alkyl chloride in 5-10 minutes.

(iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.

Do you know?

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.

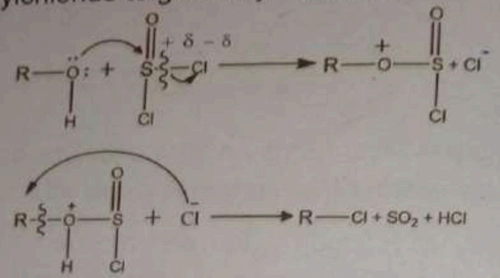
Methanol does not give iodoform Test

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{(Iodoform)}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

2. Reaction with $SOCl_2$, PX_3 to give Alkyl Halides (review)

(i) Thionylchloride ($SOCl_2$)

Alcohols react with thionylchloride to give alkyl chlorides.



(ii) Phosphorus Tribromide and Triodide (PBr_3 and PI_3)

$$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$$

Similarly,

$$3ROH + PI_3 \longrightarrow 3RI + H_3PO_3$$

Alkyl bromides and iodides are best prepared by treating alcohols with PBr_3 and PI_3.

3. Acid catalyzed Dehydration

Synthesis of Ethers via Acid-catalyzed Condensation of Alcohols

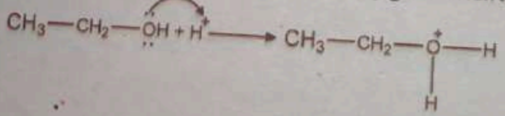
Elaboration

- Reagents typically H_2SO_4 and heat.
- In general, typically limited to **symmetrical** ethers of **primary** alcohols.
- The method is not suitable for unsymmetrical ethers.
- The substitution involves the O nucleophile of one alcohol attacking the electrophilic C in the other displacing a water molecule.

MECHANISM FOR ALCOHOL CONDENSATION TO GIVE AN ETHER

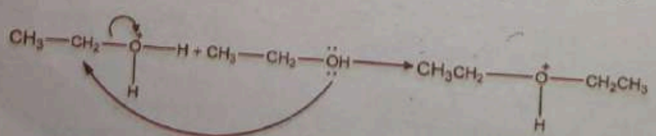
Step 1:

An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and reversible. The lone pairs on the oxygen make it a Lewis base.



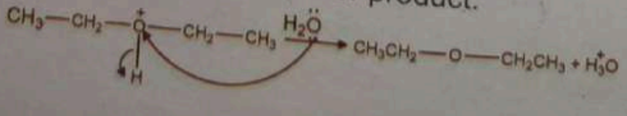
Step 2:

The O of the second alcohol molecule functions as the nucleophile and attacks to displace the good *leaving group*, a neutral water molecule, by cleaving the C-O bond. This creates an oxonium ion intermediate.



Step 3:

Another acid / base reaction. The proton is removed by a suitable base (here a water molecule, ROH is another alternative) to give the ether product.

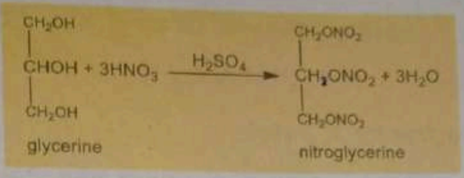


4. Preparation of Esters

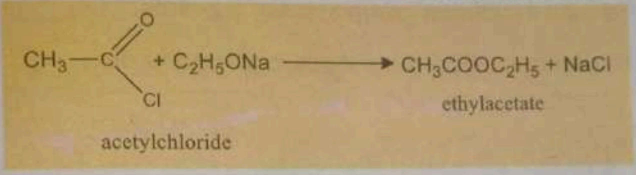
Alcohols react with organic as well as inorganic acid to form their respective esters.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

Glycerine reacts with a mixture of concentrated HNO_3 and H_2SO_4 to give an ester called Nitroglecerine or Glyceryltrinitrate.Nitroglycerine is highly explosive liquid. It is mixed with fine sand and moulded into sticks called Dynamite.



Esters are also formed by treating acid chlorides with sodium alkoxides.



5. Oxidation

Alcohols are easily oxidized by alkaline $KMnO_4$ or $K_2Cr_2O_7$ + H_2SO_4 solutions to give different products.

(i) Primary Alcohol:

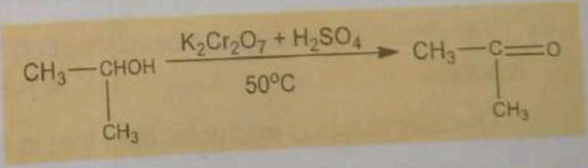
A primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.

$$\underset{}{CH_3-CH_2OH} \xrightarrow[50^{\circ}C]{K_2Cr_2O_7 + H_2SO_4} \underset{\substack{\text{acetaldehyde}\\(21^{\circ}C)}}{CH_3CHO} + H_2O$$

$$CH_3CHO \xrightarrow[50^{\circ}C]{K_2Cr_2O_7 + H_2SO_4} \underset{\text{acetic acid}}{CH_3COOH}$$

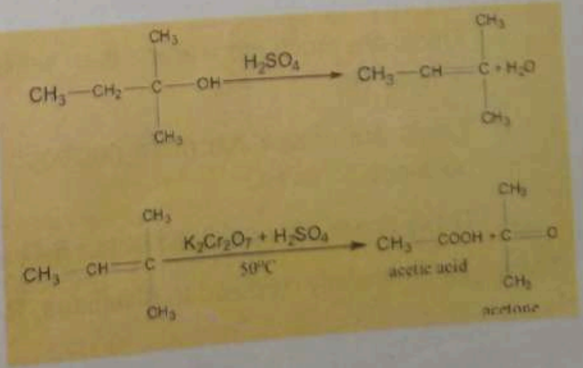
(ii) Secondary Alcohol:

A secondary alcohol is oxidized under similar condition to give a ketone which is not further oxidized.



(iii) Tertiary Alcohol:

A tertiary alcohol is not oxidized by alkaline $KMnO_4$. When heated with a mixture of $K_2Cr_2O_7$ and H_2SO_4, it is first dehydrated to an alkene in the presence of acid. Then alkene is oxidized to a ketone and a carboxylic acid by $K_2Cr_2O_7$ and H_2SO_4.

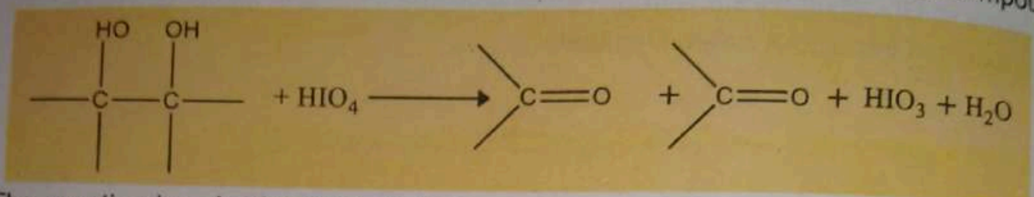


Each of the products contains lesser number of carbon atoms than the parent alcohol molecule.

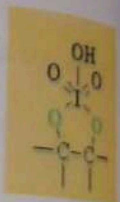
6. Cleavage of 1, 2-Diols

Oxidative Cleavage of Diols

- 1, 2- or vicinal diols are cleaved by periodic acid, HIO_4, into two carbonyl compounds.



- The reaction is selective for 1, 2-diols.
- The reaction occurs via the formation of a cyclic periodate ester.
- This can be used as a functional group test for 1,2-diols.
- The products are determined by the substituents on the diol.



18.1.8 The Sulfur Analogues (Thiols, RSH)

Thiols

Nomenclature:

Thiols are the sulfur analogues of alcohols. These are named by adding the suffix –thiol to the name of corresponding alkanes. e.g. H_3CSH (Thio methanol)

I - Physical Properties:

- Hydrogen bonding is much weaker than that in alcohols.
- Lower boiling points than similar alcohols.

II - Structure:

- Generally similar to alcohols, but bonds to S are longer and weaker than those to O.
- The thiol functional group consists of an S atom bonded to a C atom and a H atom via δ-bonds.
- The **S-H** bonds is *less* polar than that in alcohols since S is less electronegative than O.

IV - Reactivity:

- Thiols are much more acidic than similar alcohols, *e.g.* RSH (pKa = 10) versus ROH (pKa = 16 to 19)
- Thiols are also much more nucleophilic than similar alcohols, in fact RSH is about as nucleophilic as RO^-
- Thiols are readily oxidized but to **S-O** systems rather than **C=S** systems.

Thiols are commonly oxidized to disulfides, **R-S-S-R**, a biologically important reaction.

Quick Quiz

1. What are monohydric and polyhydric alcohols?
2. Why some alcohols are readily soluble in water
3. Write the structures of water and methyl alcohol.
4. Write the formulas of primary, secondary and tertiary alcohols.
5. How Grignard's reagent is used for the preparation of alcohols.

18.2 PHENOLS

Introduction

First prepared by	Runge
Melting point of phenol	41°C
Boiling point of phenol	182°C
Simplest example phenol	Carbolic acid (C_6H_5OH)

"Aromatic compounds containing 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 form coaltar by Runge in 1834.

Phenol is derived from the old name for benzene (phene), to include the suffix that indicates it possesses a hydroxyl group (ol).

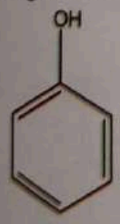
CAUTION: The word **phenol** (**C_6H_5-OH**) is often confused with **phenyl** (**C_6H_5-**). Phenols can be obtained via **substitution** reactions, with the hydrolysis of diazonium salts being the most important laboratory method.

Phenols are acidic and are important intermediates in the preparation of aryl ethers, **C_6H_5-OR**

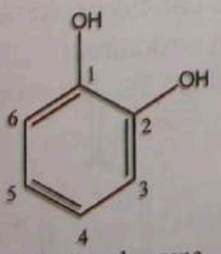
18.2.1 Nomenclature:

Phenols are named just like other derivatives of benzene. Anyhow, most of the members of this family have special names.

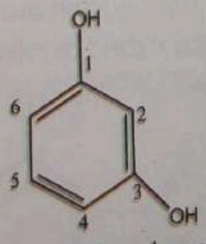
In IUPAC system, -OH group is represented by name hydroxyl. It is used as a prefix, while the benzene part of the molecule is used as a suffix. Some common names, and their IUPAC names are given below:



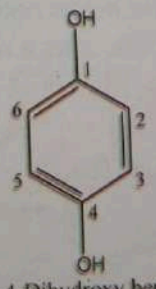
Phenol



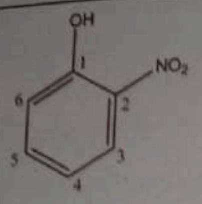
1, 2-Dihydroxybenzene
o-Hydroxyl phenol
(Catechol)



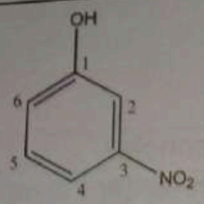
1, 3-Dihydroxy benzene
m-Hydroxy phenol
(Resorcinol)



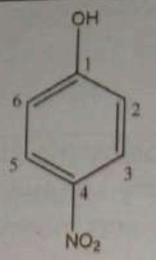
1, 4-Dihydroxy benzene
p-Hydroxy phenol
(Hydroquinone)



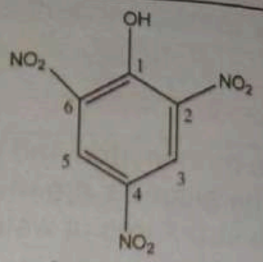
2-Nitrophenol
o-Nitrophenol



3-Nitrophenol
m-Nitrophenol



4-Nitrophenol
p-Nitrophenol



2, 4, 6-Trintrophenol
(Picric acid)

18.2.2. Structure:

- The alcohol functional group consists of an O atom bonded to an sp^2-hybridized aromatic C atom and a H atom via δ bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.
- Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.
- This results is, compared to simple alcohols:

a shorter carbon-oxygen bond distance
a more basic hydroxyl oxygen
a more acidic hydroxyl proton (-OH)

18.2.3. Physical Properties:

- Phenol is a colorless, crystalline, poisonous solid with characteristic phenolic odor having melting paint 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 causes blisters on the skin.
- It is used as disinfectants and in washrooms.
- It has distinctive odour.

Imp

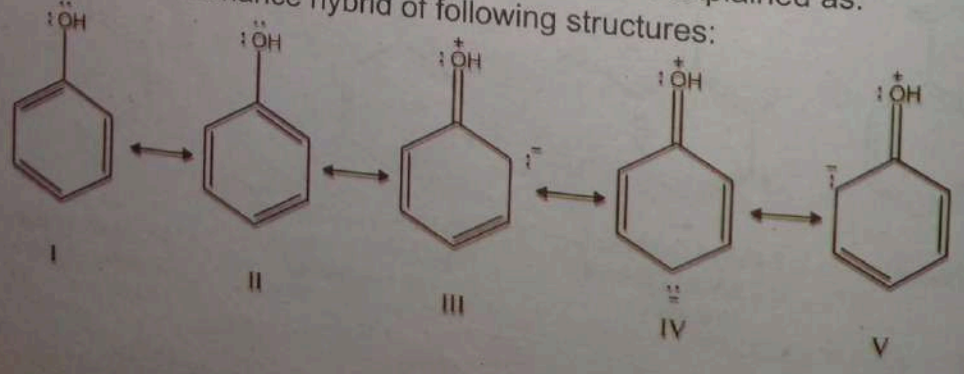
18.2.4. Acidity:

- Phenols are more acidic ($pK_a \approx 10$) than alcohols ($pK_a \approx 16 - 20$), but less acidic than carboxylic acids ($pK_a \approx 5$). Lets explain it:

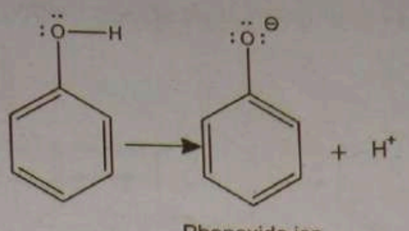
(I) Comparison of Acidity of Phenols and Alcohols

The stronger acidic nature of Phenols than alcohols can be explained as:

(a) Phenol exists as a resonance hybrid of following structures:



Thus due to resonance oxygen atom of the —OH group acquires a positive charge (as in structures III to V) and hence attracts electron pair of O—H bond leading to the release of hydrogen atom as proton.



Phenoxide ion

Carbon atom of the > COH group in phenol being sp^2 – hybridized is more electron attracting than the sp^3- hybridized carbon atom in alcohols. Thus in phenols there is greater Inductive-effect which facilitates proton release. Thus phenols are more acidic than alcohols. Since resonance is impossible in alcohols (due to the absence of conjugation of the lone electron pair of oxygen with a double bond), the hydrogen atom is more firmly held to the oxygen atom. Hence alcohols are neutral in nature.

b) The negative Phenoxide ion formed after the release of hydrogen atom is more resonance stabilized than phenol. Since there is no possibility for the delocalization of negative charge in the alkoxide ion, the latter is not stable. Hence alcohols have no tendency to form alkoxide and hydrogen ion.

ii) **Comparison of Acidity of Phenols and carboxylic acid:**

Resonating structures of carboxylic acids are:

$$R-\overset{\overset{O}{\|}}{C}-\ddot{O}H \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=\overset{+}{\ddot{O}}H$$

I

II (involves charge separation)

Carboxylic acids ionize as:

$$R-COOH \longrightarrow RCOO^- + H^+$$

(carboxylate ion)

The carboxylate anion so formed exhibits the following resonating structures:

$$R-\overset{\overset{O}{\|}}{C}-O^- \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=O$$

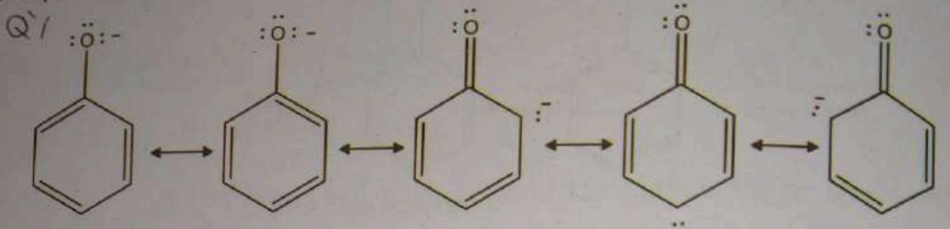
III

IV

Now the resonating structures I and II of carboxylic acid are non-equivalent and hence much less stable than the equivalent resonating structures III and IV for the carboxylate ion. Thus carboxylic acids have a tendency to undergo ionization to form more stable carboxylate ion and protons.

Now let us compare the acidic strengths of carboxylic acids and phenols. The resonating structures of phenoxide ion are not equivalent as shown below:

Q1



V VI VII VIII IX

The resonating structures III and IV of corboxylate anions are equivalent. Hence carboxylate anion is relatively more resonance stabilized than the phenoxide ion. Thus a carboxylic acid is more acidic than a phenol.) Q2

Q6 **(iii) Relative acidity of some common compounds follow the order:**

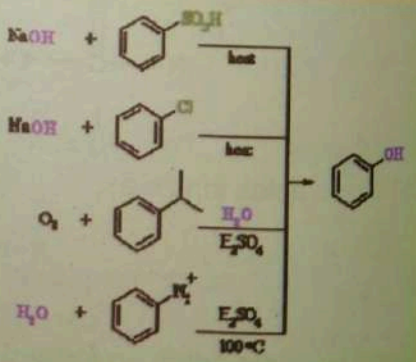
$RCOOH > H_2CO_3 > C_6H_5OH > HOH > R-OH$)

Q2 **(iv). Effect of substituents on the acidity of Phenols**

Electron attracting substituents tend to disperse the negative charge of the phenoxide ion, thus stabilise the ion and increase the acidity of phenols. Electron releasing substituents tend to intensify the charge, destablise the ion, diminish the resonance and decrease its acidity.)

18.2.5. Preparations of Phenols:

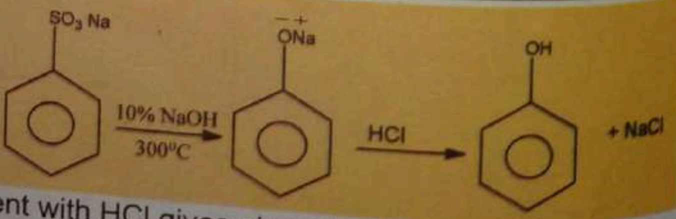
Summary



- Reaction of benzene sulfonic acid with base
- Reaction of chlorobenzene with base
- Acidic oxidation of cumene
- Hydrolysis of diazonium salts

Note: The first three methods are primarily industrial methods while the hydrolysis of diazonium salts is the most important laboratory method.

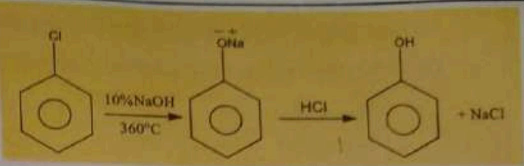
1. Reaction of Sodium salt of Benzene Sulfonic Acid with Sodium Hydroxide



Sodium benzene sulphonate on fusion with strong alkali like NaOH at 300 °C give sodium phenoxide which on treatment with HCl gives phenol.

2. Base Hydrolysis of Chlorobenzene (Dow's Method)

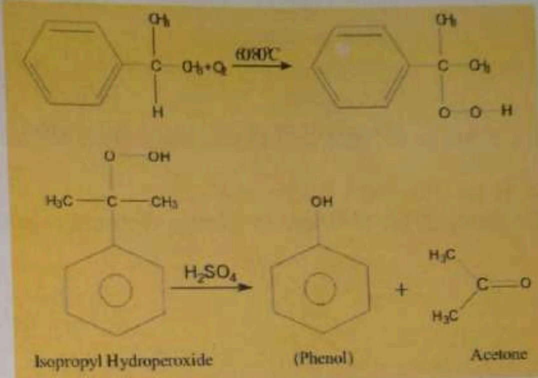
Chlorobenzene is hydrolyzed by heating with 10% NaOH at 360°C and under high pressure to form sodium phenoxide which on treating with HCl gives phenol.



3. Acidic Oxidation of Cumene

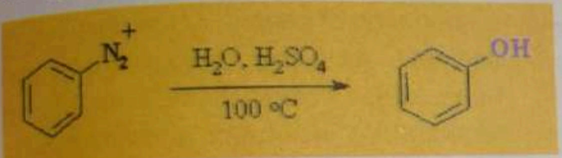
It is recently developed commercial method for the preparation of phenol. Cumene is oxidized by atmospheric oxygen in presence of metal catalyst, into cumene hydroperoxide.

The hydroperoxide is converted into phenol through an acid catalyzed rearrangement.

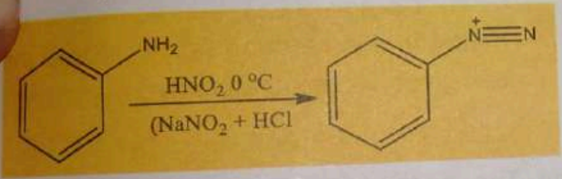


4. Preparation of Phenols from Aryl Diazonium Salts

Elaboration



- Aryl diazonium salts can be converted into phenols using H_2O / H_2SO_4 / heat



- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid, HNO_2

18.2.6 Reactivity:

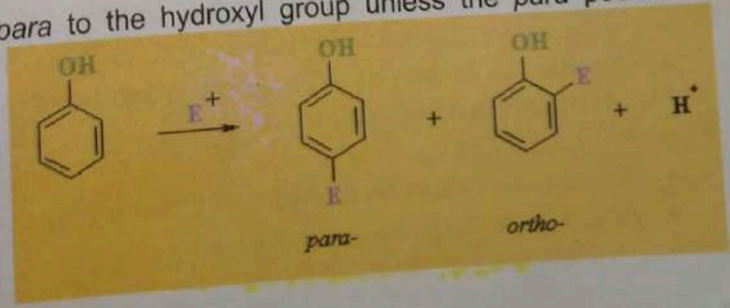
Phenols are very reactive towards electrophilic aromatic substitution. This is because the hydroxy group, **-OH**, is a strongly activating, *ortho- / para-* directing substituent.

18.2.7 Reactions of Phenols

1. Electrophilic Aromatic Substitution

Elaboration

- *Phenols* are potentially very reactive towards electrophilic aromatic substitution.
- This is because the hydroxyl group, **-OH**, is a strongly activating, *ortho- / para-* directing substituent
- Substitution typically occurs *para* to the hydroxyl group unless the *para* position is blocked, then *ortho* substitution occurs.
- The strong activation often means that milder reaction conditions than those used



for benzene itself can be used (see table below for a comparison)

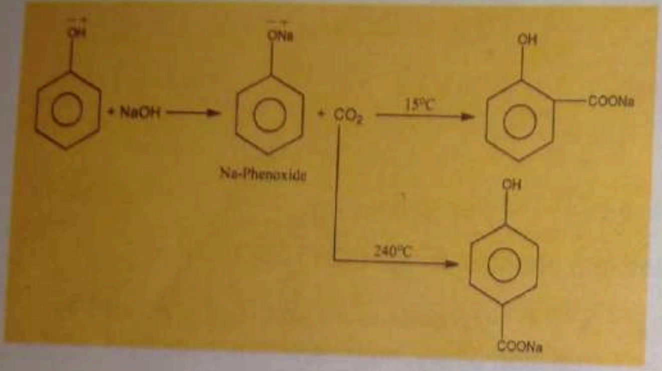
- Phenols are so activated that polysubstitution can be a problem

Reaction	Phenol	Benzene
Nitration	dil. HNO_3 in H_2O or CH_3CO_2H	Conc. HNO_3 / H_2SO_4
Sulfonation	conc. H_2SO_4	H_2SO_4 or SO_3 / H_2SO_4
Halogenation	X_2	X_2 / Fe or FeX_3
Alkylation	ROH / H^+ or RCl / $AlCl_3$	RCl / $AlCl_3$
Acylation	RCOCl / $AlCl_3$	RCOCl / $AlCl_3$
Nitrosation	aq. $NaNO_2$ / H^+	

Q4:

2. Reaction with Sodium Metal

Carboxylation of Phenols (Kolbe-Schmitt reaction)



"The reaction of sodium salt of phenol with CO_2 is called Kolbe reaction. It is carbonation of phenol. At low temperature sodium salicylate (sodium-o-hydroxy benzoate), where as at higher temperature o-product isomerizes to p-isomer,

Carbon of CO_2 acts as electrophilic centre in this reaction Acidification of the salt gives corresponding hydroxyl acid.

3. Oxidation of Phenols

Phenols are very reactive towards oxidizing agents. The oxidation takes place through several steps eventually destroying the ring.

Q5

18.2.8 Difference between Alcohols and Phenol

The main difference between alcohols and phenols are as follow;

Alcohol: with Sodium metal.

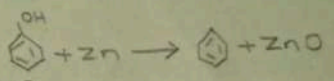
- The compounds in which hydroxyl group is attached to an alkyl group.
- Alcohols are hydroxyl derivatives of alkanes.
- The compounds in which one hydrogen of water is replaced by an alkyl group.
- The general formula of alcohol is R-OH.
- Lower alcohols are generally colorless liquids.
- Alcohols have a characteristic sweet smell and bumming taste. burning
- They are readily soluble in water but solubility decreases in higher alcohols.
- Alcohol reacts with other reagents in two ways, either in which C-O bond breaks or in which O-H bond breaks.

Phenol: with NaOH

- The compounds in which hydroxyl group is attached to an aryl group.
- Phenols are derivatives of benzene.

- The compounds in which one hydrogen of water is replaced by an aryl group.
- The general formula of phenol is C_6H_5OH. It is also known as carbolic acid.
- They are colorless, crystalline, deliquescent solids.
- They have characteristic phenolic odor.
- Its melting point is 41° C.
- Phenols are more acidic ($pK_a \approx 10$) than alcohols ($pK_a \approx 16 - 20$).
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5 °C.
- Phenolate ions have resonance structures but alcohols do not have such type structures.)

Quick Quiz

1. How negative charge of phenolate ion is stable?
2. What is acidity order of phenoles
3. Why phenols are very reactive towards electrohiplic aromatic substitution
4. Explain carbonation of phenols.
5. Alcohols and phenols both contain –OH group. What is difference between them
6. Why phenol is more acidic than ethyl alcohol?
7. What happens when phenol is heated with zinc dust? 

8. What happens when phenol is treated with bromine water?

18.3 ETHERS

18.3.1 Nomenclature

Common Names

(i) Common System of Naming:

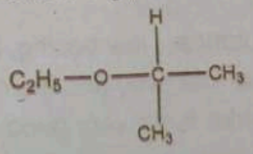
In common system of naming simple and mixed (or unsymmetrical) ethers are names by naming the two groups bonded to oxygen followed by the word ether, e.g.,

$CH_3—O—CH_3$

(Dimethyl ether)

$C_6H_5—O—CH_3$

Phenyl methyl ether (Anisole)



$$C_2H_5—O—\underset{CH_3}{\overset{H}{C}}—CH_3$$

Iso propyl ethyl ether

(ii) IUPAC System

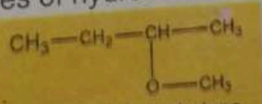
CH_3-O-CH_3	C_2H_5-O-C_2H_5
Dimethyl ether	Diethyl ether

In IUPAC system of naming simple ethers are named by naming the two groups linked to oxygen atom followed by the word ether, e.g.

Mixed ether are named as alkyl derivatives of hydrocarbons, e.g.

$CH_3—O—C_2H_5$

Methoxy ethane



$$CH_3—CH_2—\underset{O—CH_3}{CH}—CH_3$$

Methoxy butane

18.3.2. Preparation

Ethers are prepared by the following methods:

(i) **Williamson synthesis (conversion of alcohols to ethers)**

The reaction of primary alcohol with sodium gives an alkoxide.

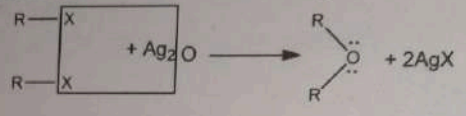
$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2\overset{-}{O}\overset{+}{Na}$$

Alkoxide when treated with alkyl halide, it forms ether.

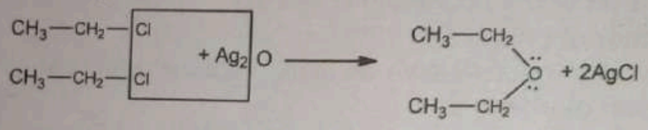
$$2CH_3CH_2\overset{-}{O}\overset{+}{Na} + CH_3CH_2Cl \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + NaCl$$

(ii) **Reaction of alkyl halides with dry Ag_2O:**

When alkyl halides are heated with dry silver oxide, then ethers are produced



Alkyl halide Ether



Ethylchloride Diethyl ether

(iii) **Dehydration of alcohols:**

Ether can be prepared by heating an excess of alcohol with conc. H_2SO_4 at 140°C. For example, ethanol with conc. H_2SO_4 at 140°C gives diethyl ether but at 180°C it gives ether.

$$2CH_3CH_2OH \xrightarrow[140^\circ C]{H_2SO_4} C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$$

When alcohols are of different types, then mixed ethers can be prepared. For example, when methanol and ethanol on mixing and heated with conc. H_2SO_4, it gives mixture of ethers, e.g;

$$CH_3CH_2OH + CH_3OH \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2OCH_2CH_3 + CH_3OCH_3 + C_2H_5OCH_3 + H_2O$$

18.3.3. Physical Properties

- Ethers are colorless, low boiling, highly inflammable compounds.
- Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compound make them very good solvent.
- Ethers are soluble in concentrated sulphuric acid, a characteristic of oxygen containing compounds. This property is used as a test to distinguish between ethers and saturate hydrocarbons.
- Lower ethers act as anaesthetics.
- Ethers are lighter than water.

18.3.4 Chemical Reactivity:

The image shows the electrostatic potential for dimethyl ether. The more red area is, the higher the electron density and the more blue area is, the lower the electron density.

- The ethereal O atom is a region of high electron density (red) due to the lone pairs.

Fig. 18.1

- Ether oxygen atoms are Lewis bases.
- Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.

The most important reaction of ethers is their cleavage by strong acids such as HI or HBr.

Q. How ethers show resistance to oxidation?

Resistance to Oxidation:

Ethers are resistant to attack by the usual chemical oxidizing agents. Moreover, reagent like NH_3, Na, alkali and acids have no action on ethers.

Q. How ethers react with H-Br?

Reaction with H-Br:

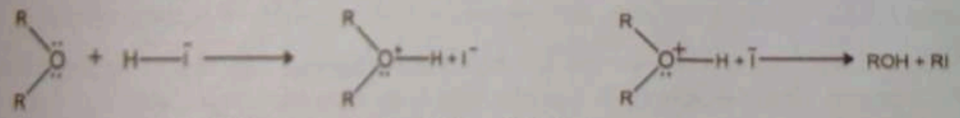
The oxygen atom of an ether molecule possesses unshared electron pair, which, accepts a portion of H-Br to form oxonium ion.

No further reaction takes place.

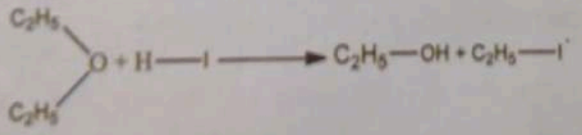
Q. How ethers react with H-I?

Reaction with H-I:

The oxygen atom of an ether molecule possesses unshared electron pair, which accepts a proton of H-I to form oxonium in, which reacts with I to form R-OH and RI.



Diethyl ether reacts with HI to form C_2H_5-OH and C_2H_5I.



Quick Quiz

1. How is diethyl ether prepared in the laboratory?
2. What are symmetrical and unsymmetrical ethers?
3. What is Williamson's synthesis?
4. "Ethers are good solvent". How?

Society, Technology and Science

1. Antiseptics and Disinfectants

Antiseptics and disinfectants are an essential part of infection control practices. They are extensively used in hospitals and other health care settings. A wide variety of active chemical agents or biocides are found in these products many of which have been used for hundred of years for antiseptics, disinfection and preservation. In general, biocides have a broader spectrum of activity than antibiotics. The widespread use of antiseptic and disinfectant products has promoted some speculation on the development of microbial resistance, in particular cross-resistance to antibiotics. Anti microbial activity of antiseptics and disinfectants can be influenced by many factors e.g. formulation effects, presence of an organic load, temperature, dilution etc.

Antiseptics

An antiseptic is a substance which inhibits the growth and development of micro organisms. For practical purposes, antiseptics are thought of as topical agents for application to skin, mucous membrane and inanimate objects. They can be either bactericidal or bacteriostatic. Their uses include cleansing of skin and wound, surfaces after injury preparation of skin surface prior to injection or surgical procedure and routine disinfection.

Disinfectants

Disinfectants were introduced by Listen who introduced carbolic acid (phenol) as the first disinfectant. Today disinfectants are widely used in the health care, food and pharmaceutical sectors to prevent unwanted micro-organisms from cuisine disease. Disinfectants chemicals disrupt significant cellular structures or processes in order to kill or eliminate micro-organism.

2. Ether – An effective Anaesthetic

Before the advent of anaesthetics, surgery was a savage and primitive affair. It was agony for the patient, and surgeons were therefore only prepared to operate if it was absolutely essential, for example the amputation of a damaged limb that would otherwise become gangrenous. Anaesthetics enable surgery to develop from crude carpentry to it present sophisticated forms.

Three of the most important early anaesthetics were nitrous oxide) dinitrogen oxide, N_2O), ether (ethoxyethane, $CH_3CH_2OCH_2CH_3$) and chloroform (trichloromethane, $CHCl_3$). Nitrous oxide is non-toxic and non-flammable, but it only produces light anaesthesia. Chloroform produces deep anaesthesia and is non-flammable, but it is toxic and carries the risk of liver damage.

Key Points

- Alcohols and phenols are hydroxyl derivatives of aliphatic and aromatic hydrocarbons.
- General formula for alcohol is ROH, for Phenol PhOH, and for ether it is ROR.
- Alcohols are usually named by replacing 'e' from the Alkane with 'ol'.
- Primary alcohols can be oxidized.
- Secondary alcohols can be oxidized to ketones but no further.
- Tertiary alcohols cannot be oxidized (no carbinol C-H).
- The thiol functional group consists of an S atom bonded to a C atom and a H atom via □ bonds.
- Thiols are much more acidic than similar alcohols, e.g. RSH (pKa = 10) versus ROH (pKa = 16 to 19)

- Phenols are more acidic (pKa»10) than alcohols (pKa»16 - 20), but less acidic than carboxylic acids (pKa»5).
- Epoxides are more reactive than simple ethers.
- In IUPAC system, ethers are named as alkoxy derivatives of alkanes.
- In contrast to alcohol, ethers are fairly unreactive.
- Alcohols are soluble in water while phenols are sparingly soluble.
- General formula for alcohol is R-OH while for phenol is Ar-OH.
- Methyl alcohol has proved to be excellent fuel for racing car.
- Ethyl alcohol may be the first organic chemical routinely manufactured by humans.
- Ethyl alcohol is also named as wine, beer and whiskey.
- Fuel oil mainly consists of amyl alcohol ($C_5H_{11}OH$)
- 95% ethyl alcohol is known as rectified spirit or commercial alcohol.
- Ethylene glycol is the major component in commercial coolants and anti-freeze.
- Glycerol is an excellent moisture retaining agent. It is used in vanishing creams, body lotions shaving foams and tooth pastes.
- Phenol is used as starting material for drugs such as salol, aspirin, phenolphthalein and several other dyes.
- Diethyl ether has been used in surgery for anaesthesia
- Cyclic ethers are known as epoxides.

Exercise

1: Select the right answer from the choices given with each question.

i. Which compound shows hydrogen bonding?

a. C_2H_6
b. C_2H_5Cl
c. $CH_3\text{-}O\text{-}CH_3$
[✓ d. C_2H_5OH]

ii. Which compound is called a universal solvent?

[✓ a. H_2O]
b. CH_3OH
c. C_2H_5OH
d. $CH_3\text{-}O\text{-}CH_3$

iii. According to Lewis concept ethers behave as

a. Acid
[✓ b. Base]
c. Acid as well as base
d. None of them

iv. Ethanol can be converted into ethanoic acid by

a: Hydrogenation
b: Hydration
[✓ c: Oxidation]
d: . Fermentation

v. Ethanol is denatured by adding;
[✓ a. methanol]
b. Carbolic acid
c. Acetone
d. Propanol

vi. Williamsons synthesis of ethers is superior to alcohols because it makes
a. Symmetrical ethers
b. Asymmetrical ethers
c. Ether at room temperature
[✓ d. Both symmetrical and asymmetrical Ethers.]

vii. Which one of the following compounds does not contain carboxylic group?
a. Acetic acid
b. Formic acid
c. Benzoic acid
[✓ d. Picric acid]

viii. Hydrogen bonding is maximum in
a. Diethyl ether
[✓ b. Ethanol]
[✓ c. Ethyl alcohol]
d. Triethyl amine

ix. Which of the following compounds have no attraction at all with water?
[✓ a. C_6H_6]
b. C_2H_5OH
c. $CH_3CH_2CH_2OH$d. CH_3-O-CH_3

x. Phenols are more acidic than alcohols which statement is correct?
a. Phenol turns blue litmus paper red
b. Alcohol liberates CO_2 with carbonate solution
[✓ c. Phenoxide ion is stabilized due to resonance]
d. Alkoxide ion is stabilized due to resonance

xi. Carbolic acid is treated with dilute nitric acid at 25 °C, the product is
a. o-nitrophenol
b. p-nitrophenol
c. m-nitrophenol
[✓ d. Both a and b]

xii. Oxonium ion is formed when
a. Ethnol reacts with Na metal
b. Phenol reacts NaOH solution
[✓ c. Ether is treated with HI]
d. Ethanol is treated with aq. NaOH and iodine

xiii. 2,4,6-Trinitrophenol is commercially called as
a. TNT
[✓ b. Picric acid]
c. Carbolic acid
d. Fumeric acid

2: Give brief answers for the following questions.

i. What are alcohols? How are they classified? (v)
ii. How are monohydric alcohols classified?
iii. Compare the acidity of primary, secondary and tertiary alcohols.
iv. 2-butene is the major product when n-butyl alcohol is heated with conc. H_2SO_4. Explain.
v. Give the mechanism of dehydration of alcohols.

vi. How will you obtain benzene from alcohol?

vii. Alcohols phenols both have OH group but phenols are more acidic than alcohols.

viii. How will you differentiate between an alcohol and phenol?

ix. Write the nomenclature of ether by IUPAC system.

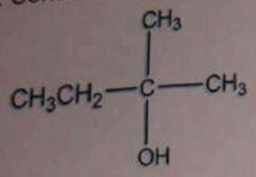
x. Why is phenol more soluble in water than toluene?

3. Give detailed answers for the following questions.

1. How will you prepare alcohols on industrial scale?
2. Distinguish ethanol from methanol and ethanol from phenol.
3. How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.
4. Give IUPAC names and structures of the following compounds.
   (i) Sec.butyl alcohol (ii) Lactic acid
   (iii) ter-butyl alcohol (iv) Tartaric acid
5. Give the reactivity of ethers.
6. Give at least two methods for the preparation of phenol.
7. How does phenol react with;
   (i) HNO_3 (ii) H_2SO_4 (iii) H_2/Pt (iv) NaOH (v) Ag_2O.
8. What is oxonium ion? Describe the chemical reactivity of ether.
9. Explain following terms using ethyl alcohol as an example;
   (i) Oxidation (ii) Dehydration (iii) Esterification (iv) Ether formation
10. How does ethyl alcohol react with the following reagents?
    (i) Conc.H_2SO_4 (ii) Na (iii) PCl_5 (iv) CH_3COOH (v) $SOCl_2$
11. How will you distinguish between?
    i. an alcohol and a phenol
    ii. an alcohol and an ether Lucas, iodo, Bromine
    iii. Methanol and ethanol.
    iv. A tertiary alcohol and a primary alcohol
    v. 1-propanol and 2-propanol
12. Give reason for the followings:
    i. Ethyl alcohol is a liquid while ethyl 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.

Skilled Activities

1. Consider the following compounds:



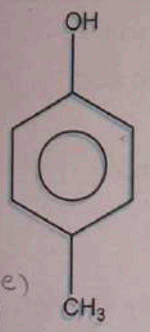
$CH_3CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$ 2-methyl 2-butanol

(a)

(b) CH_3OH Methanol

(c) $CH_3CH_2CHOHCH_3$ 2-butanol

(d) $CH_3CH_2CH_2CH_2OH$ 1-butanol



4-hydroxy toluene

~~(d)~~ (e)

(i) Name each compound. (ii) Which is a primary alcohol? (d)

(iii) Which is a tertiary alcohol? (a) (iv) Which is a phenol? (e)

(v) Which is an ether?

2. Consider again the compounds in question 1.

(a) Which react with sodium metal? (a)(b)(c)(d)

(b) Which could be oxidized to an aldehyde? (b)(d)

(c) Which could be oxidized to a ketone? (c)

(d) Which would be the strongest acid? (e)

(e) Which would form an alkene when heated with excess concentrated sulphuric acid? (c)(d)(a)

(f) Which has the lowest boiling point? [illegible]

3. Following table gives some physical properties of water, ethanol and ethoxyethane.

Name	water	ethanol	Ethoxyethane
Formula	H_2O	CH_3CH_2OH	$CH_3CH_2OCH_2CH_3$
M_r	18	46	74
Boiling point /°C	100	78	35
Density at 273 K/g cm^{-3}	1.00	0.79	0.71
Surface tension at 293 K/N m^{-1}	7.28	2.23	1.69

Suggest explanations in terms of intermolecular forces, why

(a) The boiling point of ethanol (Hydroge is greater than that of ethoxyethane? (Dipole-Dipole)

(b) The density of water is greater than that of ethanol, 1 hydrongen bond per mole

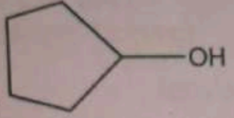
(c) The surface tension of water is greater than that of ethoxyethane.

4. Five different bottles contain the following liquids:

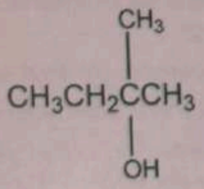
(a) Propan-1-ol $CH_3CH_2CH_2OH$

(b) Butoxybutane $CH_3CH_2CH_2CH_2—O—CH_2CH_2CH_2CH_3$

(c) Cyclopentanol



(d) 2-Methylbutan -2-ol



$CH_3CH_2C(CH_3)(OH)CH_3$

(e) Methanol CH_3OH

If the bottles were unlabeled, what *chemical* tests would you use to find out which liquid was which?

19

ALDEHYDES AND KETONES

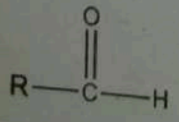
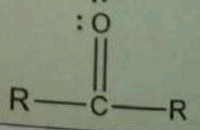
After completing this lesson, you will be able to:

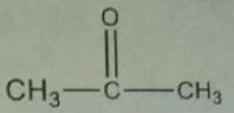
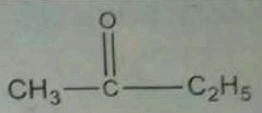
This is 5 days lesson (period including homework)

- Explain nomenclature and structure of aldehydes and ketones. (Applying)
- Discuss the preparation of aldeydes and ketones by ozonlysis of alkene, hydration of lkynes, oxidation of alcohols and Friedal Craft's acylation of armatics. (Applying)
- Describe reactivity of aldeydes and ketones and their comparison. (Analyzing)
- Describe acid and base catalysed nucleophlic addition reaction of aldehydesa nd ketones. (Applying)
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrcarbns, alcohols, by using carbons nucleophiles, nitrogen nucleophiles oxygen nucleophiles. (Applying)
- Describe oxidation reactions of aldehydes and ketones. (Applying)
- Describe isomerism in aldehydes and ketones. (Understanding)

Reading

Organic compounds containing the carbonyl functional group are called aldehydes and ketones.

Aldehydes	Ketones
(1) Functional Group	
In aldehydes, the C-atom of carbonyl group is directly attached at least One H-atom.	In ketones, the C-atom of carbonyl group is bonded to two carbon atoms called ketonic group.
(2) General Formula	
The homologous series of aldehydes have general formula $C_nH_{2n}O$.	The homologous series of ketones have general formula $C_nH_{2n}O$.
(3) General Formula Structure	
An aldehyde may be represented by the general formula structure  $R-\overset{\overset{\displaystyle O}{\|}}{C}-H$	A ketone may be represented by the general formula structure  $R-\overset{\overset{\displaystyle :\ddot{O}}{\|}}{C}-R$

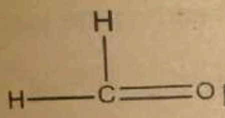
(4) Occurrence	
Aldehyde groups are present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavors.	Ketonic group is present in camphor and fructose.
(5) Examples	
(i) H-CHO (Formaldehyde) (ii) CH_3-CHO (Acetaldehyde)	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ Acetone (ii)  $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$ Methyl ethyl ketone

19.1 NOMENCLATURE:

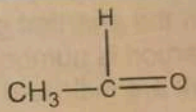
Aldehydes:

(a) Common names:

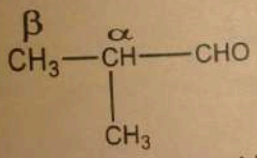
An aldehydes is named after the name of carboxylic acid obtained on its oxidation, the ending –ic acid is replaced by "aldehyde". For naming substituted aldehyde, the chain is labeled by using α, β, γ ... etc. the carbon next to carbon of the carbonyl group is indicated by 'α' and so on.



$H-\overset{\overset{\displaystyle H}{|}}{C}=O$ **Formaldehyde**

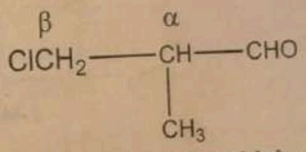


$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O$ **Acetaldehyde**



$\overset{\beta}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\alpha}{CH}}-CHO$

α- methyl propion aldehyde



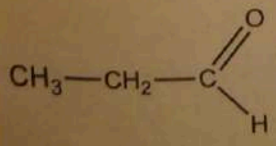
$\overset{\beta}{ClCH_2}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\alpha}{CH}}-CHO$

(β-chloro-α-methyl propionaldehyde)

(b) IUPAC Names:

1. The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon.
2. The ending 'e' of the alkane is replaced by 'al'
3. The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number 1.
4. The position of the substituent is indicated by numbers which is written before their number.

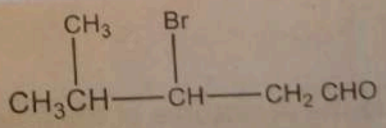
Examples:



Propanal

Cl—CH_2CHO

2 - Chloro ethanal



$CH_3\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_2\,CHO$

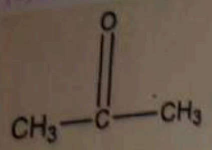
(3-Bromo-4-methyl pentanal)

Ketones:

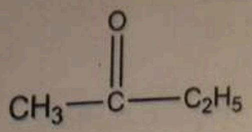
(a) Common names:

Ketones are named by adding the word ketone after writing the names of alkyl or aryl group linked to carbonyl carbon in alphabetical order.

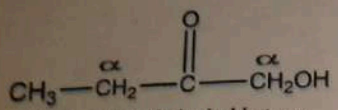
Substituted ketones are named by labeling the chain using α, β, γ ... etc, the carbon next to carbon of carbonyl group is indicated by 'α' and so on, e.g.


$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$

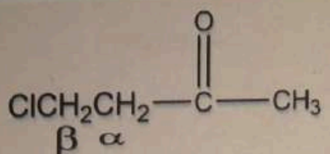
Dimethyl Ketone
(Acetone)


$CH_3-\overset{O}{\overset{\parallel}{C}}-C_2H_5$

Ethyl methyl
Ketone


$CH_3-\overset{\alpha}{CH_2}-\overset{O}{\overset{\parallel}{C}}-\overset{\alpha}{CH_2OH}$

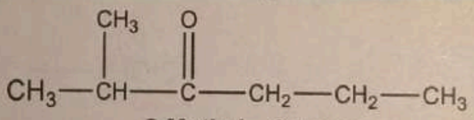
α – hydroxyl-methyl ethyl ketone


$Cl\underset{\beta}{CH_2}\underset{\alpha}{CH_2}-\overset{O}{\overset{\parallel}{C}}-CH_3$

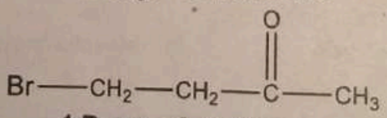
Methyl β-chloroethyl ketone

(b) IUPAC Names:

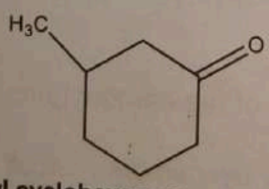
1. The longest chain containing the carbonyl group is taken a parent hydrocarbon.
2. The ending 'e' of hydrocarbon is replaces by 'one'
3. The numbering starts from the end that gives the carbonyl carbon the lower number. In cyclic ketones, carbonyl carbon is number 1
4. The positions of substituent are indicated by numbers before their names.


$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-CH_3$

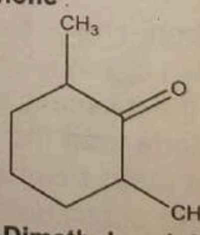
2-Methyl – 3-hexanone


$Br-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3$

4-Bromo- 2- butanone



3-Methyl cyclohexanone



2,6-Dimethyl cyclohexanone

Quick Quiz

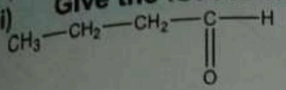
(i) Write the structures of the following compounds:

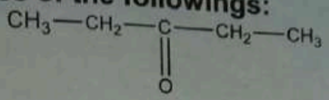
a) 2-hexanone
b) Pentanal
c) 2,4-dihexanone hexadione
d) 1-phenyl-2-butanone

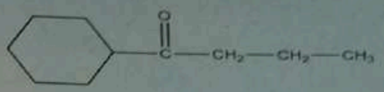
e) 4-methyl-2.pentanone

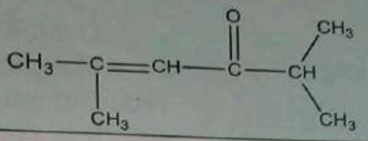
f) 1-phenyl-3-(2-methoxy phenyl)-1,3-propane dione

(ii) **Give the IUPAC names of the followings:**


$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-H$


$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$





19.2 PHYSICAL PROPERTIES:

- The polar nature of the **C=O** (due to the electronegativity difference of the atoms) means dipole-dipole interactions will occur.
- Though **C=O** can not form hydrogen-bond to each other, the **C=O** can accept hydrogen bonds from hydrogen bond donors (*e.g.* water, alcohols).

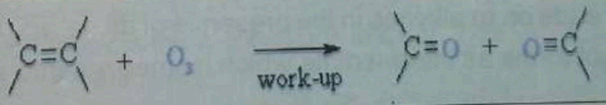
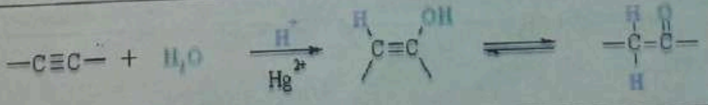
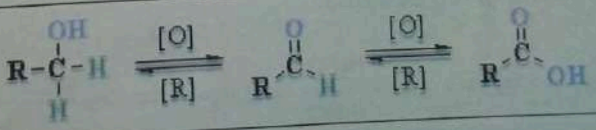
The implications of these effects are:

- higher melting and boiling points compared to analogous alkanes
- lower boiling points than analogous alcohols
- more soluble than alkanes but less soluble than alcohols in aqueous media

19.3 STRUCTURE:

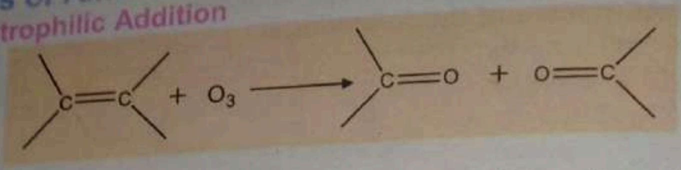
- The carbonyl group consists of an O atom bonded to a C atom via a double bonds via an sp^2 hybridization model similar to that of ethene.

19.4 PREPARATIONS OF ALDEHYDES AND KETONES

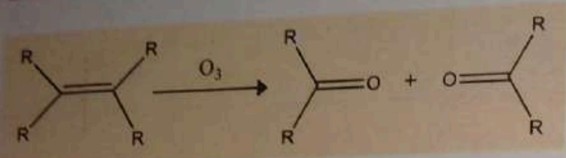
Ozonolysis of Alkenes	
Hydration of Alkynes	
Oxidation of Alcohols	
Friedel-Crafts Acylation of Aromatics	

19.4.1 Ozonolysis of Alkenes

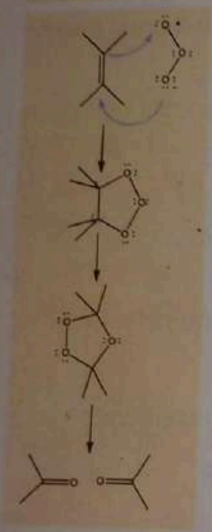
Reaction type: Electrophilic Addition



Elaboration



- Overall transformation : **C=C** to 2**C=O**
- Reagents: ozone, O_3, followed by a reducing work-up, usually Zn in acetic acid.
- It is convenient to view the process as cleaving the alkene into two carbonyl
- The substituents on the **C=O** depend on the substituents on the **C=C**.



Mechanism for Reaction of Alkenes With O_3

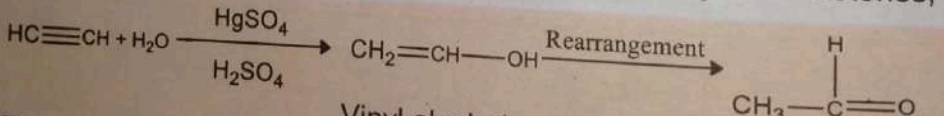
Step 1:
The Pi electrons act as the nucleophile, attacking the ozone at the electrophilic terminal O. A second C-O is formed by the nucleophilic O attacking the other end of the C=C.

Step 2:
The cyclic species called the molozonide rearranges to the ozonide.

Step 3:
On work-up (usually Zn / acetic acid) the malozonide decomposes to give two carbonyl compounds.

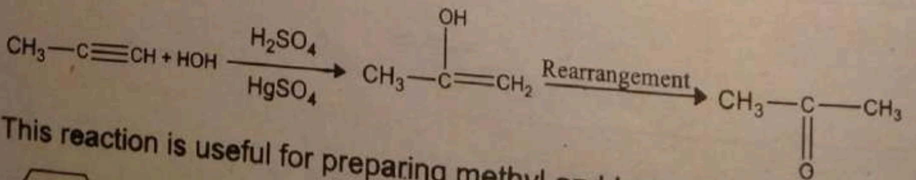
19.4.2 Hydration of Alkynes

Water adds on to alkynes in the presence of dil. H_2SO_4 and $HgSO_4$ to produce an aldehyde or ketone. Enol forms as intermediate which isomerizes into aldehydes or ketones, e.g.,



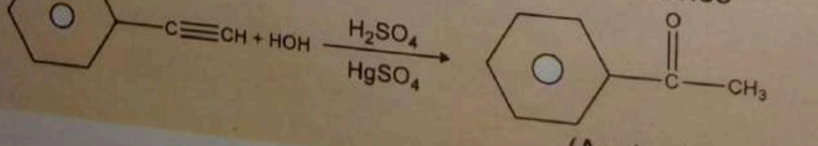
$$HC\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_2{=}CH{-}OH \xrightarrow{\text{Rearrangement}} CH_3{-}\overset{H}{\overset{|}{C}}{=}O$$

Propyne gives acetone:



$$CH_3{-}C\equiv CH + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH_2 \xrightarrow{\text{Rearrangement}} CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3$$

This reaction is useful for preparing methyl aryl ketones



(Acetophenone)

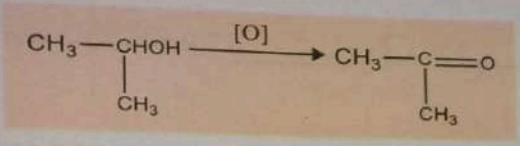
19.4.3 Oxidation of Primary and Secondary Alcohols

Primary alcohols are oxidized to aldehydes by (i) warming with acidic dichromate solution (ii) Jone reagent (CrO_3 + dil. H_2SO_4 + acetone) (iii) Sarett reagent (CrO_3 in pyridine)

$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[Na_2Cr_2O_7]{\text{Conc. } H_2SO_4} \underset{\text{Butanal}}{CH_3CH_2CH_2CHO}$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[\text{reagent}]{\text{Sarett}} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

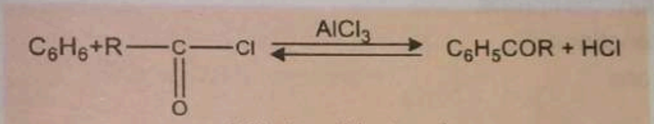
Non-aqueous solvents are employed to avoid further oxidation. Secondary alcohols are oxidized to ketones.



$$CH_3-\underset{CH_3}{\underset{|}{CHOH}} \xrightarrow{[O]} CH_3-\underset{CH_3}{\underset{|}{C}}=O$$

19.4.4 Friedel-Crafts Acylation of Benzene

It is the substitution of acyl group in an organic compound in the presence of $AlCl_3$ or some other Lewis acid

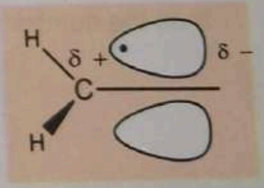


$$C_6H_6 + R-\underset{O}{\underset{\|}{C}}-Cl \xrightleftharpoons{AlCl_3} C_6H_5COR + HCl$$

(Alkyl aryl ketone)

$AlCl_3$ generates acylenium ion (electrophile) which is substituted in the aromatic ring

19.5 REACTIVITY



The double bond of the carbonyl group has a σ-bond and a π-bond. As oxygen is more electronegative, it attracts 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 the carbon atom has partial positive charge. The π electron cloud is pulled more strongly by the oxygen atom than the carbon atom. It makes oxygen atom nucleophile and carbon atom becomes electrophile.

19.6 REACTIONS OF ALDEHYDES AND KETONES

19.6.1 Nucleophilic Addition

There are two types of nucleophilic addition reactions of carbonyl compounds.

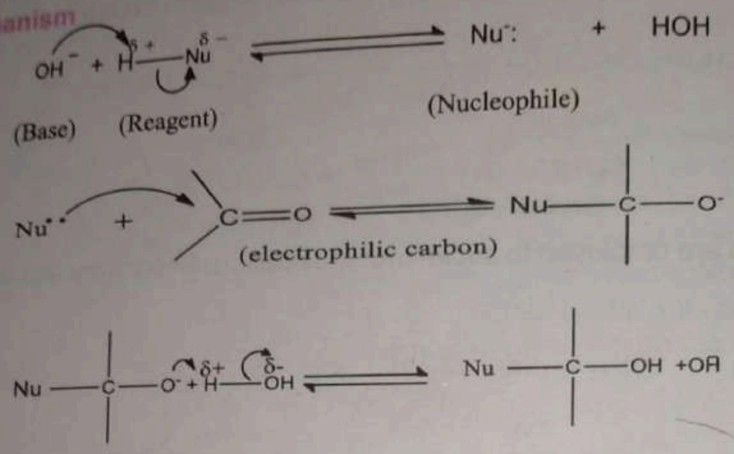
I- Base catalysed nucleophilic addition reaction

II- Acid catalysed nucleophilic addition reaction

I- Base Catalysed Nucleophilic Addition Reaction

A base catalysed nucleophilic addition reaction takes place with a strong nucleophilic reagent. The base reacts with the reagent ad 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 fallows:

General Mechanism



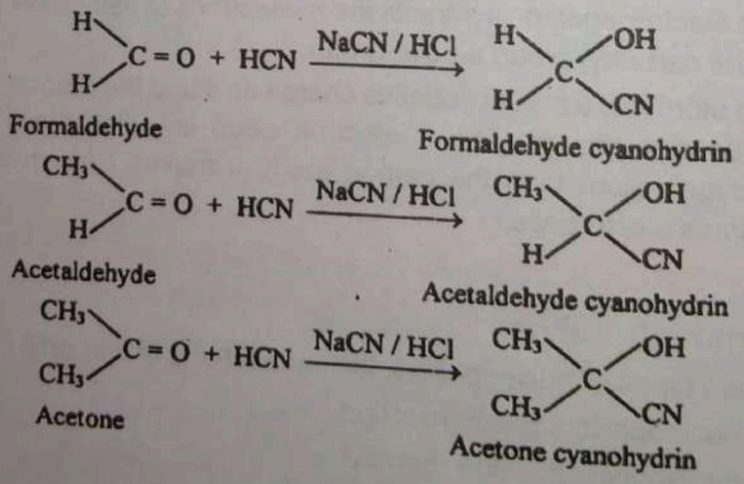
There are five types of base catalysed nucleophilic addition reactions of carbonyl compounds.

1) Addition of hydrogen cyanide
2) Addition of Grignard's reagent
3) Addition of sodium bisulphate
4) Condensation reactions
5) Haloform reactions

1. Addition of hydrogen cyanide

Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The acid generates HCN form sodium cyanide in HCl.

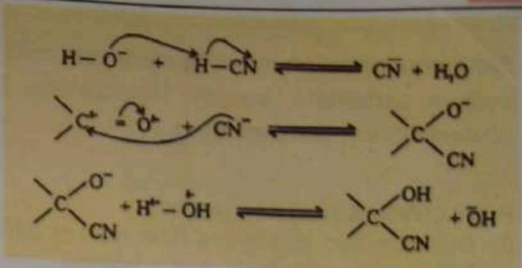
The reaction is used in the synthesis of α hydroxyl acid that contains one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.



Mechanism

The reaction is base catalysed. The base (OH^-) generates cyanide ions which act as nucleophile. 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.



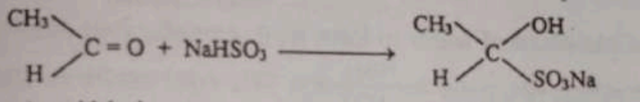
2) Addition of Grignard's reagent

Grignard's reagents add to aldehydes and ketones to form adduct which on hydrolysis with a dilute mineral acid give alcohols. (Chapter 17)

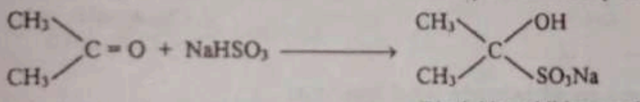
3) Addition of sodium bisulphate

Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphate to form a crystalline white precipitate of sodium bisulphate adduct.

Formaldehyde Bisulphite addition product

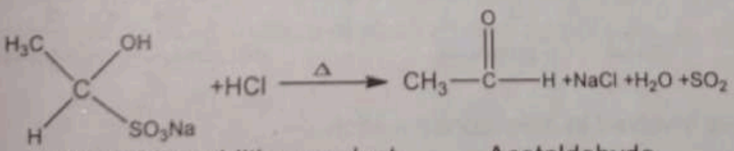


Acetaldehyde Bisulphite addition product



Acetone Bisulphite addition product

Bisulphite on heating a dilute mineral acid (HCl or H_2SO_4) regenerates the parent aldehydes or ketone.



Bisulphite addition product Acetaldehyde

The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

4) Condensation reactions

The reaction 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.

(a) ALDOL CONDENSATION

Imp

Definition:

Aldol condensation is a reaction in which two molecules of same or different carbonyl compound containing hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to from aldol or ketol, which usually loses water molecule.

Mild Alkaline conditions

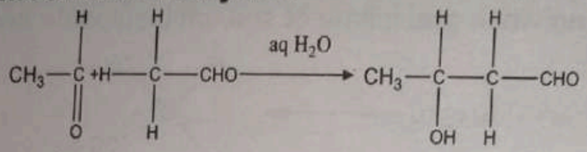
Aldol condensation takes place under mild alkaline conditions, for example in the presence of sodium carbonate, sodium bicarbonate, barium hydroxide, dilute sodium hydroxide or an alkoxide in low concentration.

Types:

Aldol condensation can occur:

(i) Between two aldehydes (identical or different)
(ii) Between an aldehyde and a ketone
(iii) Between two ketone (identical or different)

(i) Condensation between two aldehydes:

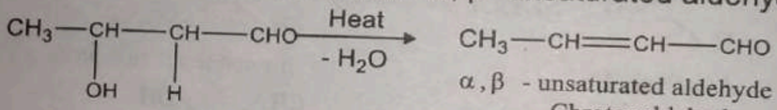


$$CH_3-CHO + H-CH_2-CHO \xrightarrow{aq\ H_2O} CH_3-CH(OH)-CH_2-CHO$$

ethanal ethanal
(Identical aldehydes)

aldol
(acetaldol)
β - hydroxy butyraldehyde
(3-hydroxybutanal)

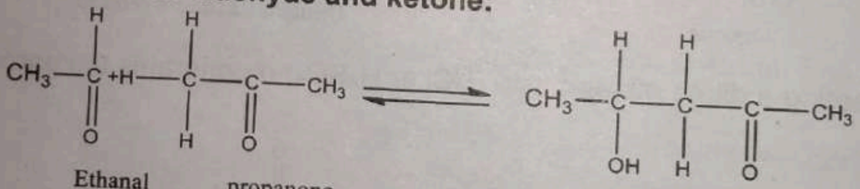
On heating aldol loses a molecule of water to form α , β –unsaturated aldehyde



$$CH_3-CH(OH)-CH(H)-CHO \xrightarrow[-H_2O]{Heat} CH_3-CH=CH-CHO$$

α , β - unsaturated aldehyde
Chrotonaldehyde
(2-butenal)

(ii) Condensation between aldehyde and ketone:



$$CH_3-CHO + H-CH_2-CO-CH_3 \rightleftharpoons CH_3-CH(OH)-CH_2-CO-CH_3$$

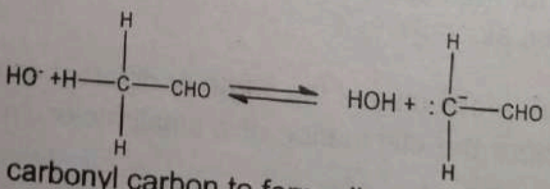
Ethanal propanone

4-Hydroxy-2-pentanone (ketol)

Mechanism of Aldol Condensation:

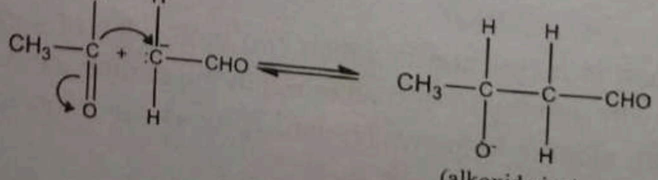
Following steps are involved in aldol condensation.

(1) Removal of a proton from α –carbon of aldehyde/ketone by base:
(Formation of nucleophile)



$$HO^- + H-CH_2-CHO \rightleftharpoons HOH + :\bar{C}H_2-CHO$$

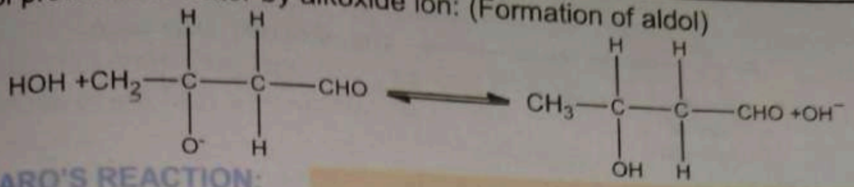
(2) Attack of nucleophile on carbonyl carbon to form alkoxide ion:
(Formation of alkoxide ion)



$$CH_3-CHO + :\bar{C}H_2-CHO \rightleftharpoons CH_3-CH(O^-)-CH_2-CHO$$

(alkoxide ion)

(3) Removal of proton from water by alkoxide ion: (Formation of aldol)

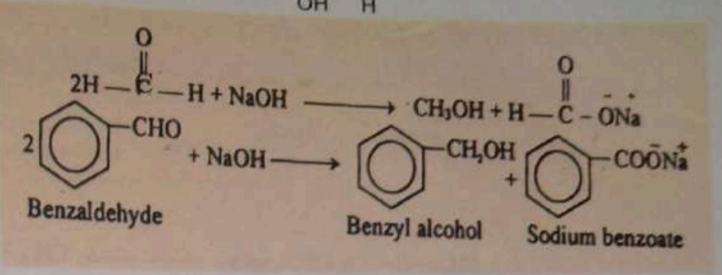


$$HOH + CH_2-\underset{O^-}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CHO \rightleftharpoons CH_3-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CHO + OH^-$$

(b) CANNIZZARO'S REACTION:

Aldehydes having no α-hydrogen atoms undergo Canizzaro's reaction. It is a disproportionate (self-oxidation-reduction) reaction.

Two molecules of the aldehyde are involved.



$$2H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow CH_3OH + H-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na}$$

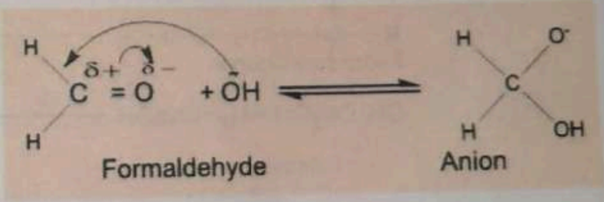
One molecule is reduced into corresponding alcohol and the other is oxidized into the acid (in the salt form). The reaction carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

Mechanism of Cannizzaro's Reaction:

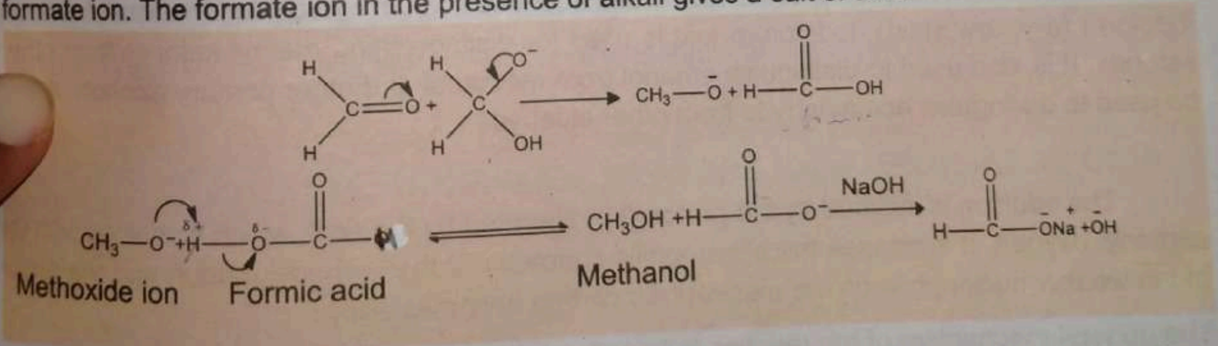
The hydroxide ion acts as a nucleophile. It attaches on the electrophilic carbonyl carbon to form a complex anion.

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.

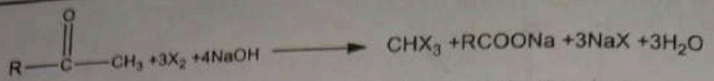


The methoxide ion acts as a base and abstracts a proton from formic acid to form methanol and formate ion. The formate ion in the presence of alkali gives a salt of acid.



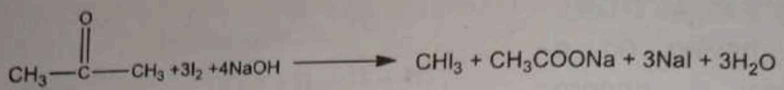
5) Haloform Reaction

Only acetaldehyde and methyl ketones react with halogens (Cl, Br, I) in the presence of sodium hydroxide to give haloform (chloroform, bromoform or iodoform) and sodium salt of the acid.



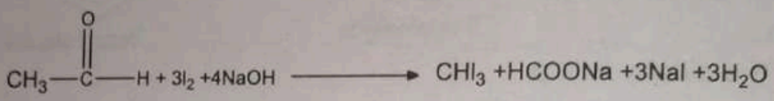
$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

R = alkyl, aryl or hydrogen — Halogen — (Haloform) (Sod carboxylate)



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

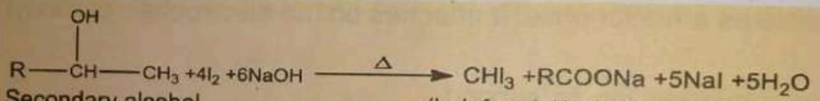
Acetone — Iodine — (Iodoform) (Sod. formate) (yellow ppt)



$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

Acetaldehyde — Iodine — (Iodoform) (Sod. formate) (yellow ppt)

Secondary alcohols containing the methyl group also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.



$$R-\overset{OH}{\overset{|}{CH}}-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NaI + 5H_2O$$

Secondary alcohol — (Iodoform) (Sod. Carboxylate)

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

Ethanol — (Iodoform) (Sod. formate)

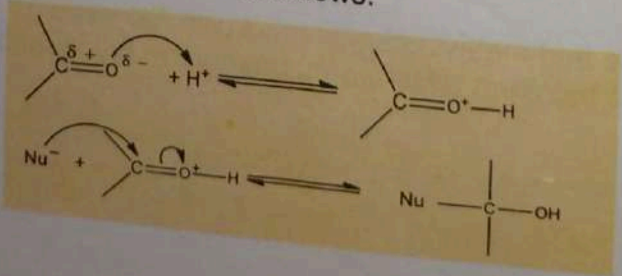
Iodoform Test:

It is halofrom reaction in which iodine and aqueous sodium hydroxide form water insoluble iodoform (a yellow solid). Iodoforum 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.

II- ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

The addition is initiated by the proton (H^+) liberated by the acid, which combines with the carbonyl oxygen. It increases the electrophilic character of the carbonyl carbon and the attack of the weaker nucleophile on the electrophilic carbon becomes easy.

The general mechanism of the reaction is as follows.

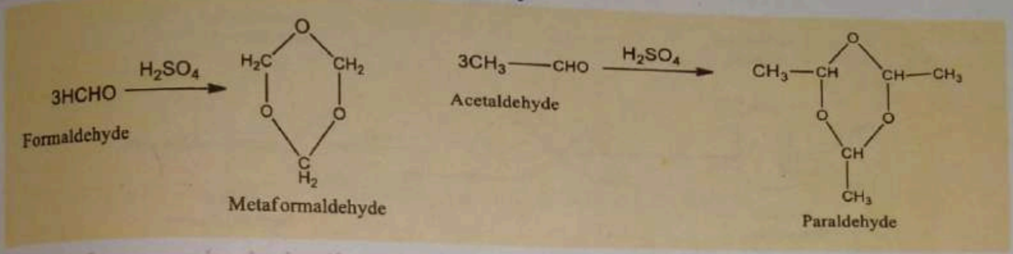


These are of three types

1. Polymerization of aldehydes
2. Addition of ammonia derivatives with aldehydes
3. Addition of alcohols with aldehydes

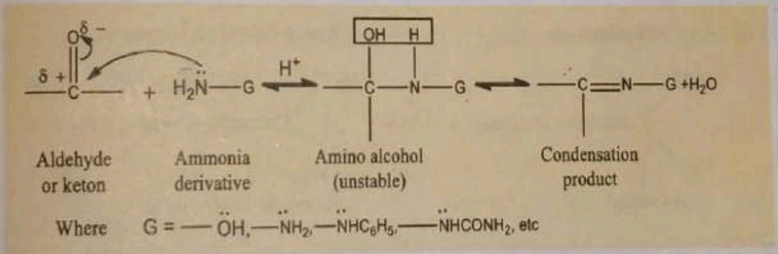
1. Polymerization of aldehydes:

Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde respectively.



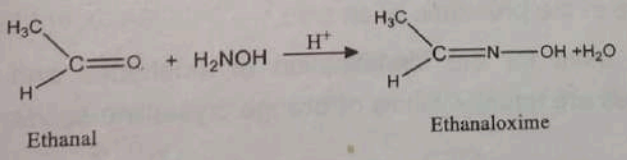
2. Addition of ammonia derivatives with aldehydes:

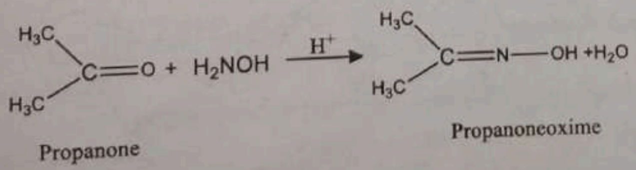
Aldehydes and ketones react with ammonia derivatives, G-NH_2 to form compounds containing the group $>C=N-G$ and water. The reaction is known as condensation reaction or addition–elimination reaction because water is lost after addition occurs. The general reaction is given below.



(i) Reaction with hydroxylamine

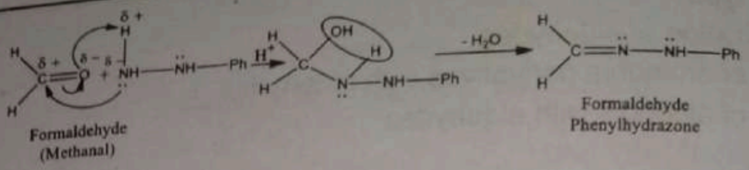
Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.





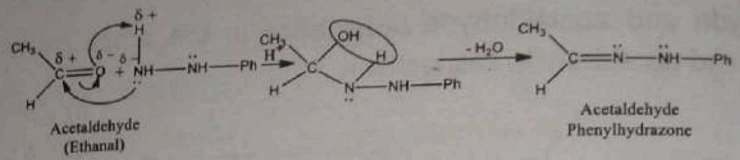
(ii) Reaction with Phenylhydrazine $(\ddot{N}H_2-\ddot{N}H-C_6H_5)$ (C_6H_5 = phenyl group = Ph -):

Aldehydes and ketones react with phenyl hydrazine to form phenylhydrazones in the presence of an acid.



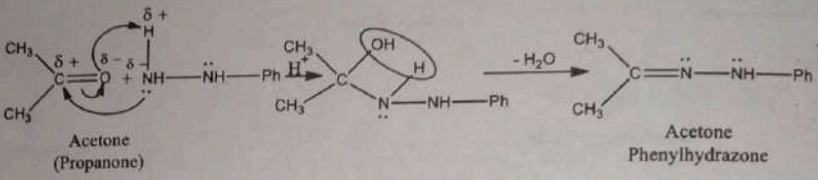
Formaldehyde (Methanal)

Formaldehyde Phenylhydrazone



Acetaldehyde (Ethanal)

Acetaldehyde Phenylhydrazone

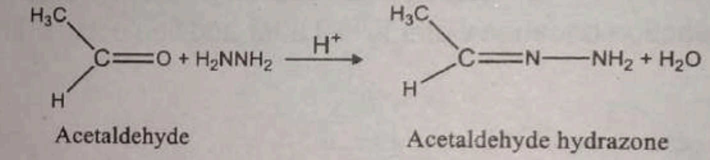


Acetone (Propanone)

Acetone Phenylhydrazone

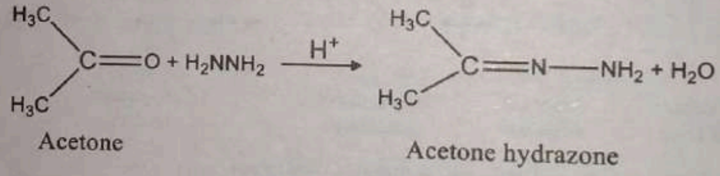
(iii) Reaction with hydrazines

Aldehydes and ketones react with hydrazine to form hyrazones in the presence of an acid.



Acetaldehyde

Acetaldehyde hydrazone



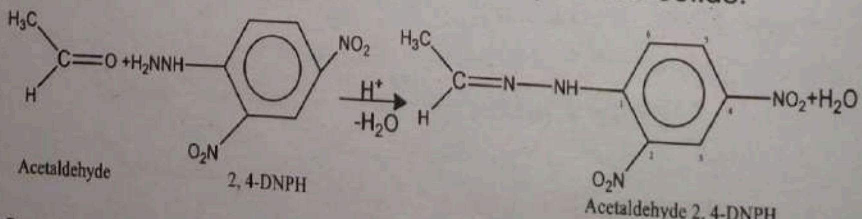
Acetone

Acetone hydrazone

(iv) Reaction with 2,4-dinitrophenylhydrazine

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazone in the presence of an acid.

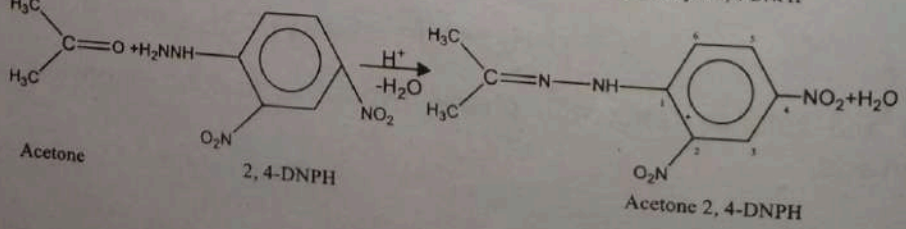
The reaction can be used for the identification of aldehydes and ketones because 2,4-dinitrophenylhydrazones are usually yellow or orange crystalline solids.



Acetaldehyde

2, 4-DNPH

Acetaldehyde 2, 4-DNPH



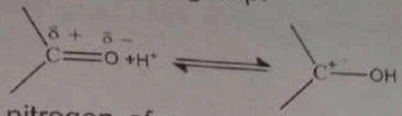
Acetone

2, 4-DNPH

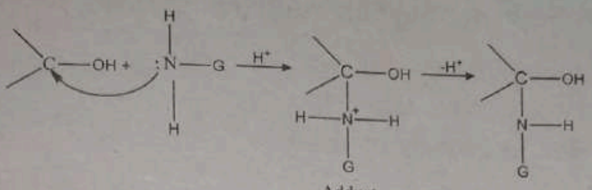
Acetone 2, 4-DNPH

Mechanism of the Reaction of ammonia derivatives

Step (i) Protonation of oxygen of the carbonyl group.

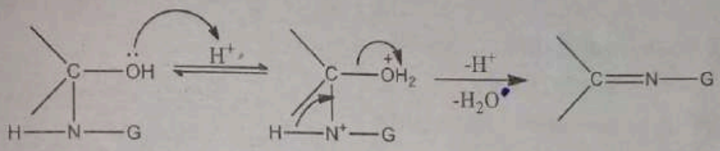


Step (ii) Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



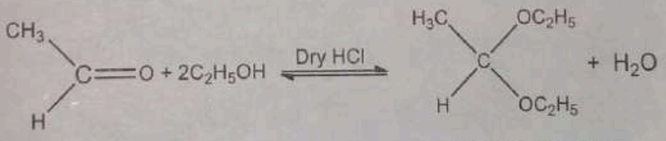
Adduct

Step (iii) Protonation of oxygen of hydroxyl group followed by the removal of water.



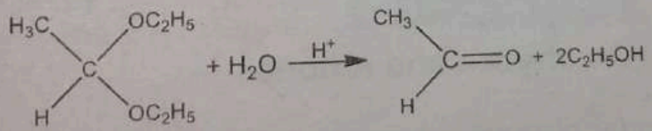
3. Addition of alcohols with aldehydes:

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride acts as a catalyst.



1, 1-Diethoxyethane

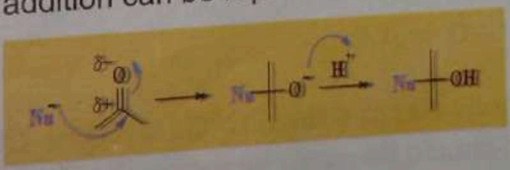
The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.



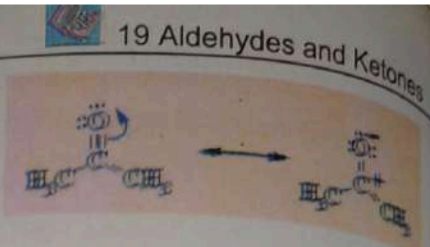
Note: Ketones do not react under these conditions.

19.6.2 Relative Reactivity

Overall a simple nucleophilic addition can be represented with curly arrows as follows:

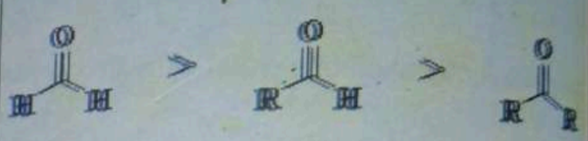


The reactivity of aldehydes and ketones can be easily rationalised by considering the important resonance contributor which has charge separation with a +ve C and -ve O.



In general the reactivity order towards nucleophiles is : **aldehydes > ketones** (see below)
The substituents have two contributing factors on the reactivity at the carbonyl C:

1. Size of the substituents attached to the **C=O**. Larger groups will tend to sterically hinder the approach of the **Nucleophile**.
2. The electronic effect of the substituent. Alkyl groups are weakly electron donating so they make the **C** in the carbonyl *less* electrophilic and therefore *less* reactive towards nucleophiles.



These trends are supported by the trends in the equilibrium data for the formation of hydrate.

Carbonyl	K / M^{-1}	% Hydrate
methanal	41	99.96
ethanal	1.8×10^{-2}	50
2,2-dimethylpropanal	4.1×10^{-3}	19
propanone	2.5×10^{-5}	0.14

19.6.3 Reduction of Aldehydes and Ketones

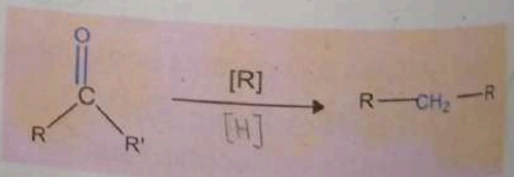
1. Reduction to Hydrocarbons

Clemmensen Reduction (acidic conditions)

- Zn(Hg) in HCl reduced the **C=O** into CH_2-

Wolff-Kishner Reduction (basic conditions)

- NH_2NH_2 / KOH / ethylene glycol (a high boiling solvent) reduces the **C=O** into CH_2-



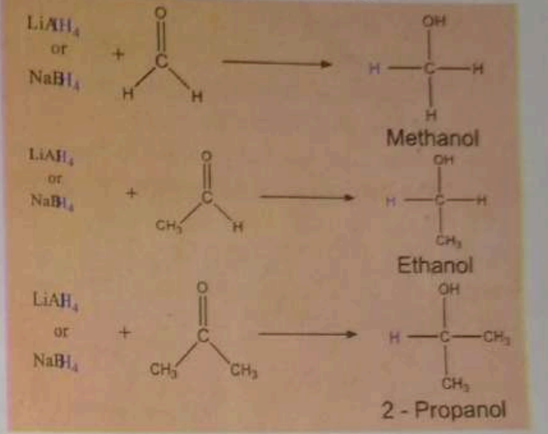
Overview

- These reduction methods do not reduce **C=C** , **C≡C** or **-CO_2H**
- The choice of method should be made based on the tolerance of other functional groups to the acidic or basic reaction conditions.

Chem Book 12

2. Hydride Reductions of Aldehydes and Ketones

- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents $LiAlH_4$ and $NaBH_4$ act as a source of H^- (hydride ion).
- Overall 2 H atoms are added across the  to give **H-C-O-H.**
- Hydride reacts with the carbonyl group, , in aldehydes or ketones to give alcohols.
- The substituents on the carbonyl tell the nature of the product alcohol.
- Reduction of methanal (formaldehyde) gives methanol.
- Reduction of other aldehydes gives **primary** alcohols.
- Reduction of ketones gives **secondary** alcohols.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction.

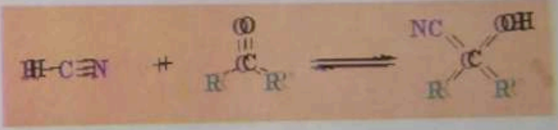


3. Using Carbon Nucleophiles

Cyanohydrin Formation

Cyanide adds to aldehydes and ketones to give a cyanohydrin.

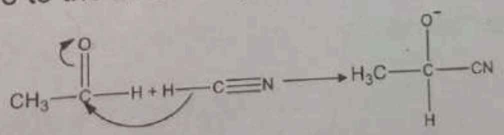
- The reaction is usually carried out using NaCN or KCN with HCl.
- HCN is a fairly weak acid, but *very toxic*.
- The reaction is useful since the cyano group can be converted into other useful functional groups ($-CO_2H$ or $-CH_2NH_2$)



Nucleophilic Addition of Cyanide to an Aldehyde

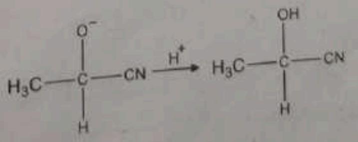
Step 1:

The nucleophilic C in the cyanide adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate alkoxide.



Step 2:

An acid/base reaction. Protonation of the alkoxide oxygen creates the cyanohydrin product.



4. Using Nitrogen Nucleophiles

Reactions of Primary Amine derivatives


Imine

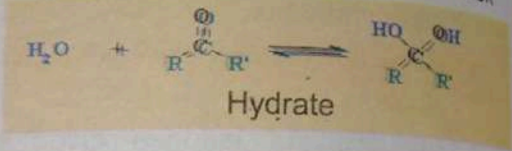
Primary amines, **R-NH₂** or **ArNH₂**, undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.

- The reactions are usually carried out in an acidic buffer to activate the C=O and facilitate dehydration but without inhibiting the nucleophile.

5. Using Oxygen Nucleophiles

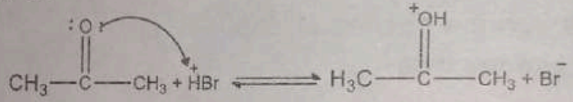
Formation of Hydrates

- Aldehydes and ketones react with water to give 1,1-geminal diols known as **hydrates**.
- In general, hydrates are not stable enough to be isolated as the equilibrium shifts back to starting materials.
- However, hydrates are the reactive species in the oxidation of aldehydes to acids.

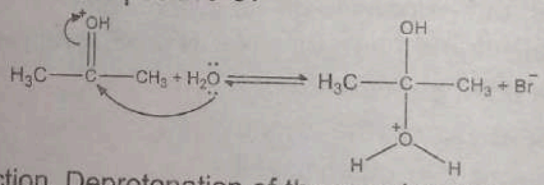

Hydrate

MECHANISM FOR THE ACID Catalyzed FORMATION OF HYDRATES

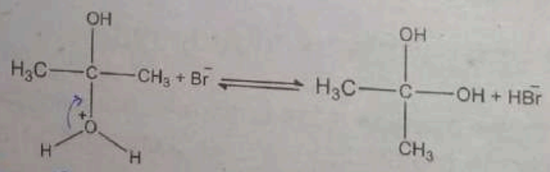
Step 1: An acid/base reaction. Since there is only a weak nucleophile, we need to activate the carbonyl by protonating on O.



Step 2: The nucleophilic O in the water attacks the electrophilic C in the C=O, breaking the π bond and giving the electrons to the positive O.



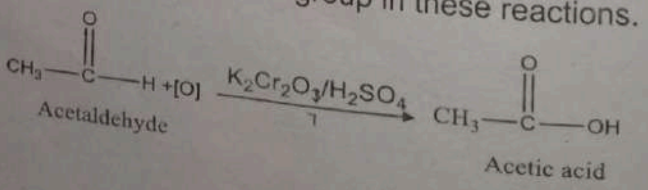
Step 3: An acid/base reaction. Deprotonation of the oxonium ion neutralizes the charge giving the hydrate.

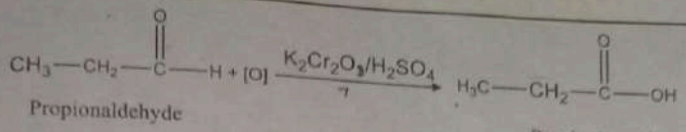


19.6.4. Oxidation Reactions

I. Oxidation of Aldehydes:

Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids. They are also oxidized by strong oxidizing 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 oxidized to OH group in these reactions.



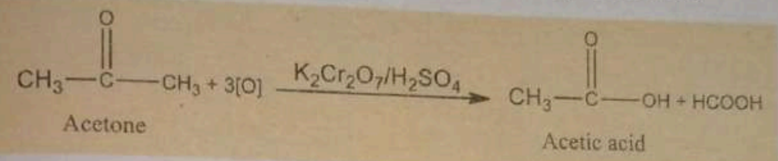


$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-H + [O] \xrightarrow[7]{K_2Cr_2O_3/H_2SO_4} H_3C-CH_2-\overset{\overset{O}{||}}{C}-OH$$

Propionaldehyde Propionic acid

II. Oxidation of Ketones:

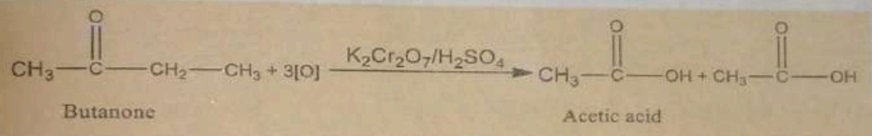
Ketones are only oxidizes by strong oxidizing agents such as $K_2Cr_2O_7$,/H_2SO_4, $KMnO_4/H_2SO_4$ and conc. HNO_3. The carbon atom joined to the smaller number of hydrogen atoms is oxidized. In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and mixture of two carboxylic acids is always obtained.



$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{\overset{O}{||}}{C}-OH + HCOOH$$

Acetone Acetic acid

However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{\overset{O}{||}}{C}-OH + CH_3-\overset{\overset{O}{||}}{C}-OH$$

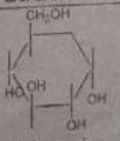
Butanone Acetic acid

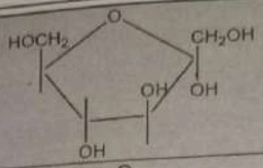
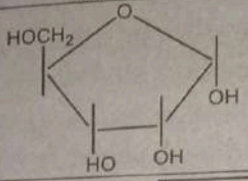
Society, Technology and Science

Sugars Glucose and Fructose – Naturally occurring carbonyl compounds

Sugars are sweet tasting soluble carbohydrates. Carbohydrates derive their name for the fact that they are composed of carbon, hydrogen and oxygen with H and O in the ratio of 2:1 as in water. Monosaccharides such as glucose are usually pentoses or hexoses, i.e. they contain 5 or 6 carbon atoms in their molecules. Disaccharides such as sucrose consist of two monosaccharide molecules joined by the elimination of a molecule of water. Polysaccharides such as starch are made up of many Monosaccharides units joined together. Notice that the Monosaccharides all have asymmetric molecules. They therefore exhibit optical isomerism.

Some common carbohydrates, with their structures are as follow:

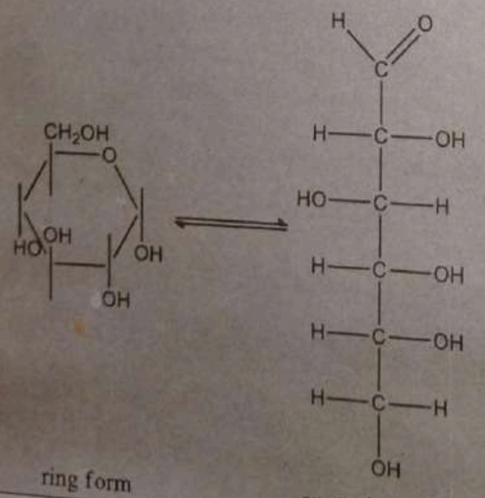
Name	Type	Structures	Occurrence
glucose	Monosaccharide, aldose, hexose	 (this is α-glucose: see section 9.8 for details of α- and β - glucose)	Occurs abundantly in plants and animals

fructose	Monosaccharide, ketose, hexose		In fruit and honey
ribose	Monosaccharide, aldose, pentose		Component of the molecules of ribonucleic acid (RNA) and vitamin B12
sucrose	disaccharide	glucose — fructose	Sugar cane, sugar beet (commonly simply called, 'sugar')
maltose	disaccharide	glucose — glucose	Malt
lactose	disaccharide	glucose — galactose	Milk
starch	polysaccharide	chains of glucose units	Plant storage organs, e.g. potato, wheat grain
Cellulose	polysaccharide	Chains of glucose units (linked differently to those in starch)	Structural material of plants

The carbonyl properties possessed by glucose arise from the fact that in addition to its normal ring form it can exist as an open chain form.

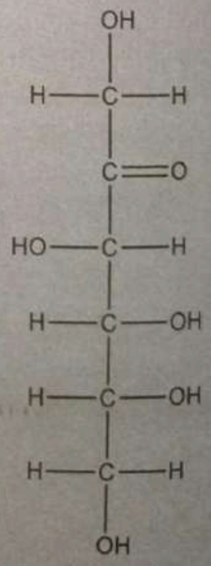
Glucose – An example of aldehyde

The two forms are readily inter-converted and in aqueous solution about 1% of glucose molecules exist in the open chain form. This form carries an aldehyde group, so glucose has several properties typical of an aldehyde. It is some times called an aldose. Thus, in addition to the condensation reaction already mentioned glucose shows the reducing properties typical of an aldehyde. The reduction of Fehling's solution (or Benedict's solution) is a standard test for glucose and other reducing sugars.



ring form

open-chain form



Fructose - An example of Ketone

The open chain form of fructose is ketose. Why does the open chain form of glucose and other sugars change to the ring form? It is a result of the tendency of the carbonyl group to undergo nucleophilic addition. The nucleophile involved in the oxygen atom of one of the –OH group of the same molecule. An internal nucleophilic addition reaction occurs, forming a ring.

Do You Know?

1. 40% aqueous solute of formaldehyde is known as formalin, which is used in the preservation of biological specimens.
2. Acetone is widely used solvents in industry, the laboratory and the home
3. Formaldehyde is used as decolourising agent in vat dyeing,

Quick Quiz

C

- i. What is functional group of carbonyl compounds? Write their general formula?
- ii. What types of aldehydes used in Cannizzaro's reactions don't have α-hydrogen.
- iii. What is Cannizzaro's reaction?
- iv. Which types of carbonyl compound condense to form an aldol?
- v. What is haloform reactions?
- vi. Give the oxidation reactions of aldehydes.

Key Points

- Primary alcohols can be oxidized to aldehydes (or further to carboxylic acids).
- Secondary alcohols can be oxidized to ketones.
- Tertiary alcohols cannot be oxidized (no carbinol C-H).
- The protonation of a carbonyl gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.
- Organolithium or Grignard reagents react with the carbonyl group, C=O, in aldehydes or ketones to give alcohols.
- The carbonyl group, -C=O, is present in aldehydes and ketones. In aldehydes it is in a terminal position in the carbon chain. In ketones it is in a non – terminal position.
- Aldehydes and ketones are named using the suffixes –al and –one, respectively.
- Aldehydes are prepared by oxidising primary alcohols, ketones by oxidising secondary alcohols.
- The carbonyl group readily undergoes nucleophilic addition. This is sometime followed by the elimination of a molecule of water, resulting in a condensation reaction.
- Aldehydes are generally more reactive then ketones.
- The tendency of aldehydes to undergo nucleophilic addition makes them polymerize readily.

- Aldehydes can be oxidized to carboxylic acids by a variety of reagents. Ketones are not readily oxidized.
- The carbonyl group activates the hydrogen atoms on neighbouring carbon atoms, making them more readily substituted than those in alkanes.

Exercise

Q1: Select the right answer from the choices given with each question.

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. Ketones are prepared by the oxidation of
a. Primary alcohol [✓ b. Secondary alcohol]
c. Tertiary alcohol d. none of these

iii. Acetone reacts with HCN to form a cyanohydrins. It is an example of
a. Electrophilic addition b. Electrophilic substitution
[✓ c. Nucleophilic addition] d. Nucleophilic substitution

iv. Cannizaro's reaction is not given by
a. Formaldehyde [✓ b. Acetaldehyde]
c. Benzaldehyde d. Trimethylacetaldehyde

v. 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

vi. Aldehydes are the oxidation product of
[✓ a. p-alcohols] b. s-alcohols c. ter-alcohols d. carboxylic acids

vii. Which of the following compounds will not given iodoform test on treatment with I_2/NaOH.
a. Acetaldehyde b. Acetone c. Butanone [✓ d. 3-pentanone]

viii. Aldehydes and ketones are carbonyl compounds. Which of them react both with $NaBH_4$ and with Tollen's reagent.
a. Both aldehydes and ketones [✓ b. Aldehydes only]
c. Ketones only d. Neither aldehydes nor ketones

ix. Which one of the following can undergo Aldol condensation reaction?
a. Farmaldehyde [✓ b. Acetaldehyde]
c. Benzeldehyde d. Trimethylacetaldehyde

x. Aldol condensation is not successful with compounds
[✓ a. Having no α-hydrogen] b. Having α-hydrogen
c. Having α-methyl group d. None

xi. Phenylhydrazone is formed on treatment with carbonyl compounds with
a. Hydroxyl amines [✓ b. Phenylhydrazine]
c. Oximes d. None

xii. General formula of aldehyde and ketone is?
[✓ a. $C_nH_{2n}O$] b. $C_nH_{2n+1}O$ c. C_nH_nO d. $C_nH_{2n+2}O$

xiii. The colour of Iodoform is
a. White b. Black [✓ c. Yellow] d. Blue

Q2: Give brief answers for the following questions.

i. How is formaldehyde prepared industrially?
ii. Describe briefly the nucleophilic addition mechanism to the carbonyl compound.
iii. What is the mechanism of HCN addition to carbonyl compounds?
iv. How is ethanol converted to lactic acid?
v. What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?
vi. What is Haloform reaction?
vii. Which type of alcohols undergo iodoform reaction?→ Which have methyl group attached to CH_2-OH.
viii. Why formaldehyde do not give aldol condensation reaction?
ix. Give the mechanism of addition of sodium bisulphate to ketones.

Q3: Give detailed answers for the following questions.

i. What is the reactivity of the carbonyl group? 234
ii. How formaldehyde reacts with following? (i) HCN (ii) $\overset{239}{H_2SO_4}$ (iii) $NaHSO_4$ 3
iii. Define and explain aldol condensation along with mechanism.
iv. Give detail of haloform reaction. Why it is called so?
v. Give the following reductions of aldehydes and ketones along with mechanism.
(i) $NaBH_4$ (ii) Catalytic reduction
vii. What is the mechanism for addition of ammonia derivatives to carbonyl group?
viii. Which type of aldehydes give Cannizaro's reaction? Explain with mechanism.
ix. How do you distinguish a ketone and an aldehyde by chemical method?
x. How will you differentiate between acetophenone and benzophenone?

Skilled Activities

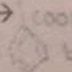
i. Predict the formulas of the products of the following reaction

$CH_3COCH_2CH_3 + H_2 \rightarrow$ $CH_3-\overset{OH}{CH}-CH_2-CH_3$ 2-butanol

$C_6H_5CHOCH_3 + NH_2OH \rightarrow$ $C_6H_5-\overset{CH_3}{C}=N-OH + H_2O$ acetophenone oxime

$CH_3CH_2COCH_2CH_3 + HCN \rightarrow$ $CH_3-CH_2-\underset{CN}{\overset{OH}{C}}-CH_2-CH_3$ 3-cyno-3-hydroxy pentane

$C_6H_5CHO + KMnO_4 \xrightarrow[{[O]}]{H_2SO_4}$



benzoic acid

$CH_3CH_2CHO + Cl_2 \rightarrow$

ii. Write structural formulas for all compounds of molecular formula C_4H_8O containing a carbonyl group.

iii. Predicts the formulas of the compounds formed when the following are treated with the Grignard's reagent methyl magnesium bromide, followed by water.

a. Methanol, Ethanol, Propanone, Carbon dioxide

20

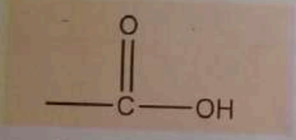
CARBOXYLIC ACIDS AND FUNCTIONAL DERIVATIVES

After completing this lesson, you will be able to:

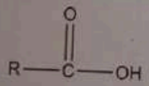
This is 8 days lesson (period including homework)

- Describe preparation of carboxylic acids by carbonation of Grignard's Reagent, hydrolysis of nitriles, oxidation of primary alcohols oxidation aldehydes and oxidation of alkyl benzenes. (Applying)
- Discuss reactivity of carboxylic acids. (Applying)
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid derivatives: acyl halides, acid anhydrides, esters, amides and reactions involving interconversion of these. (Analyzing)
- Describe e reactions of carboxylic acid derivatives. (Applying)
- Describe isomerism in carboxylic acids.. (Understanding)

Reading



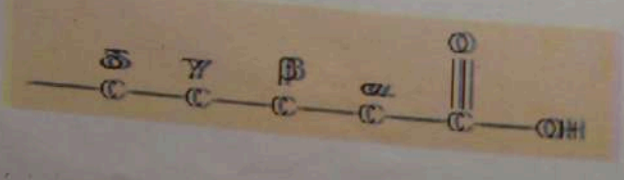
Organic compounds which contain functional group $C_nH_{2n+1}COOH$ in their molecule are called carboxylic acids. Aliphatic carboxylic acids have the carboxyl group attached with an open chain of carbon atoms. They may be represented by the general formula



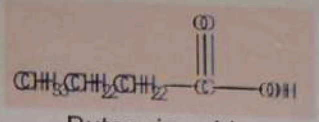
$R-\overset{O}{\overset{\|}{C}}-OH$ where R = H or any alkyl group. Aromatic carboxylic acids have the carboxylic group with phenyl or aryl group. There are organic compounds which contain more than one carboxylic groups in their molecule.

20.1. NOMENCLATURE:

(1) Common Names: Many carboxylic acids are known by their common names, which were given to them before the systematic names were evolved. The positions of other groups attached with the chain containing the carboxyl group are indicated by the Greek letters α, β, γ etc. the carbon adjacent to the carboxylic group is called α (alpha) carbon and the carbon atom in the carboxyl group is not the α carbon e.g.



(2) The IUPAC system: From the name of alkane, which contains the same number of carbon atoms as the longest continuous chain the carboxyl group the ending -e is dropped and in its place the ending -oic acid added. For example the carboxylic acid has four carbon atoms in the chain containing carboxyl group. The name of the alkane having a straight chain of four carbon atoms is butane. Therefore the name of the four carbon acid, will be butanoic acid

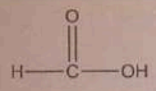


$CH_3CH_2CH_2-\overset{O}{\overset{\parallel}{C}}-OH$

Butanoic acid

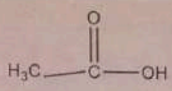
The carbon atoms of the chain containing the carboxyl group are numbered to indicate the positions of other groups attached with it. The carbon atom of the carboxyl group is given the number 1.

The names and the structural formulas of a few carboxyl acids are given below. Boiling points and melting points are also given.



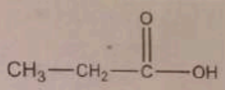
$H-\overset{O}{\overset{\parallel}{C}}-OH$

Formic acid
or
Methanoic acid
b.p., 101°C
m.p., 8.4°C



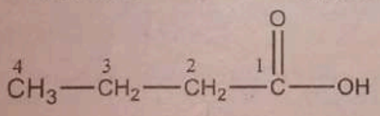
$H_3C-\overset{O}{\overset{\parallel}{C}}-OH$

Acetic acid
or
ethanoic acid
b.p., 118°C
m.p., 16°C



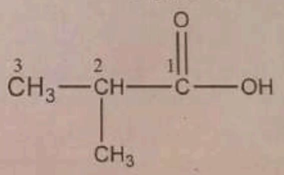
$CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-OH$

Propionic acid
or
Propanoic acid
b.p., 142°C
m.p., 21°C



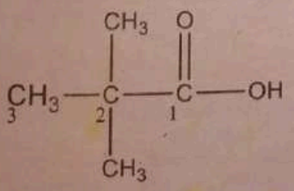
$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{O}{\overset{\parallel}{\overset{1}{C}}}-OH$

n-Butyric acid
or
Butanoic acid
b.p., 164°C
m.p., 5°C



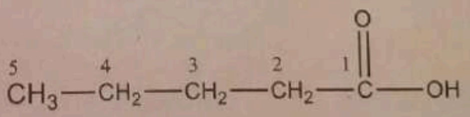
$\overset{3}{C}H_3-\underset{CH_3}{\overset{2}{C}H}-\overset{O}{\overset{\parallel}{\overset{1}{C}}}-OH$

Isobutyric acid or
2-Methyl propanoic acid
b.p., 154°C
m.p., 47°C



$\underset{3}{C}H_3-\underset{CH_3}{\overset{CH_3}{\underset{2}{C}}}-\overset{O}{\overset{\parallel}{\underset{1}{C}}}-OH$

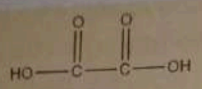
Trimethylacetic acid
or
2,2-Dimethylpropanoic acid
b.p., 164°C
m.p., 35.5°C



$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{O}{\overset{\parallel}{\overset{1}{C}}}-OH$

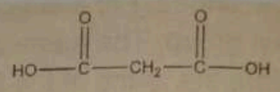
n-Valeric acid
or
Pentanoic acid
b.p., 186°C
m.p., 35°C

Carboxylic acids may be classified as mono, di or poly carboxylic acids as they contain one, two or many carboxylic groups respectively in their molecules e.g.



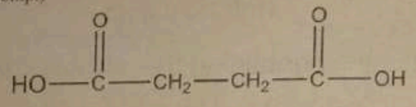
$$HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

Oxalic acid
or
Ethanedioic acid
m.p., 186°C
(decomp.)



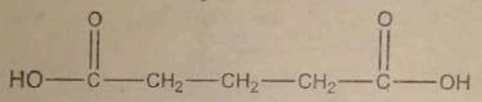
$$HO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Malonic acid
or
Propanedioic acid
m.p., 130 - 135°C
(decomp.)



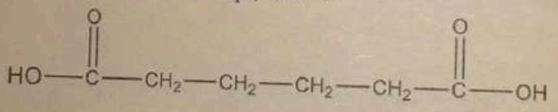
$$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Succinic acid
or
Butanedioic acid
m.p., 182°C



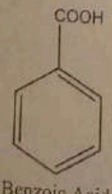
$$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Glutaric acid
or
Pentanedioic acid
m.p., 97.7°C

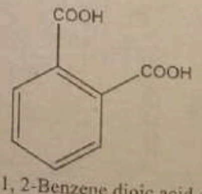


$$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Adipic acid
or
Hexanedioic acid
m.p., 151 - 153°C



Benzoic Acid
(monocarboxylic acid)



1, 2-Benzene dioic acid or
phthalic acid
(Dicarboxylic acid)

20.2. PHYSICAL PROPERTIES

- The polar nature of both the **O-H** and **C=O** bonds (due to the electronegativity difference of the atoms) results in the formation of strong hydrogen bonds with other carboxylic acid molecules or other H-bonding systems (*e.g.* water). The implications are:
  - Higher melting and boiling points compared to analogous alcohols

- High solubility in aqueous media
- Hydrogen bonded dimers in gas phase and dimers or aggregates in pure liquid

20.3. STRUCTURE

- The **-COOH** unit is planar and consistent with sp^2 hybridization and a resonance interaction of the lone pairs of the hydroxyl oxygen with the π system of the carbonyl.

20.4 ACIDITY

Carboxylic acids are the most acidic simple organic compounds (pKa ~ 5). But they are only weak acids compared to acids like HCl or H_2SO_4. (Remember the lower the pKa, the stronger the acid)

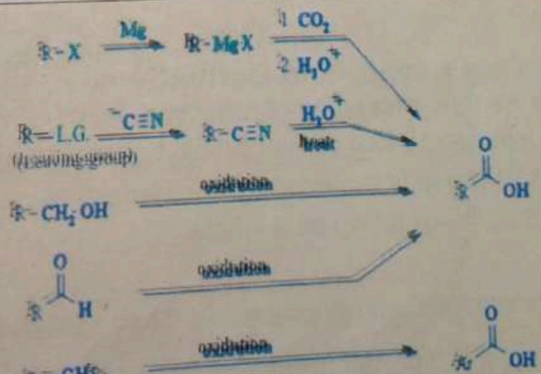
Resonance stabilization of the carboxylate ion allows the negative charge to be delocalized between the two electronegative oxygen atoms (compare with alcohols, pKa ~ 16).

Adjacent electron withdrawing substituents increase the acidity by further stabilizing the carboxylate.

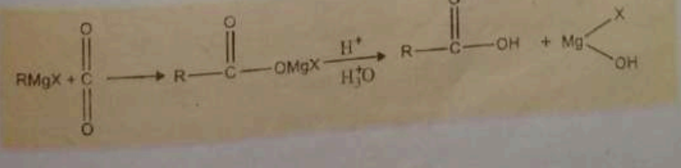
Carboxylic Acid	Structure	pKa	
Ethanoic acid	CH_3CO_2H	4.7	
Propanoic acid	$CH_3CH_2CO_2H$	4.9	
Fluoroethanoic acid	CH_2FCO_2H	2.6	
Chloroethanoic acid	CH_2ClCO_2H	2.9	
Dichloroethanoic acid	$CHCl_2CO_2H$	1.3	
Trichloroethanoic acid	CCl_3CO_2H	0.9	
Nitroethanoic acid	$O_2NCH_2CO_2H$	1.7	

20.5 PREPARATIONS OF CARBOXYLIC ACIDS

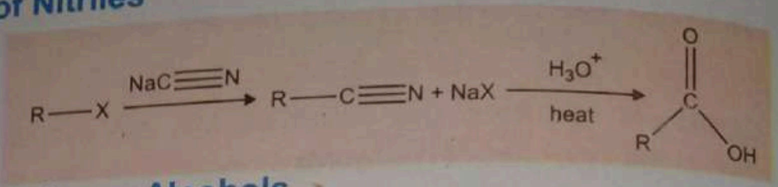
Summary



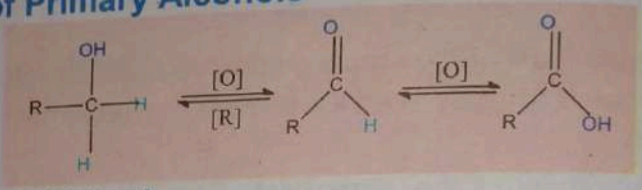
20.5.1 Carbonation of Grignard Reagents, RMgX, by CO_2



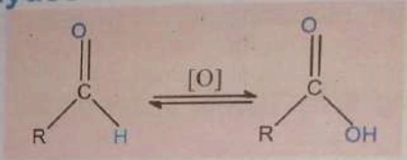
20.5.2. Hydrolysis of Nitriles



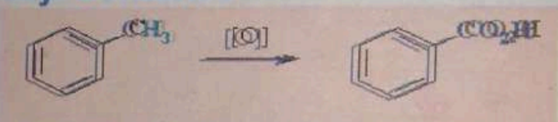
20.5.3. Oxidation of Primary Alcohols



20.5.4. Oxidation of Aldehydes



20.5.5. Oxidation of Alkyl Benzenes



[O] = $Cr_2O_7^{2-}$ or MnO_4^- / H_2SO_4 / heat

20.6 REACTIVITY

The carboxyl group shows the chemistry of both the carbonyl ($-\overset{O}{\overset{\|}{C}}-$) and the hydroxyl (-OH) groups. In most reactions, the carboxyl group is retained. However the reactivity of these molecules is due to the presence of carbonyl group.

20.7 REACTIONS OF CARBOXYLIC ACIDS

20.7.1 Conversion to Carboxylic Acid Derivatives

Carboxylic acids undergo the following types of reactions.

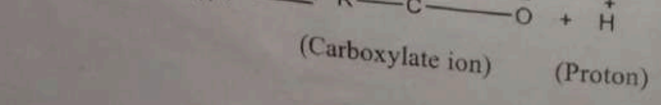
i) The reaction in which hydrogen atom of the carboxyl group is involved (salt formation).

ii) The reaction in which OH group is replaced by another group.

iii) The reactions involving carboxyl group as a whole.

(i) Reaction 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.



(Carboxylate ion) (Proton)

1. Reactions with bases

Carboxylic acids react with bases (NaOH, KOH) to form salts

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

2. Reaction with carbonates and bicarbonates

Carboxylic acids decompose carbonate and bicarbonates evolving carbon dioxide gas with effervescence.

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

3. Reactions with metals

Carboxylic acids react with active metals such as Na, K, Ca, Mg etc to form their salts with the evolution of hydrogen gas,

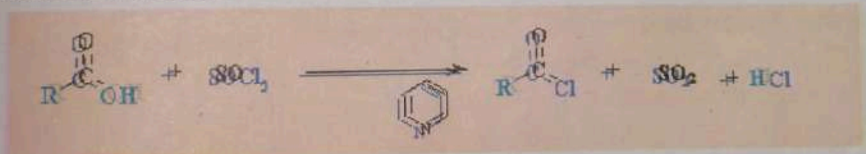
$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$

(ii) Reaction involving the OH group of Carboxylic acid:

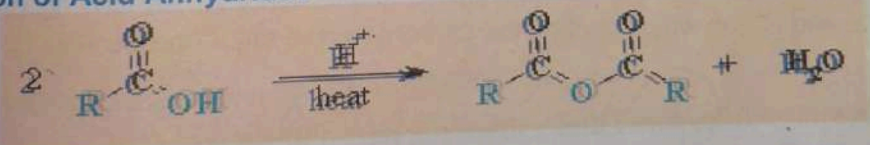
The addition of a nucleophile to the carboxyl group is always followed by the displacement of the –OH group by some other group producing a carboxylic acid derivatives.The –OH group can thus be replaced by x, OR and NH_2 to form halides,esters and amide respectively.

1. Preparation of Acyl Chlorides

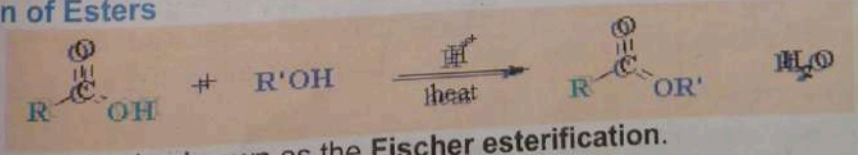
- Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride, $SOCl_2$, in the presence of a base.



2. Preparation of Acid Anhydrides



3. Preparation of Esters



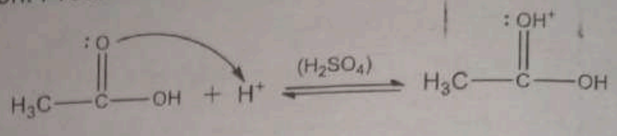
- This reaction is also known as the **Fischer esterification**.
- Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst.
- The equilibrium can be driven to completion by using an excess of either the alcohol or the carboxylic acid, or by removing the water as it forms.
- Alcohol reactivity order : $CH_3OH > 1^o > 2^o > 3^o$ (steric effects)

- Esters can also be made from other carboxylic acid derivatives, especially acyl halides and anhydrides, by reacting them with the appropriate alcohol in the presence of a weak base

Mechanism for Reaction for Acid Catalyzed Esterification

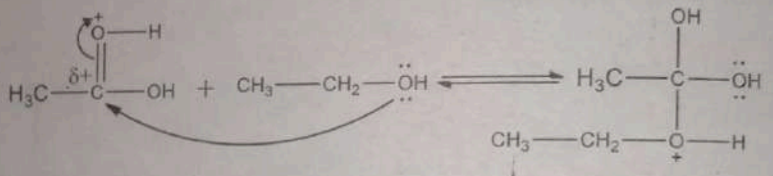
Step 1:

An acid/base reaction. Protonation of the carbonyl makes it more electrophilic.



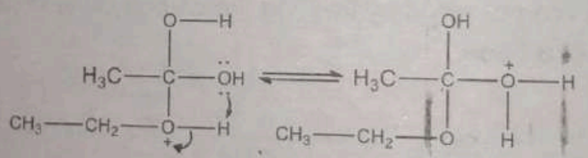
Step 2:

The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.



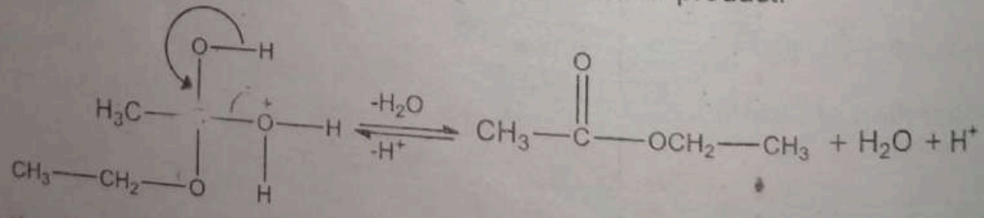
Step 3:

An acid/base reaction. Deprotonate the alcoholic oxygen. Need to make an -OH leave, it doesn't matter which one, so convert it into a good leaving group by protonation.



Step 4:

Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral water molecule and H^+ ion which reveals the carbonyl in the ester product.



4. Preparation of Amides (Reaction with Ammonia)

Carboxylic acids react with ammonia to form ammonium salt which on heating produce acid amide.

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3\,CO\bar{O}\overset{+}{N}H_4 \xrightarrow{\text{heat}} CH_3\,CO\cancel{O}NH_2 + H_2O$$

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20.7.2. Reduction to Alcohols

Reduction of Carboxylic Acids to alcohol:

$$CH_3\,COOH + 4[H] \xrightarrow{LiAlH_4} CH_3\,CH_2OH + H_2O$$

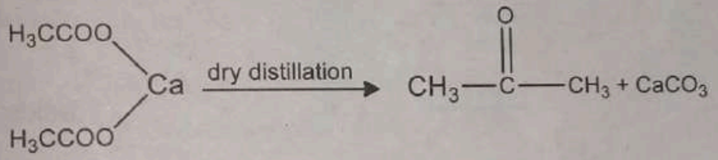
- Carboxylic acids are less reactive to reduction by hydride than aldehydes, ketones or esters.
- Carboxylic acids are reduced to **primary alcohols**.
- As a result of their low reactivity, carboxylic acids can only be reduced by $LiAlH_4$ to form primary alcohol.

20.7.3. Decarboxylation (Ketones)

Loss of carbon dioxide is called **decarboxylation**.

Simple carboxylic acids rarely undergo decarboxylation.

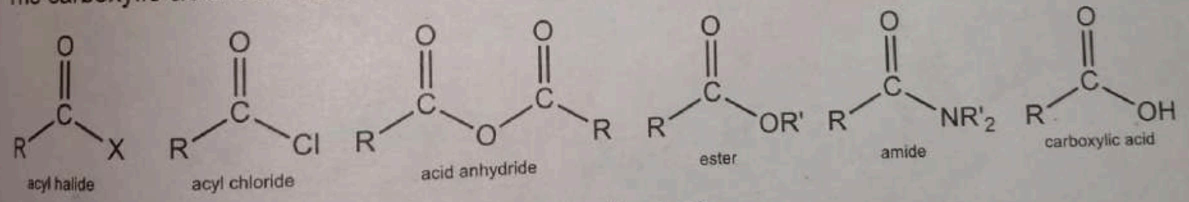
Dry distillation of calcium salt of carboxylic acids give ketone.



$$\begin{matrix} H_3CCOO \\ H_3CCOO \end{matrix}\!\!>Ca \xrightarrow{\text{dry distillation}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$

20.7.4. Summary of Reactions that Interconvert Carboxylic Acids

The carboxylic acid derivatives are a **family** of closely related functional groups:



Each contain a **C=O** group with a **heteroatom** attached

(Note: This is what distinguishes them from **aldehydes and ketones**) they can all be **prepared** from the "parent" carboxylic acid on hydrolysis they all convert back to the parent carboxylic acid, they share a common reactivity pathway with nucleophiles: **nucleophilic acyl substitution**.

IMPORTANT Reactivity order: acyl chloride > anhydride > ester = carboxylic acid > amide > carboxylate $(R-\overset{O}{\overset{\|}{C}}-O^-)$

The most important things to know about carboxylic acid derivatives are:

- How to prepare the derivatives from the carboxylic acid itself (Chapter 19)
- The relative reactivity of the carboxylic acid derivatives.

- The hydrolysis of derivatives gets back to the carboxylic acid.
- The mechanism of nucleophilic acyl substitution.

20.7.8. Reactions of Carboxylic Acid Derivatives

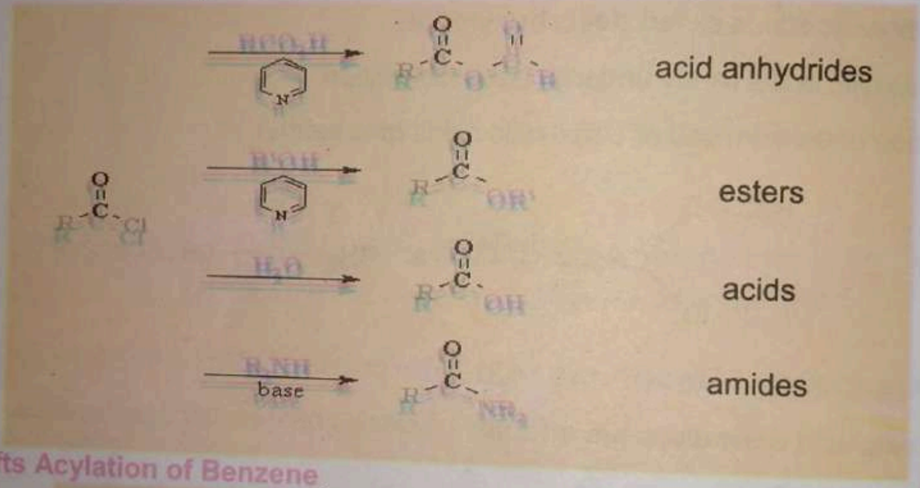
(Elaboration of Reactions that Interconvert Carboxylic Acids Derivatives)

1. Reactions of Acyl Halides, Friedel-Crafts Acylation (review)
2. Reactions of Acid Anhydrides,
3. Reactions of Esters, Hydrolysis, Reduction, and with Grignard reagents
4. Reactions of Amides, Hydrolysis and Reduction
5. Reactions of Nitriles, Hydrolysis, Reduction, and with Grignard reagents

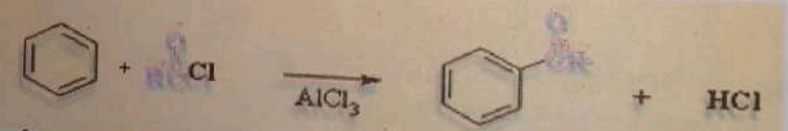
1. Reactions of Acyl Halides, Friedel-Crafts Acylation

Reactions of Acyl Halides

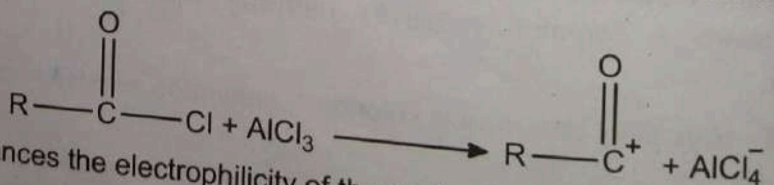
Interconversion Reactions of Acyl Chlorides with carboxylic acid, alcohol, water and primary amine gives acid anhydride, esters, acids and amides respectively.



Friedel-Crafts Acylation of Benzene



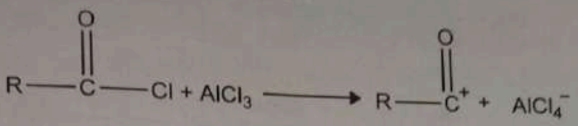
- Overall transformation : **Ar-H** to**Ar-COR**(a ketone)
- Named after Friedel and Crafts who discovered the reaction.
- Reagent : normally the acyl halide (*e.g.* usually RCOCl) with aluminum trichloride, $AlCl_3$, a Lewis acid catalyst.



$$R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C^+}} + AlCl_4^-$$

- The $AlCl_3$ enhances the electrophilicity of the acyl halide by complexing with the halide.

- Electrophilic species : the acyl cation or **acylium ion** (*i.e.* RCO^+) formed by the "removal" of the halide by the Lewis acid catalyst, e.g.,



$$R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C^+}} + AlCl_4^-$$

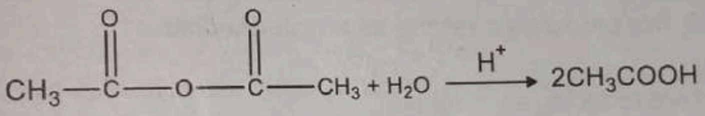
- Friedel-Crafts reactions are limited to arenes as or more reactive than mono-halobenzenes.
- Other sources of acylium can also be used such as acid anhydrides with $AlCl_3$
- Note how the reaction can still be reviewed as a ***Nucleophilic Acyl Substitution***of the acyl halide since overall we have a nucleophile (here the pi bond of an aromatic ring) replaces the leaving group (chloride) at the electrophilic C=O.

2. Reactions of Acid Anhydrides

Imp

i. Hydrolysis (Reaction with water)

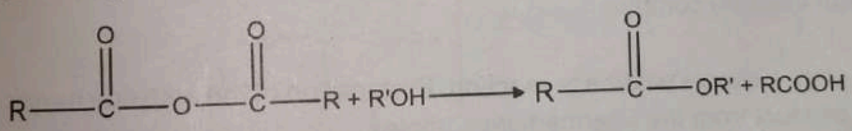
Acid anhydrides are hydrolysed under acidic or basic conditions to form the parent acid.



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \xrightarrow{H^+} 2CH_3COOH$$

ii. Alcoholysis:

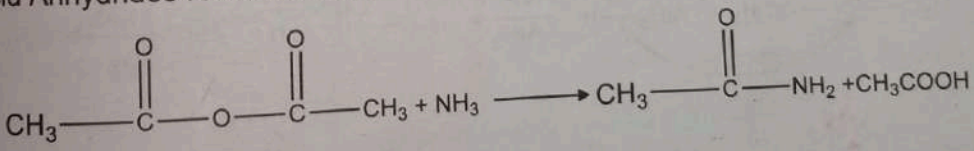
Acid Anhydrides react with alcohols to form esters.



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + R'OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR' + RCOOH$$

iii. Formation of Amide:

Acid Anhydrides react with Ammonia to form amide.



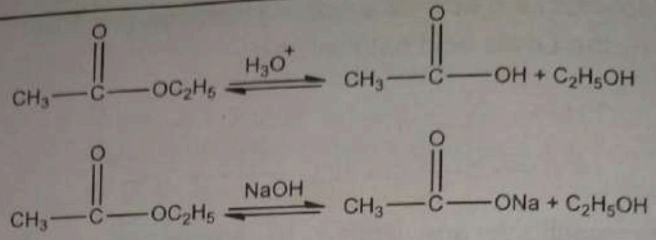
$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3COOH$$

3. Reactions of Esters (Hydrolysis, Reduction, and with Grignard's Reagent Interconversion)

i. Hydrolysis of Esters

Esters can by hydrolysed to acid and alcohol under acidic or basic conditions.

Basic hydrolysis of esters is known as **saponification** because it leads to the formation of alkali salt of carboxylic acids which is soap.



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \underset{}{\overset{H_3O^+}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \underset{}{\overset{NaOH}{\rightleftharpoons}} CH_3-\overset{O}{\overset{\|}{C}}-ONa + C_2H_5OH$$

ii. Reduction of Esters

Esters can be reduced either catalytically or by the use of chemical reducing agents; such as $LiAlH_4$. In either case, the ester is cleaved to yield in addition to alcohol (or phenol) from which it is derived a primary alcohol.

Mechanism

Step 1:

The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O, creating an intermediate metal alkoxide complex.

Step 2:

The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group, this produces a ~~ketone~~ aldehyde as an intermediate.

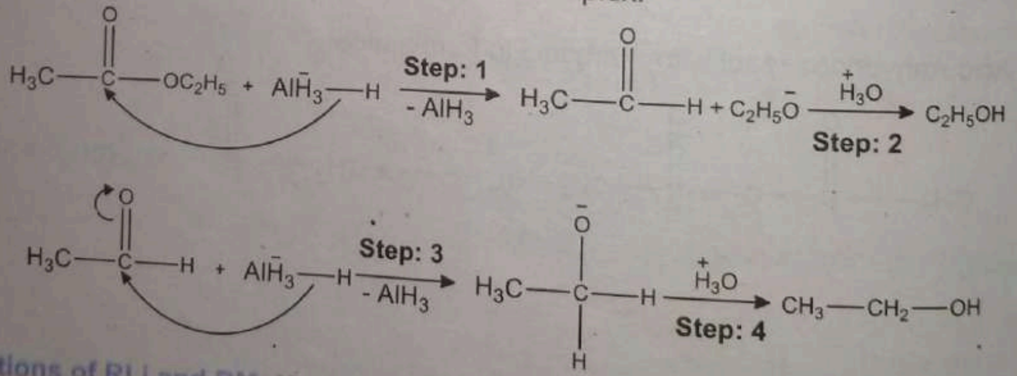
Step 3:

Now we are reducing an aldehyde.

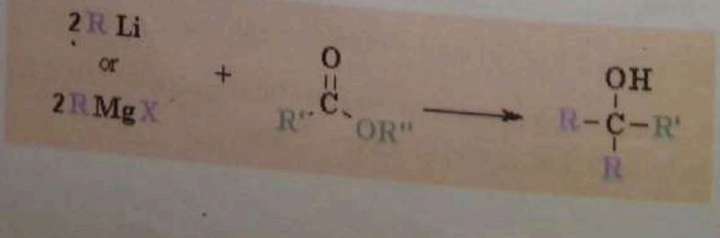
The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the aldehyde. Electrons from the C=O move to the electronegative O, creating an intermediate metal alkoxide complex.

Step 4:

This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the primary alcohol product from the intermediate complex.



iii. Reactions of RLi and RMgX with Esters



Carboxylic esters, **R'CO₂R"**, react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.

The tertiary alcohol that results contains 2 identical alkyl groups (from R in the scheme)

The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent (review)

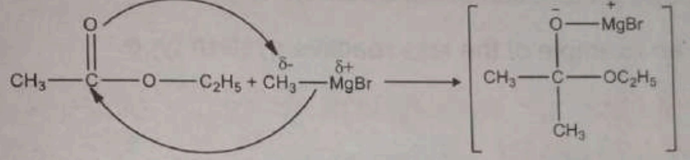
Since the ketone is more reactive than the ester, the reaction *cannot* be used as a preparation of ketones.

The mechanism is an example of the reactive system type.

Mechanism

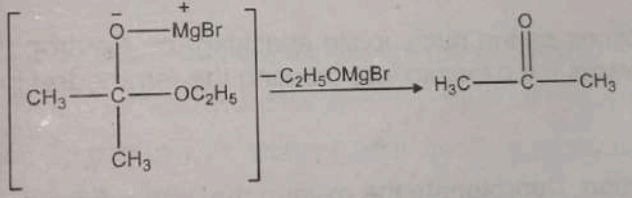
Step 1:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O, creating an intermediate metal alkoxide complex.



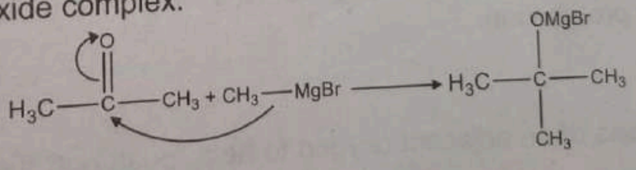
Step 2:

The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group; this produces a ketone as an intermediate.



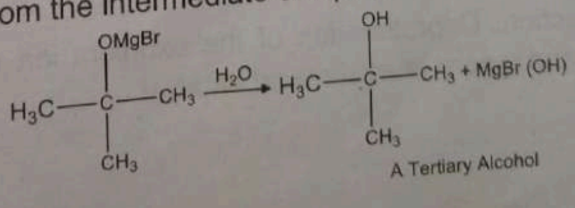
Step 3:

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C=O move to the electronegative O, creating an intermediate metal alkoxide complex.



Step 4:

This is the work-up step, a simple acid/base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.



A Tertiary Alcohol

4. Reactions of Amides (Hydrolysis and Reduction) P

Interconversion Reactions of Amides

I. Hydrolysis of Amides

$$RC(=O)NR'_2 \xrightarrow[\text{heat}]{H_2O} RC(=O)OH + R'_2NH$$

- Amides hydrolyze to the parent carboxylic acid and the appropriate amine.
- The mechanisms are similar to those of esters.
- Reagents : Strong acid (*e.g.* H_2SO_4) / heat (preferred) or strong base (*e.g.* NaOH) / heat.

Reaction under ACIDIC conditions:

Note that the acid catalyzed mechanism is analogous to the acid catalyzed hydrolysis of esters.

The mechanism shows protonation of the carbonyl not the amide N (see **step 1**).

The mechanism is an example of the less reactive system type.

Mechanism of the Acid Catalyzed Hydrolysis of Amides

Step 1:

An acid/base reaction. Since we only have a weak nucleophile and a poor electrophile, we need to activate the ester. Protonation of the amide carbonyl makes it more electrophilic.

Step 2:

The water O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3:

An acid/base reaction. Deprotonate the oxygen that came from the water molecule.

Step 4:

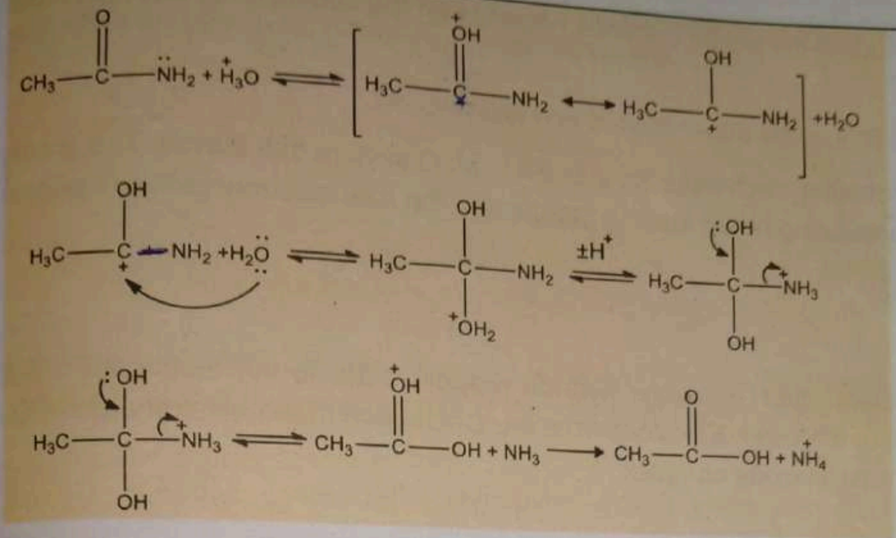
An acid/base reaction. Need to make the -NH_2 leave, but need to convert it into a good leaving group first by protonation.

Step 5:

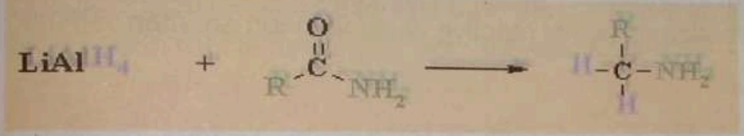
Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral ammonia molecule.

Step 6:

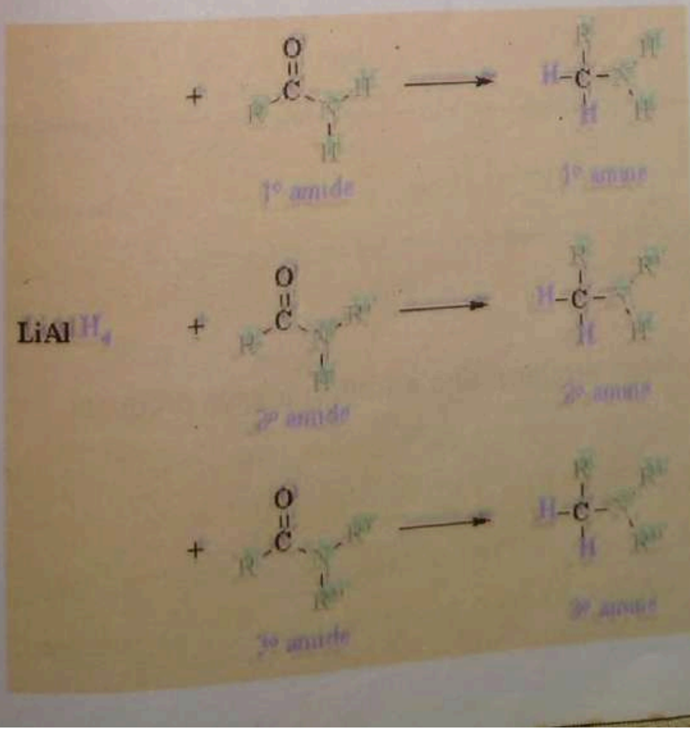
An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the carboxylic acid product and regenerates the acid catalyst.



Reduction of Amides



- Amides, **RCONR'₂**, can be reduced to the amine, **RCH₂NR'₂** by conversion of the C=O to -CH₂-
- Amides can be reduced by $LiAlH_4$ but not the less reactive $NaBH_4$
- Typical reagents : $LiAlH_4$ / ether solvent followed by aqueous work-up.
- Note that this reaction is different to that of other C=O compounds which reduce to ***alcohols***



- The nature of the amine obtained depends on the substituents present on the original amide.
- R, R' or R" may be either alkyl or aryl substituent.
- In the potential mechanism note that it is an O system that leaves. This is consistent with O systems being better leaving groups that the less electronegative N systems.

Mechanism

Step 1:

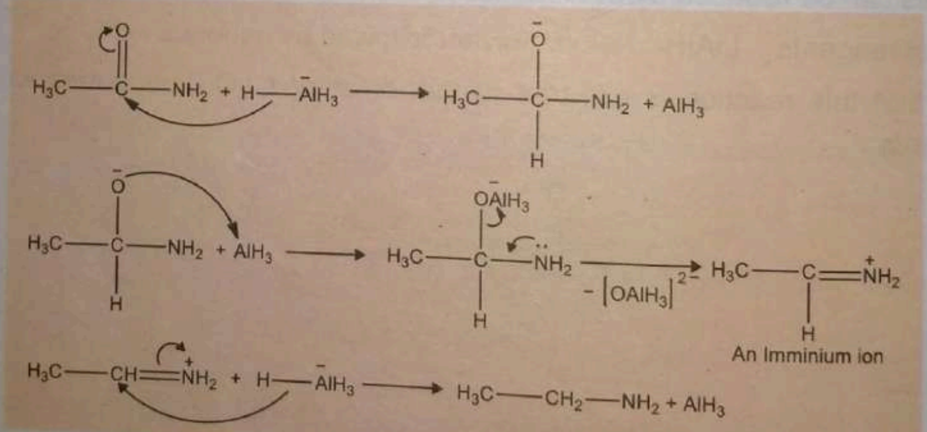
The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 2:

The tetrahedral intermediate collapses and displaces the O as part of a metal alkoxide leaving group, this produces a highly reactive aluminium ion an intermediate.

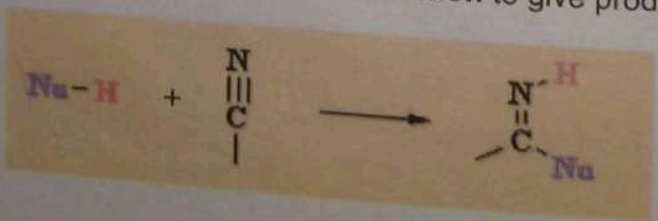
Step 3:

Rapid reduction by the nucleophilic H from the hydride reagent as it adds to the electrophilic C in the iminium ion. π - electrons from the C=N move to the cationic N neutralizing the charge creating the amine product.

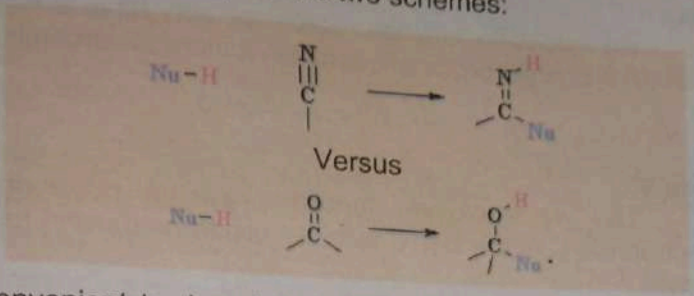


5. Reactions of Nitriles (Hydrolysis, Reduction, and reactions with Grignard's Reagent)

Nitriles typically undergo **nucleophilic addition** to give products.



The chemistry of the nitrile functional group, **C≡N**, is very similar to that of the carbonyl, C=O of aldehydes and ketones. Compare the two schemes:

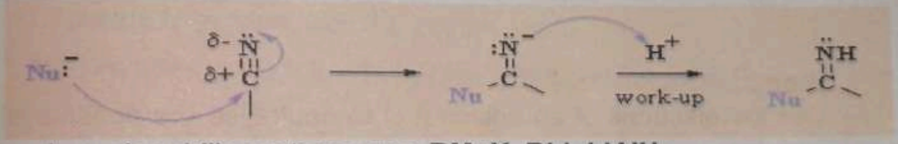


However, it is convenient to describe nitriles as carboxylic acid derivatives because: the oxidation state of the C is the same as that of the carboxylic acid derivatives.

Hydrolysis produces the carboxylic acid

Like the carbonyl containing compounds, nitriles react with nucleophiles via two scenarios:

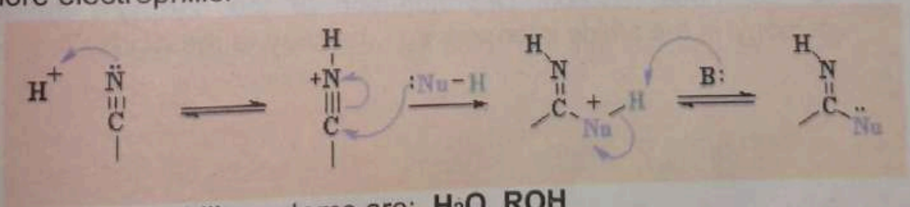
Strong nucleophiles (anionic) add directly to the **C≡N** to form an intermediate imine salt that protonates (and often reacts further) on work-up with dilute acid.



Examples of such nucleophilic systems are: **RMgX, RLi, LiAlH$_4$**

Weaker nucleophiles (neutral) require that the **C≡N** be activated prior to attack of the Nu.

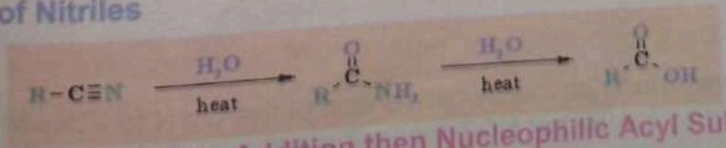
This can be done using an acid catalyst which protonates on the Lewis basic N and makes the system more electrophilic.



Examples of such nucleophilic systems are: **H$_2$O, ROH**

The protonation of a nitrile gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.

i. Hydrolysis of Nitriles



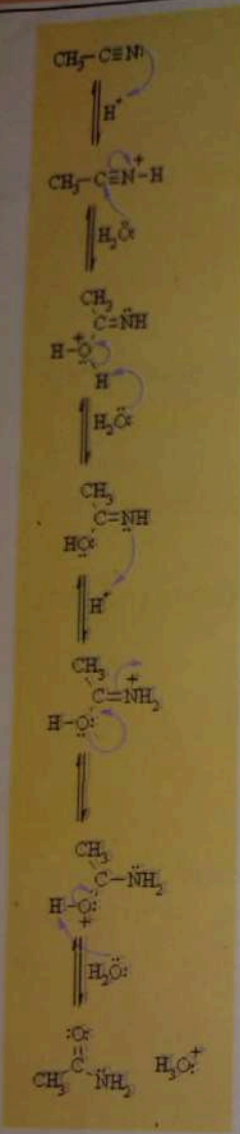
Reaction type: Nucleophilic Addition then Nucleophilic Acyl Substitution

Elaboration

Nitriles, **RC≡N**, can be hydrolyzed to carboxylic acids, **RCO$_2$H** via the amide, **RCONH$_2$**.

Reagents: Strong acid (*e.g.* H$_2$SO$_4$) or strong base (*e.g.* NaOH) / heat.

Mechanism of the Acid Catalyzed Hydrolysis of Nitriles



Step 1:

An acid/base reaction. Since we only have a weak nucleophile so activate the nitrile, protonation makes it more electrophilic.

Step 2:

The water oxygen functions as the nucleophile attacking the electrophilic C in the C≡N, with the electrons moving towards the positive center.

Step 3:

An acid/base reaction. Deprotonate the oxygen that came from the water molecule. The remaining task is a tautomerization at N and O centers.

Step 4:

An acid/base reaction. Protonate the N gives us the -NH_2 we need....

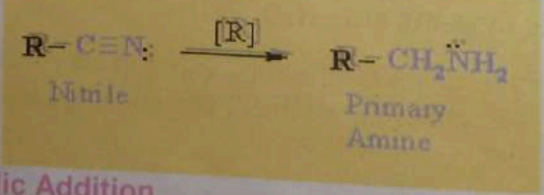
Step 5:

Use the electrons of an adjacent O to neutralise the positive at the N and form the π bond in the C=O.

Step 6:

An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the amide intermediate....halfway to the acid.....

ii. Reduction of Nitriles



Reaction type: Nucleophilic Addition

Elaboration

The nitrile, **RC≡N**, gives the 1° amine by conversion of the **C≡N** to **-CH_2-NH_2**

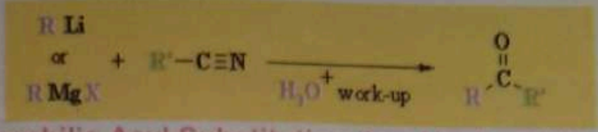
Nitriles can be reduced by $LiAlH_4$ but **NOT** the less reactive $NaBH_4$

Typical reagents: $LiAlH_4$ /ether solvent followed by aqueous work-up.

Catalytic hydrogenation (H_2/catalyst) can also be used giving the same products.

R may be either alkyl or aryl substituents

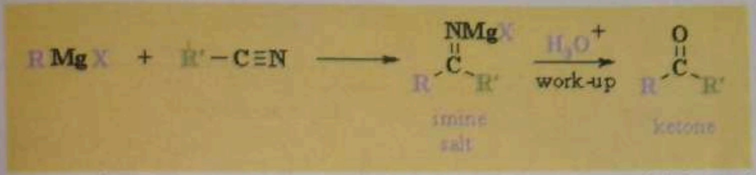
iii. Reactions of RLi or RMgX with Nitriles



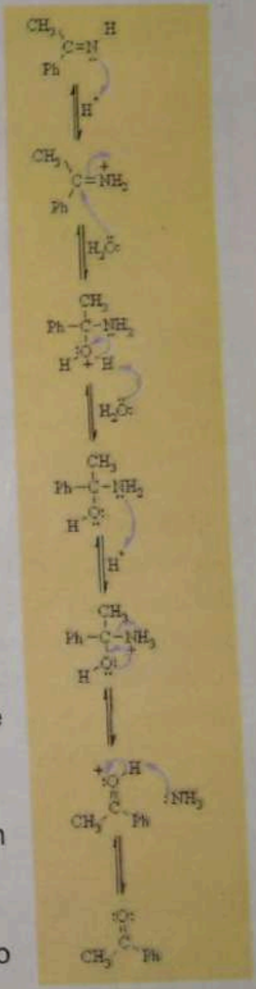
Reaction type: Nucleophilic Acyl Substitution then Nucleophilic Addition

Elaboration:

- Nitriles, **RC≡N**, react with Grignard reagents or organolithium reagents to give ketones.
- The strongly nucleophilic organometallic reagents add to the **C≡N** bond in a similar fashion to that seen for aldehydes and ketones.
- The reaction proceeds via an imine salt intermediate that is then hydrolyzed to give the ketone product.



- Since the ketone is not formed until after the addition of water, the organometallic reagent does not get the opportunity to react with the ketone product.
- Nitriles are less reactive than aldehydes and ketones.



Mechanism

Step 1:
The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar nitrile group. Electrons from the C≡N move to the electronegative N creating an intermediate imine salt complex.

Step 2:
An acid/base reaction. On addition of aqueous acid, the intermediate salt protonates giving the imine.

Step 3:
An acid/base reaction. Imines undergo nucleophilic addition, but require activation by protonation (*i.e.* acid catalysis)

Step 4:
Now the nucleophilic O of a water molecule attacks the electrophilic C with the pi-bond breaking to neutralize the change on the N.

Step 5:
An acid/base reaction. Deprotonate the O from the water molecule to neutralize the positive charge.

Step 6:
An acid/base reaction. Before the N system leaves, it needs to be made into a better leaving group by protonation.

Step 7:

Use the electrons on the O in order to push out the N leaving group, a neutral molecule of ammonia.

Step 8:

An acid/base reaction. Deprotonation reveals the carbonyl group of the ketone product.

Quick Quiz

1. Define Steric effect?
2. What is alcohol's reactivity order?
3. How oxonium ion creates the tetrahedral intermediate?
4. Define tautomerization?
5. Define saponification?

Society, Technology and Science

1. Carboxylic acids occurence.

Sorbic acid

Caprylic acid is present in coconut

Lauric acid is also present in coconut

Myristic acid is present in nutmeg

Arachidic acid is present in peanut oil

Citric acid is present in citrus fruits e.g. lemon, limes, grapes, oranges.

Tartaric acid is present in tamarind.

Lactic acid is present in apples, tomatoes and molasses.

Acetic acid is present in grapes.

Malic acid is present in green apples and plums.

Benzoic acid is found in berries.

Butyric acid is present in rancid butter.

Caproic acid is present in goat fat.

Caprylic acid is present in milk.

Palmitic acid is present in palm oil.

Stearic acid is present in waxes, animal fats and oils.

Amino acids are the building blocks of proteins.

Acetoacetic acid and pyruvic acid are the acids of biochemical significance.

Lactic acid is found in sour milk.

Tartaric acid is found in wine.

Acetic acid is found in vinegar.

Do You Know?

1. The carboxylic acid (3-methyl-3-hexanoic acid is one of the compounds associated with the odour of human perspiration
2. The vinegaroon (whip-tail scorpion) expels a spray of acetic acid to repel predators
3. Flavour of some esters

❖ Amylacetate	Banana
❖ Isobutyl formate	Raspberry
❖ Benzyl acetate	Jasmine
❖ Ethyl butyrate	Pineapple
❖ Amyl butyrate	Apricot
❖ Octyl Acetate	Orange

4. A peptide containing mass more than 10000 is known as protein.

2. Carboxylic acids as food preservatives.

Formic acid is used as preservative for silage (including fresh hay) and other livestock feed.

Boric acid was used as a food preservative in caviar (a product made from salt-cured fish-eggs) but its use has been banned now.

Salicylic acid Its use has been banned now.

Benzoic acid is used as a preservative in jams, beer, preserved fruit, pickles, fruit juice, desert sauces and syrups.

Acetic acid is used as a preservative in fish fingers, butter, margarine, processed cheese, curry powder, cooking oil.

Lactic acid is used as a preservative in beer, tinned foods especially vegetables and fruit, fresh fruit and vegetables.

Propionic acid is used as a preservative in dairy products, particularly in cheese and in baking products.

Taste of different carboxylic acids.

Esters are derived from carboxylic acids by reaction of carboxylic acids and alcohols in the presence of hydrochloric acid or sulfuric acid, a process called esterification.

Ester flavors are a range of fruity, sugary and sweet that occur in many beer types as a normal part of their brewing process.

Examples of ester flavors are

Ethyl formate gives raspberries their characteristic taste.

Ethyl acetate has a bittersweet, wine-like burning *taste.*

Isoamyl acetate has a taste reminiscent of pears or bananas.

Ethyl propionate *has rum like taste. (Rum is* distilled alcoholic beverage made from sugarcane byproducts).

Ethyl butyrate *–found in pineapples- tastes like sugar water.*

Ethyl valerate *has apple like taste.*

Ethyl hexanoateis an apple-flavoured ester.

Ethyl heptanoate has wine-like odour and taste with a burning after-taste.

Ethyl octanoate found in pineapples has sweet taste.

Key Points

- Carboxylic acids are the most acidic of the common organic functional groups.
- The **CO_2H** unit is planar and consistent with sp^2 hybridization and a resonance interaction of the lone pairs of the hydroxyl oxygen with the π system of the carbonyl.
- The most important reactions of carboxylic acids converts them into carboxylic acid derivatives such as acyl halides, esters and amides via nucleophilic acyl substitution reactions.
- Esters can also be made from other carboxylic acid derivatives, especially acyl halides and anhydrides, by reacting them with the appropriate alcohol in the presence of a weak base.
- Loss of carbon dioxide is called **decarboxylation**.
- Simple carboxylic acids rarely undergo decarboxylation

- Esters are less reactive towards Nu than aldehydes or ketones.
- Carboxylic esters, **R'CO$_2$R"**, react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- Amides hydrolyze to the parent carboxylic acid and the appropriate amine.
- Amides can be reduced by LiAlH$_4$ but **NOT** the less reactive NaBH$_4$
- The chemistry of the nitrile functional group, **C≡N**, is very similar to that of the carbonyl, **C=O** of aldehydes and ketones.

Nitriles, **RC≡N**, react with Grignard reagents or organolithium reagents to give ketones.

Exercise

Q1: Select the right answer from the choices given with each question.

i. A carboxyl acid contains functional group;
   a. A Hydroxyl group
   [✓ b] A Carboxyl group
   c. Hydroxyl and Carboxyl group
   d. A Carboxyl and aldehyde group

ii. From the following carboxylic acids which acid has higher acidity;
   a. Ethanoic acid
   b. Propanoic acid
   c. Chloroethanoic acid
   [✓ d] Nitroethanoic acid

iii. Which reagent is used to reduce a carboxylic acid?
   a. He/Ni
   b. H$_2$/Pt
   c. NaBH$_4$
   [✓ d] LiAlH$_4$

iv. Stronger acid is
   a. CH$_3$COOH
   [✓ b] HCOOH
   c. CH$_3$CH$_2$COOH
   d. CH$_3$CH$_2$CH$_2$COOH

v. Acetamide is prepared by;
   [✓ a] Heating ammonium acetate
   b. Heating methyl cyanide
   c. Heating ethyl acetate
   d. The hydrolysis of methyl cyanide

vi. Carboxylic acids react with metal to form salts with the evolution of
   a. CO$_2$
   [✓ b] H$_2$
   c. CO
   d. CH$_4$

vii. Ethane-1,2-dioic acid is also called;
   a. Benzoic acid
   [✓ b] Oxalic acid
   c. Formic acid
   d. Malonic acid

viii. Carboxylic acid can be prepared by the action of Grignard's reagent with
   a. O$_2$
   [✓ b] CO$_2$
   c. KCl
   d. N$_2$

ix. The IUPAC name for formic acid is
   [✓ a] Methanoic acid
   b. Acetic acid
   c. Ethanoic acid
   d. Butanoic acid

x. The reaction of alcohol with acetic acid is known as
   a. sponification
   [✓ b] estrification
   c. ammonolysis
   d. hydrolysis

xi. Esters are formed by the reaction of carboxylic acids with
[✓ a. alcohols] b. ethers
c. aldehydes d. Alkyl halides

xii. Which one of the following has both hydroxyl and carboxylic acid groups?
a. phenol b. picric acid
c. phthalic acid [✓ d. Salicylic acid]

xiii. Which of the following cannot be prepared directly from acetic acid.
[✓ a. acetamide] b. acetyl chloride
c. acetic anhydride d. Ethyl acetate

xiv. Reaction between caustic soda and a fat is called
a. esterification b. hydrogenation
c. neutralization [✓ d. saponification]

xv. When a carboxylic acid reacts with alcohol, it produces a new class of compounds.
a. ethers [✓ b. esters]
c. anhydride d. amide

Q 2: Give brief answers for the following questions.

i. What are aliphatic and aromatic carboxylic acids?
ii. Give probable mechanism of alkaline hydrolysis of an ester.
iii. A carboxylic acid does not form phenyl hydrazone when treated with phenyl hydrazine. Explain
iv. Give the mechanism for the acid catalyzed hydrolysis of a nitrile,?
v. Why acetic acid is often called Glacial acetic acid?
vi. What is use of esters?
vii. How may nitriles be converted into carboxylic acid?
viii. What are acidic amino acids give example?
ix. How does carboxylic acids exist in nonpolar solvent

Q3: Give detailed answers for the following questions.

i. How will you prepare carboxylic acids from?
(i) alkyl nitrile (ii) Hydrolysis of esters
ii. Give the reaction of amine with Grignard reagent with mechanism.
iii. Write down the mechanism of the following reactions.
- Between acetic acid and ethanol (esterification)
- Between acetic acid ammonia
- Between acetic acid and thionyl chloride

iv. How would convert the following?
- Acetic acid into acetamide
- Acetic acid into acetone

v. How amides are reduced with $LiAlH_4$? Give mechanism.
vi. What is Friedal & Craft's reaction? Explain their mechanism.
vii. Give mechanism for reaction for acid catalyzed esterification.

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BIOCHEMISTRY

After completing this lesson, you will be able to:

This is 7 days lesson (period including homework)

- Explain the basis of classification, structure, functional relationship of Carbohydrates.
- Explain the role of various carbohydrates in health and diseases.
- Identify the nutritional importance and their role as energy storage.
- Explain the basis of classification and structural–function relationship of proteins.
- Describe the role of various proteins in maintaining body function and their nutritional importance
- Describe the role of enzyme as biocatalyst and relate this role to various functions such as digestion food.
- Identify factors that affect enzyme Activity such as effect of temperature and pH.
- Explain the role of inhibitors of enzyme catalyzed reaction.
- Describe the basis of classification and structure-function relationship of Lipids.
- Identify the nutritional and Biological importance of lipids (Applying)
- Identify the structural components of DNA and RNA
- Recognize the structural differences between DNA polymer (double strand) and RNA (single strand)
- Relate DNA sequence to its function as storage of genetic information
- Relate RNA sequence (transcript) to its role in transfer of information to protein (Translation).
- Identify the sources of minerals such as Iron, Calcium, Phosphorus and Zinc

Reading

INTRODUCTION TO BIOCHEMISTRY

As the name indicates, biochemistry is a hybrid science: Biology is the science of living organisms and chemistry is the science of atoms and molecules, so biochemistry is the science of the atoms and molecules in living organisms.

Biochemistry is the branch of science concerned with studying the various molecules that occur in living cells and organisms, with their chemical reactions. Biochemistry is concerned with the complete spectrum of all forms of life, from relatively simple viruses and bacteria to complex human beings. It attempts to describe in molecular terms the structures, mechanisms, and chemical processes shared by all organisms.

Living organisms should be able to transform matter and energy into different forms, show response to changes in their environment and show growth and reproduction. All living organisms undergo changes due to large organic compounds called macromolecules. Four main types of macromolecules control all activities. They are carbohydrates, proteins, lipids and nucleic acids. Now, we discuss these one by one.

21.1 CARBOHYDRATES

Carbohydrates are called carbohydrates because they contain carbon, oxygen and hydrogen and these are generally in proportion to form water with the general formula $C_n(H_2O)_n$.

Modern Definition:

Carbohydrates are polyhydroxy compounds of aldelydes or ketones.

Carbohydrates or saccharides are the most abundant of the four types of macromolecules. These are sugars or starches. They have several roles in living organisms, including energy transportation, as well as being structural components of plants and arthropods. Carbohydrate derivates are actively involved in fertilization, immune systems, development of disease, blood clotting and growth. Most organic matter on earth is made up of carbohydrates because they are involved in so many aspects of life, including:

DO YOU KNOW?

All the organic compounds containing hydrogen and oxygen in the proportion of 2:1 are not carbohydrates. For example

i) Formaldehyde	-HCHO	$= C(H_2O)$
ii) Acetic acid	$-CH_3COOH$	$= C_2(H_2O)_2$
iii) Lactic acid	$-CH_3CH(OH)COOH$	$=C3(H_2O)_3$

Anyhow, Rhaminose $C_6H_{12}O_5$ does not have the ratio of hydrogen to oxygen as in H_2O, but it is a carbohydrate.

- Energy stores, fuels, and metabolic intermediaries.
- Ribose and deoxyribose sugars are part of the structural framework of RNA and DNA.
- The cell walls of bacteria are mainly made up of polysaccharides (types of carbohydrate).
- Cellulose (a type of carbohydrate) makes up most of plant cell walls.
- Carbohydrates are linked to many proteins and lipids (fats), where they are vitally involved in cell interactions.

21.1.1 Classification of Carbohydrates

Carbohydrates are classified into three types.

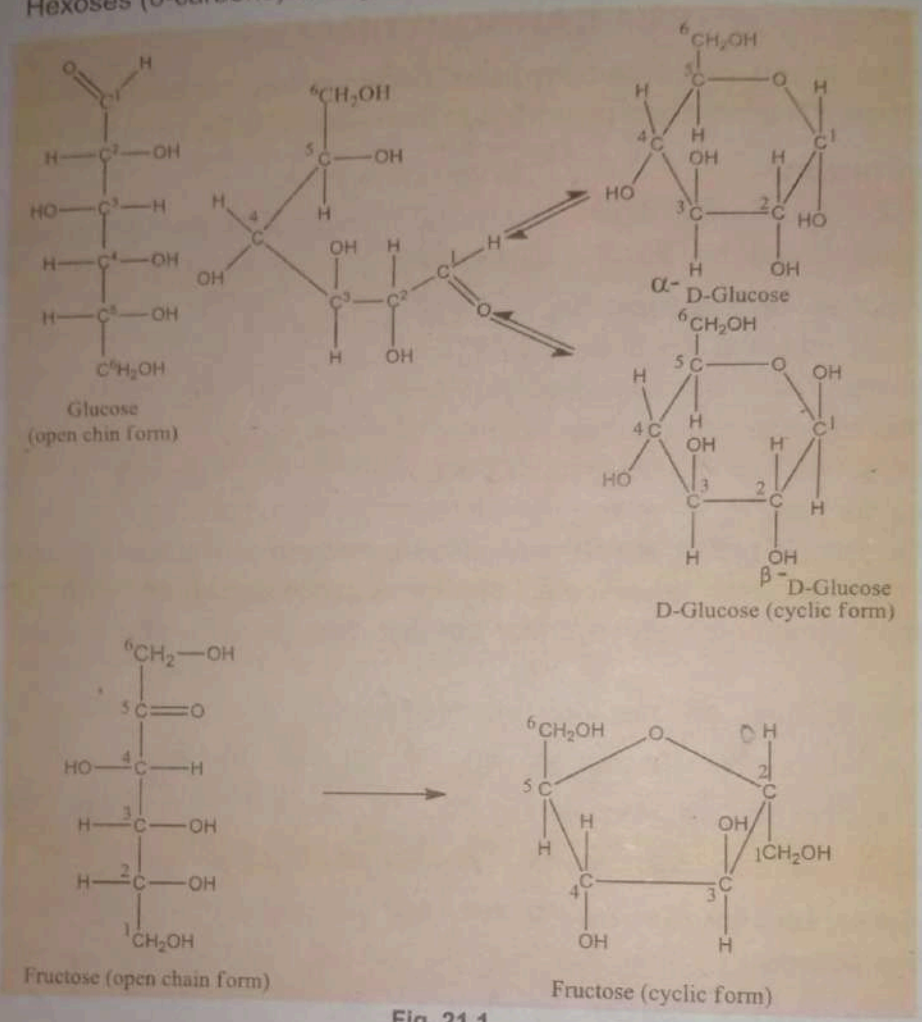
a. Monosaccharides

Definition: The carbohydrates which do not hydrolyze to simpler units are called monosaccharides.

This is the smallest possible sugar unit. Examples are glucose, galactose and fructose. When we talk about blood sugar, we refer to glucose in the blood; glucose is a major source of energy for a cell. Glucose is naturally in honey and corns. In human nutrition, galactose can be found most readily in milk and dairy products, while fructose is found mostly in vegetables and fruits (grapes).

When monosaccharides merge together in linked groups, they are called polysaccharides.

- Monosaccharides can be further classified by the number of carbons present. Hexoses (6-carbons) are by far the most prevalent.



Glucose (open chin form)

D-Glucose (cyclic form)

Fructose (open chain form)

Fructose (cyclic form)

Fig. 21.1

b. Disaccharides

Two monosaccharide molecules are bonded together to form disaccharides. Disaccharides are polysaccharides; "poly" specifies any number higher than one, while "di" specifies exactly two. Examples of disaccharides include lactose, maltose, and sucrose.

- Lactose is formed in the milk (Wheat)
- Sucrose occurs in sugarcane, sugar beet, mango, pineapple, almond and apricot.

c. Polysaccharides

Definition: The carbohydrates producing large number of mono-saccharides on hydrolysis are called polysaccharides.

Starch and cellulose are the example of polysaccharides.

It is a chain of two or more monosaccharides. The chain may be branched (molecule is like a tree with branches and twigs) or unbranched (molecule is a straight line with no twigs). Polysaccharide molecule chains may be made up of hundreds or thousands of monosaccharides.

Polysaccharides are polymers. A simple compound is a *monomer*, while a complex compound is a *polymer* which is made of two or more *monomers*.

Interesting Information

A new system for classifying carbohydrates is the glycemic index. The glycemic index ranks foods on how they affect blood sugar level by measuring how much the blood sugar increases after one eats.

A brief summary is presented below;

Carbohydrates		
Monosaccharides	**Disaccharides**	**Polysaccharides**
Glucose	Sucrose	Starch
Galactose	Maltose	Glycogen
Fructose	Lactose	Cellulose
Ribose		
Glyceraldehyde		

1.1.2 Functions of Carbohydrates

The main functions of carbohydrates are given below:

- They spare protein so that protein can concentrate on building, repairing, and maintaining body tissues instead of being used up as an energy source.
- For fat to be metabolized properly, carbohydrates must be present. If these are not enough carbohydrates, then large amounts of fat are used for energy. The body is not able to handle this large amount so quickly, so it accumulates ketone bodies, which make the body acidic. This causes a condition called ketosis.
- Carbohydrate is necessary for the regulation of nerve tissue and is the only source of energy for the brain.
- Certain types of carbohydrates support the growth of healthy bacteria in the intestines for digestion.
- Some carbohydrates are high in fibre, which helps prevent constipation and lowers the risk for certain diseases such as cancer, heart disease and diabetes.

When IP (Polysaccharides act as food stores in plants in the form of starch, or in humans and other animals in the form of glycogen) Polysaccharides also have structural roles in the plant cell wall in the form of cellulose or pectin, and the tough outer skeleton of insects in the form of chitin. Three major functions of polysaccharides are discussed below.

a. Storage Polysaccharides imp IP

- **Glycogen** - a polysaccharide that humans and animals store in the liver and muscles.

•1,4 glycosidic linkage

amylose
•water soluble
•10-20%

amylopectin
•insoluble
•80-90%

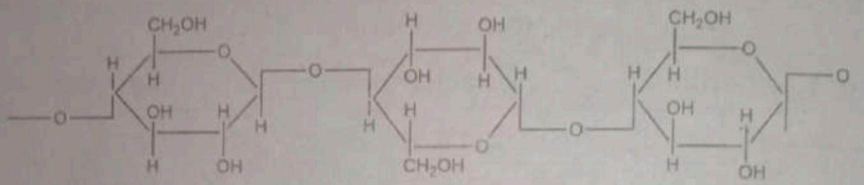
•1,4 glycosidic linkage
•1,6 glycosidic linkage

- **Starch** - these are glucose polymers made up of Amylose (10-20%) and Amylopectin (80-90%). Starches are water insoluble. Humans and animals digest them by hydrolysis; our bodies have amylases which break them down. Rich sources of starches for humans are potatoes, rice and wheat.

  Structures of Amylase and Amylopectin are given below in Fig 21.3 and 21.4

b. Structural Polysaccharides

- **Cellulose** - the structural constituents of plants are made mainly from cellulose - a type of polysaccharide. Wood is mostly made of cellulose, while paper and cotton are almost pure cellulose.



Cellulose (Polymer of β -D-glucose)

Fig. 21.3

- **Chitin** - chitin, a polysaccharide, is one of the most abundant natural materials in the world. Microorganisms, such as bacteria and fungi secrete chitinases, which over time can break down chitin.

  Chitin is the main component of fungi cell walls, the exoskeletons (hard outer shell/skin) of arthropods, such as crabs, lobsters, ants, beetles, and butterflies.

c. Bacterial Polysaccharides

They are found in bacteria, especially in bacterial capsules. Pathogenic bacteria often produce a thick layer of mucous-like polysaccharide which protects the bacteria from the host's immune system. In other words, if the bacteria were in a human, that human's immune system would less likely attack the bacteria because the polysaccharide layer covers its pathogenic properties.

21.1.3 Nutritional Importance of Carbohydrates

DO YOU KNOW?

- 1 gram of carbohydrate contains approximately 4 kilocalories (kcal)
- 1 gram of protein contains approximately 4 kcal
- 1 gram of fat contains approximately 9 kcal

- Scientific research has shown the diverse functions of carbohydrates in the body and their importance for good health. Bread, pasta, beans, potatoes, bran, rice and cereals are carbohydrate-rich foods.

  Their main functions are given by:

a) Body Weight Regulation

People eating a diet high in carbohydrates are less likely to accumulate body fat compared with those who follow a low carbohydrate/high-fat diet. The reasons for this observation are threefold:

It could be due to the lower energy density of high carbohydrate diets, as carbohydrates have fewer calories than fats. Fiber-rich foods also tend to be bulky and physically filling, so fewer calories may be consumed. Studies show that carbohydrates, both in the form of starch and sugars, work quickly to aid satiety and that those consuming high carbohydrate diets are therefore less likely to overeat. It is evident that diets high in carbohydrate, as compared with those high in fat, reduce the likelihood of developing obesity.

Interesting Information

In several studies, high sugar consumers have been found to be slimmer than low sugar consumers.

b) Diabetes

There is no evidence that sugar consumption is linked to the development of any type of diabetes. However there is now good evidence that obesity and physical inactivity increase the likelihood of developing non-insulin dependent diabetes, which usually occurs in middle age.

Weight reduction is usually necessary and is the primary dietary aim for people with non-insulin dependent (Type II) diabetes. Consuming a wide range of carbohydrate foods is an acceptable part of the diet of all diabetics, and the inclusion of low glycaemic index foods is beneficial as they help to regulate blood glucose control. Most recommendations for the dietary management of diabetes allow a modest amount of ordinary sugar as the inclusion of sugar with a meal has little impact on either blood glucose or insulin concentrations in people with diabetes.

c) Dental Health

The incidence of tooth decay is influenced by a number of factors. These include:

- degree of oral hygiene and plaque removal carried out,
- availability of fluoride,
- type of food eaten,
- frequency of consumption of any fermentable carbohydrate
- genetic factors

Foods containing sugars or starch can be broken down by the enzymes and bacteria in the mouth to produce acid which attacks the enamel of the teeth. However it is not the amount of sugar or other carbohydrate that is important but how often they are consumed. After an acid challenge, saliva provides a natural repair process which rebuilds the enamel. When carbohydrate-containing foods are consumed too frequently, or nibbled over time, this natural repair process is overwhelmed and the risk of tooth decay is increased.

d) Getting Active

There is now substantial evidence that carbohydrates can improve the performance of athletes. During high intensity exercise, carbohydrates are the main fuel for the muscles. By consuming high levels of carbohydrate before, during and after training or an event, glycogen stores are kept well stocked. These stocks help the athlete to perform for longer and help their bodies sustain the effort.

The vital role of physical activity in maintaining health and fitness in the general population is now recognized. There is no doubt that many people would benefit from increasing their Activity level as it helps in the regulation of body weight. It also reduces the risk of developing diseases such as heart disease and diabetes. For those who want to keep fit and active, a well-balanced high-carbohydrate diet is recommended.

Quick Quiz

1. What are carbohydrates? Give its general formula?
2. Quote one example of each type of carbohydrates.
3. Write structural formulae of Glucose and Fructose.
4. What do you understand by glycemic index?
5. How much calories do 1gm of carbohydrate have?
6. On what factors tooth decay depend?

21.2. PROTEINS

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The molecules which yield amino acids on complete hydrolysis are called proteins.

Proteins are probably the most important class of biochemical molecules, although of course lipids and carbohydrates are also essential for life. Proteins are the basis for the major structural components of animal and human tissue. Proteins are natural polymer molecules consisting of amino acid units. The number of amino acids in proteins may range from two to several thousand.

These molecules contain nitrogen, carbon, hydrogen and oxygen. They act as biological catalysts (enzymes), form structural parts of organisms, participate in cell signal and recognition factors, and act as molecules of immunity. Proteins can also be a source of fuel.

21.2.1. Classification of Proteins

Three classes of proteins are usually defined; 1) Simple proteins 2) Compound on conjugated proteins 3) Derived proteins.

a. Simple Proteins: These proteins on hydrolysis yield only amino acids or their derivatives. Numerous examples of simple proteins are given below.

- **Albumins:** blood (serumbumin); milk (lactalbumin); egg white (ovolbumin); lentils (legumelin); kidney beans (phaseolin); wheat (leucosin). Globular protein is soluble in water and dilute salt solution; it is precipitated by saturation with ammonium sulfate solution; coagulated by heat; usually found in plant and animal tissues.
- **Globulins:** blood (serum globulins); muscle (myosin); potato (tuberin); Brazil nuts (excelsin); hemp (edestin); lentils (legumin). Globular protein is sparingly soluble in water and soluble in neutral solutions; precipitated by dilute ammonium sulfate and coagulated by heat; distributed in both plant and animal tissues.
- **Glutelins:** wheat (glutenin); rice (oryzenin). It is insoluble in water and dilute salt solutions; soluble in dilute acids; found in grains and cereals.
- **Histones:** thymus gland, pancreas and nucleoproteins (nucleohistone). It is soluble in water, salt solutions and dilute acids; insoluble in ammonium hydroxide; yields large amounts of lysine and arginine; combined with nucleic acids within cells.

b. Conjugated Proteins: Those proteins which are attached or conjugated to some non-protein group which are called prosthetic group. Few examples are given below.

- **Nucleoproteins:** Cytoplasm of cells (ribonucleoprotein), nucleus of chromosomes (deoxyribonucleoprotein), viruses and bacteriophages. It contains nucleic acids, nitrogen and phosphorus. It is present in chromosomes and in all living forms as a combination of protein with either DNA or RNA.
- **Mucoprotein:** saliva (mucin) and egg white (ovomucoid). Proteins combined with amino sugars, sugar acids and sulfates.
- **Glycoprotein:** bone (osseomucoid), tendons (tendomucoid) and cartilage (chondromucoid). Containing more than 4% hexosamine, mucoproteins; if less than 4%, then glycoproteins.
- **Phosphoprotein:** milk (casein) and egg yolk (ovovitellin). Phosphoric acid joined in ester linkage to protein.

c. Derived Proteins: Those proteins which are derived from simple and conjugated proteins). Its typical examples are given below.

- **Proteans:** edestan (from elastin) and myosin (myosin). It results from short action of acids or enzymes; insolvent in water.
- **Proteoses;** intermediate products of protein digestion. It is soluble in water; not coagulated by heat; and precipitated by saturated ammonium sulfate; result from partial digestion of protein by pepsin or trypsin.
- **Peptones;** intermediate products of protein digestion. It has the same properties as proteases except that they can not be salted out; of smaller molecular weight than proteases.
- **Peptides;** intermediate products of protein digestion. Two or more amino acids joined by a peptide linkage; hydrolyzed to individual amino acids.

21.2.2. Structure of Proteins

The structure of a protein depends upon the spatial arrangement of polypeptide chains present in proteins. Since three spatial arrangements are possible, proteins have the following four structures.

((i) Primary structure (P Diff
(ii) Secondary structure)
(iii) Tertiary structure
(iv) Quaternary structure

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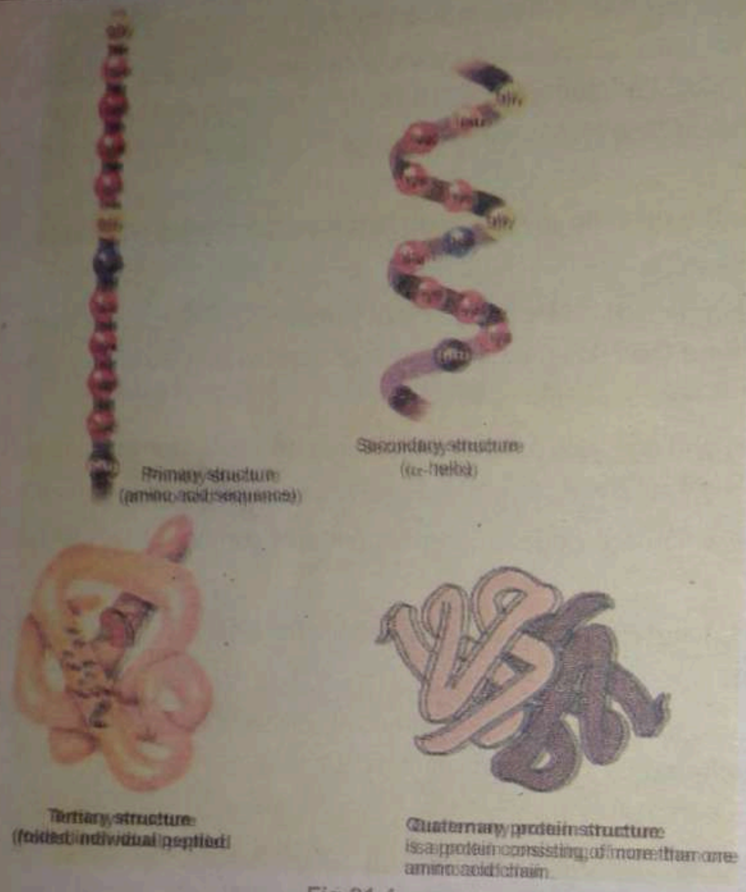
Primary structure (amino acid sequence)

Secondary structure (α-helix)

Tertiary structure (folded individual peptide)

Quaternary protein structure is a protein consisting of more than one amino acid chain

Fig 21.4

a) The Primary Structure of Proteins

The sequence of amino acids in a peptide chain is called primary structure. Amino acids are linked with one another through peptide bond. The arrangement of these acids is called primary structure.

b) The Secondary Structure of Proteins

Peptide chains may acquire spiral shape or may be present in a zig-zag manner. This coiling or zig-zagging of polypeptide is called secondary structure of protein. It is due to H-Bond

c) The Tertiary Structure of Proteins

Twisting or folding of polypeptide chains represents tertiary structure of proteins.

d) Quaternary Proteins

Quaternary means four. This is the fourth phase in the creation of a protein.

Quaternary protein is the arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex. A variety of bonding interactions including hydrogen bonding, salt bridges, and disulfide bonds hold the various chains into a particular geometry.

21.2.3. Properties of Proteins

Proteins are one of the four major groups of macromolecules that are found in all living organisms. These giant molecules carry out many of the vital functions needed by cells.

Proteins are involved in such processes as food digestion, cell structure, catalysis, movement, energy manipulation and much more. They are complex, huge associations of molecular subunits that appear impossibly difficult to understand. Fortunately they are all built using the same construction principle. As with all macromolecules, proteins are polymers, composed of smaller subunits - the amino acids - joined together in long chains.

There are about 20-22 common amino acids found in most proteins. All but one of these small molecules has the same common structure, but varies in the nature of one chemical group - termed the "R-group". Amino acids are joined together in long chains called "polypeptides".

21.2.4. Importance of Proteins

Following are the features of the protein which are considered to be very important:

1) Proteins play an important role in the formation of protoplasm. Protoplasm is the essence of all form of life.
2) Nucleoproteins are complex proteins and act as the carrier of heredity from one generation to the other.
3) Enzymes are the biological catalyst and they are also proteins. Without enzymes life is not possible.
4) Hemoglobin is a protein. It acts as carrier of oxygen.
5) Some of the proteins act as hormones. They carry out the regulatory function of the body.
6) Proteins have great importance in industry. The tanning of hides is an industrial process. This process is the precipitation of protein by tannic acid.
7) Gelatin is obtained by heating bones, skins and tendons in water. It is used in bakery goods.
8) Casein is another protein used in the manufacture of buttons and buckles.
9) Proteins obtained from the soyabean are used for the manufacture of plastics.

Quick Quiz

1. What are proteins? Give its simple classifications.
2. Differentiate primary, secondary and tertiary structure of Proteins.
3. What are polypeptides?

21.3. ENZYMES

(Greek word En means in and Zyme means yeast)

Enzymes are biocatalysts which alter the speed of metabolic activities in the living bodies.

Enzymes are complex protein molecules which are quite specific in action and sensitive to temperature and pH.

21.3.1. Role of Enzymes as a Biocatalyst:

The life of living organisms is a reflection of what is going on in their bodies. **Metabolism** is the set of biochemical reactions that occur in living organ is in order to maintain life. These processes allow organism to grow and reproduce, maintain their structures, and respond to their environments. **Anabolism** includes the biochemical reactions in which larger molecules are synthesized while catabolism includes the biochemical reactions in which larger molecules are broken down. Usually, energy is released in **catabolism** and it is utilized in anabolism. In this way the biochemical reactions are actually energy transfers.

During metabolism, chemicals are transformed from one form to the other by enzymes. Enzymes are crucial to metabolism because they act as **biocatalysts** and speed up and regulate metabolic pathways.

Enzymes are proteins that catalyze (i.e. speed up) biochemical reactions and are not changed during the reaction. The molecules at which enzymes act are called **substrates**, and enzyme converts them into different molecules, called **products**.

How does Enzyme work?

When enzyme attaches with substrate, a temporary enzyme-substrate (ES) complex is formed. Enzyme catalyzes the reactions and substrate is transformed into product. After it, the ES complex breaks enzyme product.

$$E + S \rightarrow ES\ Complex \rightarrow E + P$$

A) In order to explain the mechanism of enzyme action a German chemist Emil Fischer in 1894, proposed lock and key model. According to this model, both enzyme and substrate possess specific shapes that fit exactly into one an other. This model explains enzyme specificity.

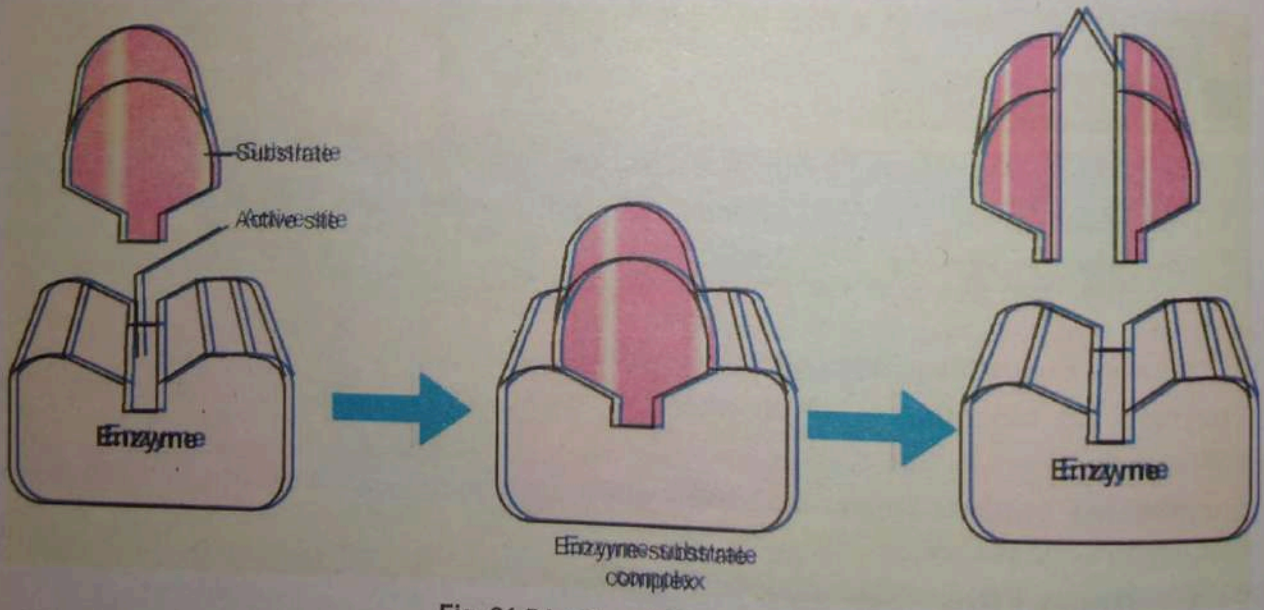

Fig. 21.5 Lock and Key Model

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b) In 1958, an American biologist **Daniel Koshland** suggested a modification to lock and key model and proposed **induced-fit model**. According to this model, active site is not a rigid structure rather is moulded into the required shape to perform its function. "Induced fit model" is more acceptable than "lock and key" model of enzyme action.

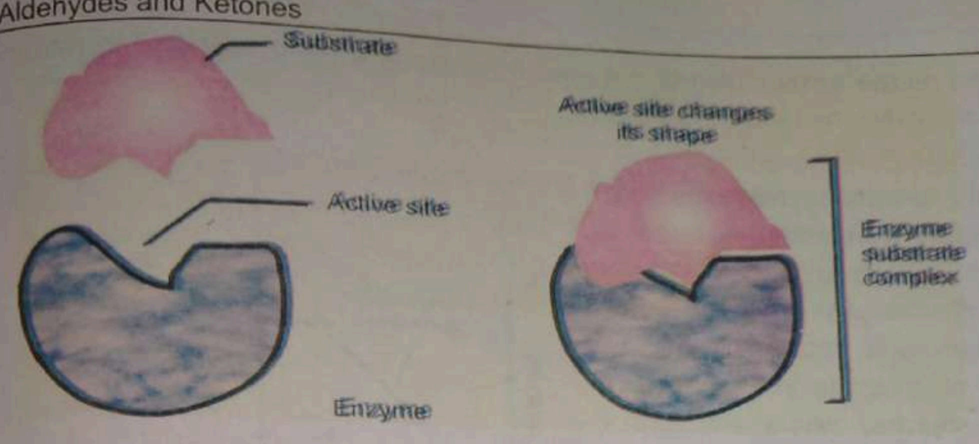

Fig. 21.6 Induced Fit Model

Interesting Information

1) Winhelm Kuhne (1978) first time used the term enzyme.
2) There are over 2000 known enzymes, each of which is involved in one specific chemical reaction.
3) Enzymes are substrate specific.
   (i) The enzyme protease (which breaks peptide bonds in proteins) will not work on starch (which is broken down by an enzyme amylase).
   (ii) Similarly lipase enzyme acts on lipids and digests them into fatty acids and glycerol.

21.3.2. Factors Affecting Enzyme Activity

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Enzymes are very sensitive to the environment in which they work. Any factor that can change the chemistry or shape of enzyme molecule, can affect its activity. Some of the factors that can affect the rate of enzyme action are being discussed here.

i) Temperature

Increase in temperature speeds up the rate of enzyme catalyzed reactions, but only to a point. Every enzyme works at its maximum rate at a specific temperature called as the optimum temperature for that enzyme.

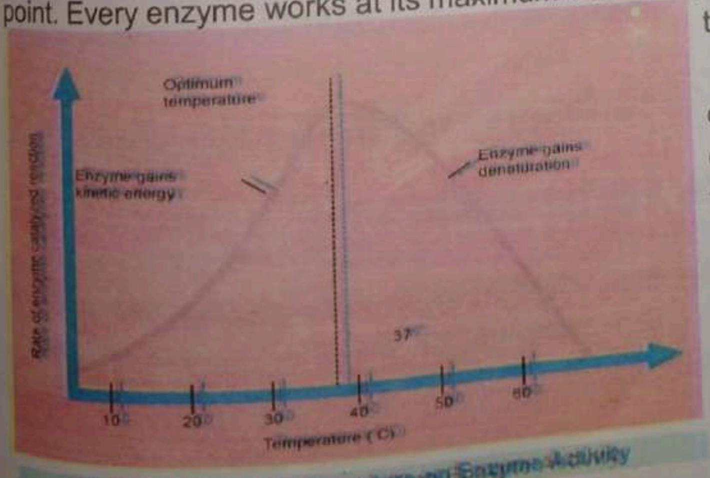


Fig. 21.7 Effect of Temperature on Enzyme Activity

When temperature rises to a certain limit, heat adds in the activation energy and also provides kinetic energy for the reaction. So reactions are accelerated. But when temperature is raised well above the optimum temperature, heat energy increases the vibrations of atoms of enzyme and the globular structure of enzyme is lost. This is known as the denaturation of enzyme, it results in a rapid decrease in rate of enzyme action and it may be blocked completely.

ii) Substrate Concentration

If enzyme molecules are available in a reaction, increase in substrate concentration increases the rate of reaction. If enzyme concentration is kept. is constant and amount of substrate ~~in~~ is increased, a point is reached where any further increase in substrate does not increase the rate of reaction any more. When the active sites of all enzymes are occupied (at high substrate concentration), any more substrate molecules do not find free active site. This state is called saturation of active site and reaction rate does not increase.

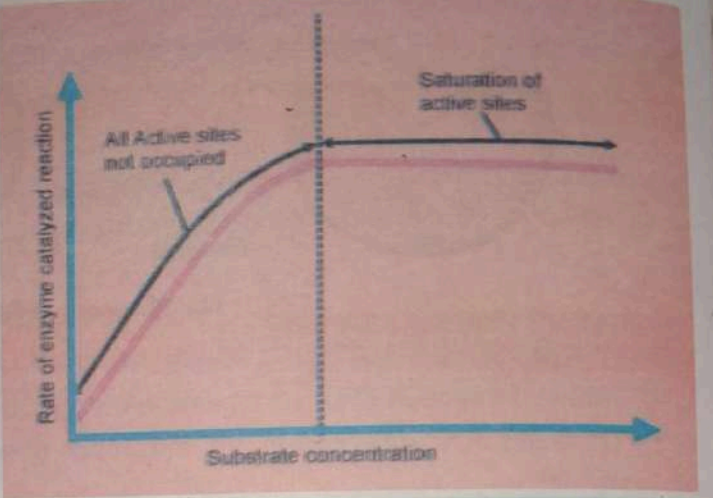


Fig 21.8 Effect of Substrate Concentration on Enzyme Activity

iii) pH

All enzymes work at their maximum rate at a narrow range of pH, called as the optimum pH. A slight change in this pH causes retardation in enzyme Activity or blocks it completely. Every enzyme has its specific optimum pH value. For example, pepsin (working in stomach) is active in acidic medium (low pH) while trypsin (working in small intestine) shows its Activity in alkaline medium (high pH). Change in pH can affect the ionization of the amino acids at the active site.

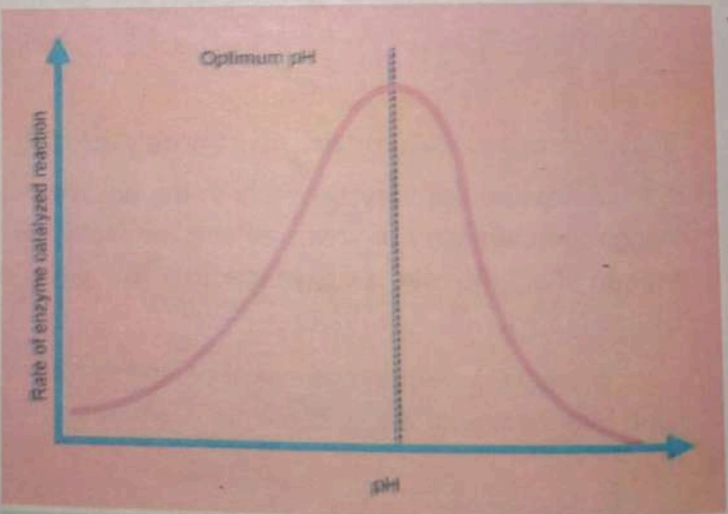


Fig 21.9 Effect of pH on Enzyme Activity

Role of Inhibitors in Enzyme Catalyzed Reactions:

Inhibitors:

Substances that tend to decrease the activity of enzymes are called inhibitors. OR An inhibitor is a chemical substance which can react (in place of substance) with the enzyme but is never transferred into products by blocking the active site of enzyme temporarily or permanently.

Examples of Inhibitors:

Poisons like cyanide, antibodies, anti-metabolics and some drugs.

Types of Inhibitors

Inhibitors can be divided into two types

(a) Irreversible inhibitors (b) Reversible inhibitors

Irreversible Inhibitors

They occupy the active sites by forming covalent bond or they may physically block the active sites. They decrease the reaction rate by occupying the active sites or destroying the globular structure of enzymes.

Reversible Inhibitors

They form weak linkages with the enzyme. Their effect can be neutralized completely or partly by an increase in the concentration of the substrate.

Role

In an enzyme catalyzed reaction, the inhibitors may decrease the activity of enzymes and thus the rate of the reaction either by combining directly with the enzyme or by reacting with the activator, so that the activator does not remain available to enzyme for activation.

Example

Succinic acid (substrate) is converted into Fumaric acid (product) by the enzyme succinic dehydrogenase.

Succinic dehydrogenase + succinic acid → Funaric acid + succinic dehydrogenase
(Enzyme) (Substrate) (Product) (Enzyme)

But in the presence of malonic acid (competitive inhibitor) having structural similarity with succinic acid (substrate), the binding sites are occupied by the malonic acid but no catalysis takes place at the active or catalytic site, hence no product is formed

Succinic dehydrogenase + Malonic acid → No reaction possible
(Enzyme) (Competitive inhibitor) (Enzyme blocked)

Another type of inhibitors, called non-competitive inhibitors cause "non competitive inhibition". Here, the inhibitor is not bound to the catalytic or active site but to some other site of enzyme. This binding distorts the enzyme's structure also affecting the catalytic site of the enzyme in such a way that even if genuine substrate binds the active sites, catalysis fails to take place.

In the reactions catalysed by enzymes irreversible inhibitors cause irreversible inhibition either by physically blocking the active sites of enzymes or by occupying the active sites and forming covalent bonds. So the rate of reaction is retarded due to the occupation of active sites of enzymes by irreversible inhibitors or due to the destruction of the globular structure of enzymes.

Note:

Competitive and non-competitive inhibitors are the two major types of reversible inhibitors.

21.3.3. Industrial Application of Enzyme:

Enzymes are extensively used in different industries for fast chemical reactions. For example;

1. **Food industry:** Enzymes that break starch into simple sugars are used in the production of white bread, buns etc.
2. **Brewing industry:** Enzymes break starch and proteins. The products are used by yeast for fermentation (to produce alcohol).
3. **Paper industry:** Enzymes break starch to lower its viscosity that aids in making paper.
4. **Biological detergent:** Protease enzymes are used for the removal of protein stains from clothes. Amylase enzymes are used in dish washing to remove resistant starch residues.

Quick Quiz

1. What are enzymes? Why are they called biocatalysts?
2. How does enzyme work?
3. Who has used the term Enzyme first time?
4. Why are following scientists famous for?
   (i) Emil Fischer (ii) Daniel Koshland
5. "Enzymes are extensively used in different industries". Comment on this statement.

21.4. LIPIDS

(Greek, lipos means fat)

Lipids are naturally occurring organic compounds of animals and plants origin, which are soluble in organic solvents and belongs to a heterogeneous group of substances.

These molecules consist of carbon, hydrogen, and oxygen atoms. The main constituents of all membranes in all cells (cell walls), food storage molecules, intermediaries in signaling pathways, Vitamins A, D, E and K, cholesterol.

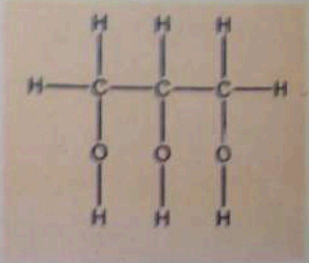


Fig 21.10

All lipids are hydrophobic: that's the one property they have in common. Fats and oils are made from two kinds of molecules: glycerol (a type of alcohol with a hydroxyl group on each of its three carbons) and three fatty acids joined by dehydration synthesis. Since there are three fatty acids attached, so these are known as triglycerides.

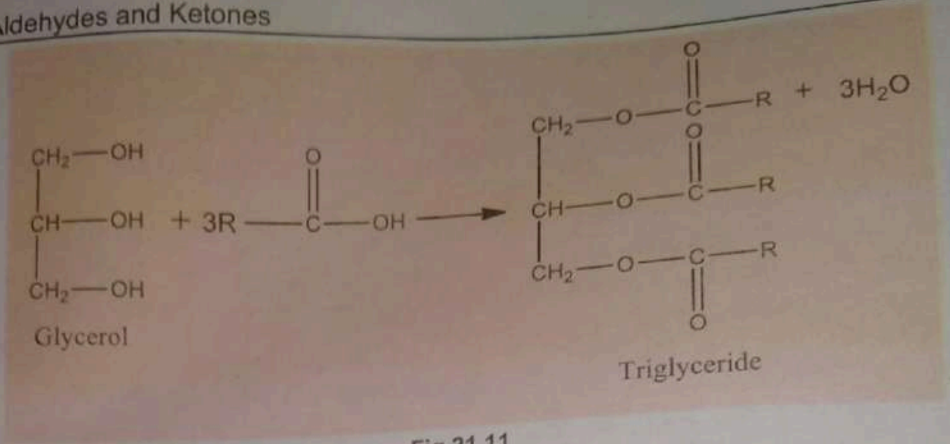


Fig 21.11

21.4.1. Classification of Lipids

There are three broad classes of lipids, discussed below.

a. **Simple Lipids**These are the ester of fatty acids with glycerol.

- **Triglycerides, neutral fats:** Found in adipose tissue, butterfat, fish oils, olive oil, and corn oil. **Waxes:** beeswax, head oil of sperm whale, carnauba oil, and lanolin of industrial and medicinal importance.

b. **Compound Lipids** --- These contain radicals in addition to fatty acids and alcohols.

- **Phospholipids (phosphatides):** Found chiefly in animal tissues.
- **Plasmalogen:** Found in brain, heart, and muscle.
- **Lipositol:** Found in brain, heart, kidneys, and plant tissues together with phytic acid. Phosphatidyl inositol; phosphatide linked to inositol; rapid synthesis and degradation in brain; evidence for role in cell transport processes.
- **Sphingomyelin:** Found in nervous tissue, brain, and red blood cells. Source of phosphoric acid in body tissue.

c. **Derived Lipids:** (These are hydrolytic product of compound lipids)

- **Fatty acids:** Occur in plant and animal foods; also exhibit in complex forms with other substances. Obtained from hydrolysis of fats; usually contains an even number of carbon atoms and are straight chain derivatives.

21.4.2. Structure of Lipids

Lipids are generally defined in terms of solubility, and not in terms of particular structures, as in the cases of proteins and nucleic acids. Lipids associate with one another via van der Waals forces and the hydrophobic effect. In particular, we discuss the structure of 'Fatty Acids'.

The "tail" of a fatty acid is a long hydrocarbon chain, making it hydrophobic. The "head" of the molecule is a carboxyl group which is hydrophilic. Fatty acids are the main component of soap, where their tails are soluble in oily dirt and their heads are soluble in water to emulsify and wash away the oily dirt. However, when the head end is attached to glycerol to form a fat, that whole molecule is hydrophobic.

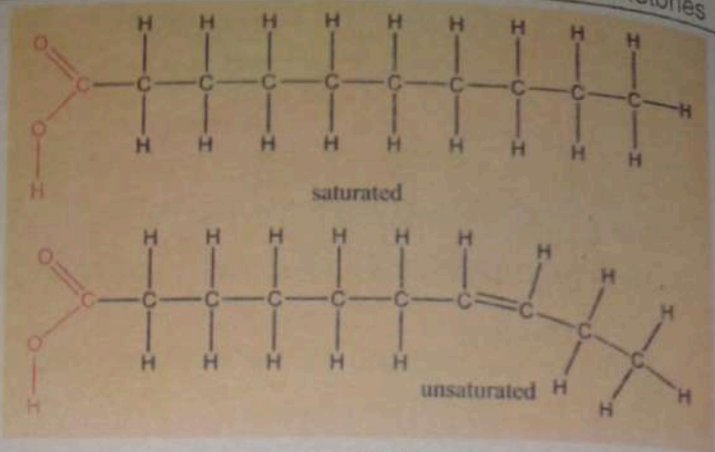


Fig 21.12

21.4.3. Properties of Lipids

1) Physical Properties

DO YOU KNOW?
The unsaturated fats are "healthier" than the saturated ones.

1. Oils and fats may be either liquids or non-crystalline solids at room temperature
2. Fats and oils in the pure states are colorless, odorless and tasteless.
3. The color fats arise due to foreign substances, for example yellow color of the butter is due to the presence of keratin.
4. They are lighter than water.
5. They are insoluble in water.
6. They are readily soluble in organic solvents like diethyl ether, carbon disulphide, acetone, benzene, chloroform and carbon tetrachloride.
7. They form emulsions when they are agitated with water in the presence of soap or other emulsifier.
8. Fats and oils are poor conductor of heat and electricity and serve as excellent insulator for the animal body.

2) Chemical Properties

1. Fats and oils undergo various types of reactions but the most important are:

i) Hydrolysis
ii) Hydrogenation

1) Hydrolysis of fats and oils:

Fats and oils are triglycerides. They are triesters. They are hydrolyzed by enzymes which act as catalysts. These enzymes are called lipases.

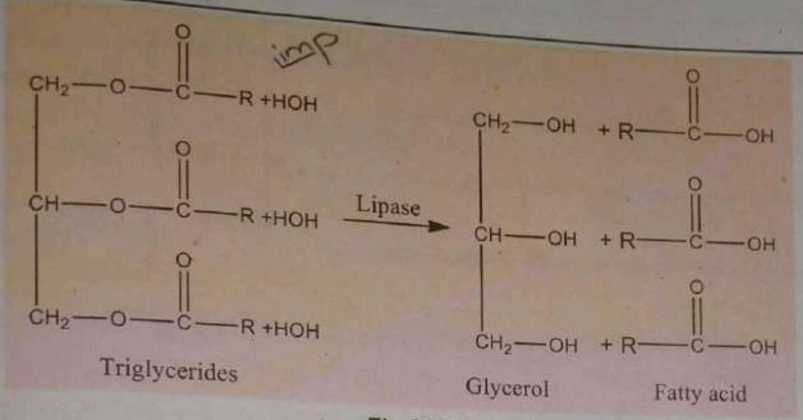


Fig 21.13

Actually this hydrolysis takes place in the digestive tract of human beings and animals. Fatty acids are produced in animal body which play an important role in the metabolic pathways.

2) Saponification: imp

Saponification is the hydrolysis of triglycerides (oils or fats) by alkalies. Glycerol is produced along with sodium or potassium salt of fatty acids. These Na and K salt are called soaps (salt of fatty acid).

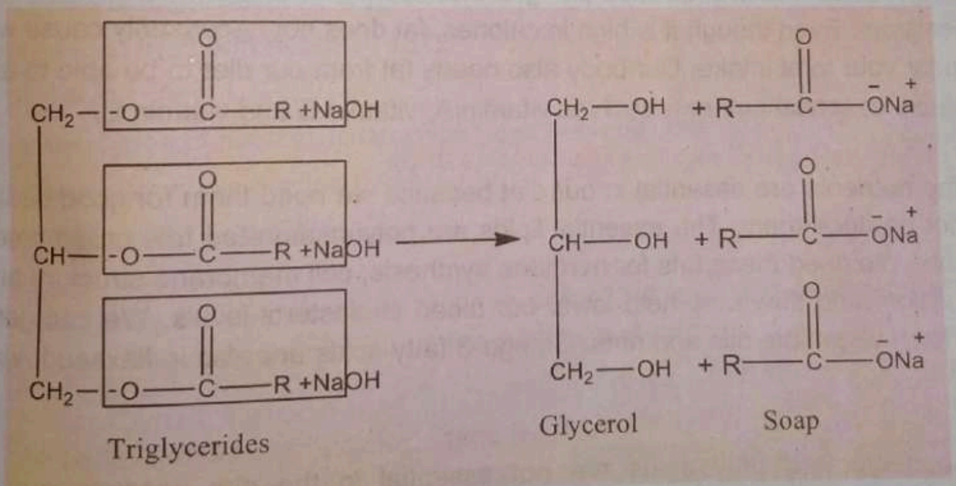


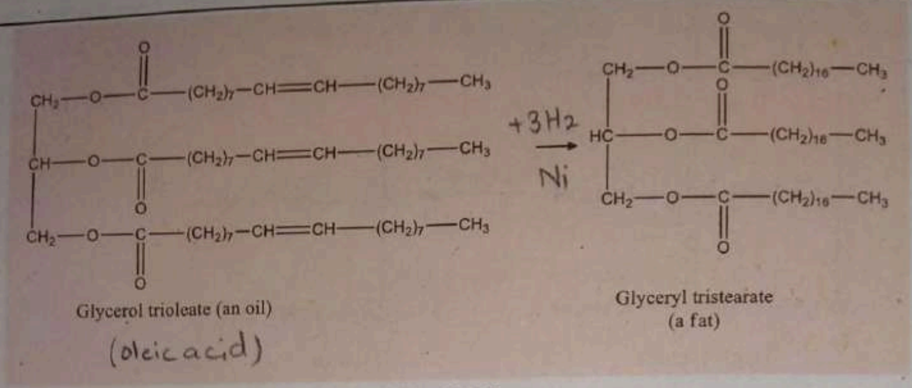
Fig 21.14

3) Hardening of Oils: imp

We know that unsaturated triglycerides are liquids at room temperature. They are called oils. They can be saturated by passing hydrogen in them in the presence of metal catalysts. The result is the conversion of liquid triglycerides into a semisolid triglyceride. In this way, liquid triglycerides are converted into a semisolid triglyceride.

This reaction is used commercially to harden the vegetable oil, for the production of vegetable ghee or margarine.

Hardened oils are also used extensively for making soaps and candles.



Glycerol trioleate (an oil)

(oleic acid)

Glyceryl tristearate
(a fat)

Fig 21.15

21.4.4. Nutritional and Biological Importance of Lipids

Lipids play three major biochemical roles:

1. As a storage form for metabolic energy (triglycerides).
2. As components of membranes.
3. As messengers (prostaglandins, steroid hormones).

A major role of lipids in nutrition is to provide energy, since unsaturated, saturated and trans fats all provide about 9 calories per gram compared to carbohydrates or protein with 4 calories per gram. Even though it is high in calories, fat does not necessarily cause weight gain if you monitor your total intake. Our body also needs fat from our diet to be able to absorb and use fat-soluble essential nutrients such as vitamin A, vitamin D and vitamin E.

* $CH_3-CH_2-CH=CH-CH_2-(CH_2)_6-\overset{O}{\overset{\|}{C}}-OH$

Essential Lipids.

Some nutrients are essential in our diet because we need them for good health but our body cannot produce them. The essential lipids are polyunsaturated fats called omega-6 and omega-3 fats. We need these fats for hormone synthesis, cell membrane structure and healthy brain and vision, and they may help lower our blood cholesterol levels. We can get omega-6 fatty acids from vegetable oils and nuts. Omega-3 fatty acids are also in flaxseed, walnuts and fatty fish.

Omega-3 in which double bond is present at C-3 from the tail end.

· Omega-6 in which double bond is present at c-6 from the tail end.

Non-Essential Lipids.

Monounsaturated fatty acids are not essential in the diet because our body can synthesize them, but they may help to reduce our risk for heart disease. They are in olive oil, peanuts and avocadoes. We do not need to get saturated fat, trans fat or cholesterol in our diet, and these lipids raise bad cholesterol levels in our blood. Saturated fat is in fatty meats and cheese, palm and coconut oil, and butter. Trans fat is in partially hydrogenated oils in processed and fried foods, while cholesterol is fatty animal foods.

> **DO YOU KNOW?**
> Our bodies make about 2 g of cholesterol per day, and that makes up about 85% of blood cholesterol, while only about 15% comes from dietary sources.

↓tail end :-

· $CH_3-(CH_2)_4-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH$

Some other functions are:

- tissues reconstruction;

- nervous system organization;
- increases and assures a normal function of the skin;
- antibodies formation;
- good function of endocrine glands(thyroid);
- water metabolism;

Quick Quiz

1. What are lipids? Shortly explain the only property that all the lipids have in common.
2. What are triglycerides? Draw its structure
3. Explain briefly the structure of lipids.

21.5. NUCLEIC ACIDS

Definition: The molecules that preserve hereditary information and that transcribe and translate that information in a way that allows the synthesis of all the varied enzymes of the cell are called the nucleic acid.

Discovery:

i. Nucleic acids were first of all demonstrated in the nuclei of puss cells in 1868 by Friedrik Miescher.

They were found in sperm heads in 1872.

Types of Nucleic Acids:

There are two types of nucleic acids which have been discovered:

1) Deoxyribonucleic acids (DNA)
2) Ribonucleic acid (RNA)

Nucleic acids and proteins:

In the human body the nucleic acids occur as part of the conjugated proteins which are called nucleoproteins. The nucleic acids direct the synthesis of proteins.

21.5.1 Structural Components of DNA and RNA

The basic structure of nucleic acids are determined by the biochemist P.A. Levene, who found that DNA contains three main components. 1) Five carbon sugars 2) Nitrogen containing bases 3) Phosphate (PO_4) groups.

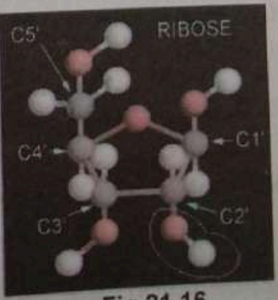


Fig 21.16

Fig 21.17

Levine concluded that DNA and RNA molecules are made of repeating units called nucleotides. In a nucleotide nitrogen base is attached to carbon number 1 of a pentose sugar and phosphate group is attached to carbon number 5 of the sugar. In addition a free hydroxyl (-OH) group is attached to the 3' carbon atom. The 5' phosphate and 3' hydroxyl groups allow DNA and RNA to form long chains of nucleotide because these two groups can react chemically with each other. The reaction between the phosphate group of one nucleotide and the hydroxyl group of another is a dehydration synthesis, eliminating a water molecule and forming a covalent bond that links the two groups. The linkage is called a phosphodiester bond because the phosphate group is now linked to the two sugars by means of a pair of ester (P-O-C) bonds. The two unit polymer resulting from this reaction still has a free 5' phosphate group at one end and a free 3' hydroxyl group at the other, so that it can link to other nucleotides. In this way, many thousands of nucleotides can join togather in long chains. Linear strands of DNA or RNA no matter how long, will almost always have a free 5' phosphate group at one end and a free 3' hydroxyl group at the other. It is analysed that the amount of adenine in DNA always equals the amount of thymine, and the amount of guanine always equals the amount of cytosine. It also implies that there is always equal proportion of purine (A+G) and pyrimidine (C+T). The X-ray diffraction pattern suggested that the RNA molecule had a shape of a helix with a diameter of 2 nm and a complete helical turn every 3.4 nm.

Fig 21.18
Pyrimidines

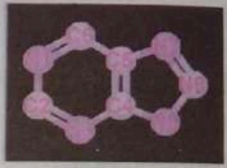


Fig 21.19
Purines

Q/

Imp

Protein Synthesis

transfer of genetic material from one generation to another

Difference between RNA and DNA:

1. RNA contains ribose sugar while DNA contains deoxyribose sugar.
2. Nitrogenous bases in DNA are cytosine, thymine, adenine and quinine while in RNA thymine is replaced by uracil.
3. DNA is double stranded while RNA is single stranded.

21.5.2 STORAGE OF GENETIC INFORMATION.

Genetic information is stored within the chemical structure of DNA. The main role of the DNA in the cell is the long term storage of genetic information. The genetic information is stored within the sequence of bases along the DNA chain. This information flows down from DNA into RNA, which is then converted into proteins.

DNA is a large molecule and therefore is a suitable molecule for storing genetic information. DNA is like a code with instructions that has the ability to not only store information but also replicate itself. The parts of DNA that carry this genetic information are called genes.

For storing genetic information, the base pairing is very important in a DNA molecule because each three base sequence gets transcribed into a 3 base codon on a mRNA molecule. This process is called transcription. This mRNA molecule leaves the nucleus of the cell and travels to a ribosome. The ribosome reads each codon and pairs it up with the anticodon of a specific tRNA molecule. Each specific tRNA molecule carries a specific amino acid to synthesize a protein. As the mRNA molecule is translated by the ribosome, a long chain of amino acids, arranged in a specific order is synthesized. This process is called translation. This chain of amino acids called a polypeptide will then be transported to Golgi Bodies where it is processed and will become part of a protein.

Functions of Nucleic Acid

(a) **Replication**: The genetic information for the cell is contained in the sequence of bases – Adenine, Thymine, Guanine and Cytosine in the DNA molecule when a cell divides – DNA molecule replicate in such a way that each daughter cell contains DNA identical to that of parent cell.

(b) **Protein Synthesis**: The genetic information coded in ENA in the form of specific base sequences must be produced in the form of synthesis of specific proteins. It is carried ou in two steps:

(i) Transcription and (ii) Translation

The **transcription** involves copying of DNA sequences into a complementary RNA molecule called messenger RNA (m-RNA).

During **translation** m-RNA directs protein synthesis in the cytoplasm of cell with the involvement of another type of RNA molecule called transfer RNA (t-RNA) and the ribo somal particles (i.e RNA protein complexes). Several enzymes coordinate with this complex process.

The DNA sequence that codes for a specific protein or a polypeptide is known as gene. Thus each protein in a cell has its corresponding gene. This relationship between the nucleotide triplets and the amino acids is known as genetic code.

Protein synthesis is fairly rapid. The $\propto$-chain of haemoglobin with 150 amino acids can be synthesized in just 2.5 minutes. Protein synthesis in micro-organisms is even faster – a complex protein molecule can be formed in just 10 seconds.

Quick Quiz

1. Write the names of structural components of DNA and RNA
2. Differentiate Transcription and Translation.
3. Which type of sugar is present in DNA?

21.6 MINERALS OF BIOLOGICAL SIGNIFICANCE

Minerals are the nutrients that exist in the body, and are as essential as our need for oxygen to sustain life. Minerals are also found in organic and inorganic combinations in food. In the body only 5% of the human body weight is mineral matter, vital to all mental & physical processes &

for total wellbeing. They are most important factors in maintaining all physiological processes, constituents of the teeth, bones, tissues, blood, muscle, and nerve cells.

Acting as catalysts for many biological reactions within the human body, they are necessary for transmission of messages through the nervous system, digestion, & metabolism or utilization of all nutrients in foods. Vitamins cannot be properly assimilated without the correct balance of minerals. For example; calcium is needed for vitamin "C" utilization, zinc for vitamin "A", magnesium for "B" complex vitamins, selenium for vitamin "E" absorption, etc.

The roles of major and minor minerals in human body are given in Table.

Important minerals in human diet and their roles		
Minerals	**Role in body**	
Major minerals		
Sodium	Fluid balance in the body Helps in absorption of other nutrients	Important for muscle contraction, nerve impulse transmission, heart function, and blood pressure
Potassium	Fluid balance in the body Acts as cofactor for enzymes	
Chloride	Fluid balance in the body Component of hydrochloric acid	
Calcium	Development and maintenance of bones and teeth and Blood clotting	
Magnesium & Phosphorus	Development and maintenance of bones and teeth	
Trace Minerals		
Iron	Oxygen transport and storage	Act as enzyme cofactors Support immune function
Zinc	Aids insulin action Helps in growth and reproduction	
Copper	Acts as enzyme cofactor	
Chromium	Helps in insulin action	
Fluoride (Shine)	Stabilizes bone mineral and hardens tooth enamel	
Iodine	Essential for normal thyroid function	

Out of all above mentioned mineral only Calcium, phosphorus, Iron and Zinc are included in our syllabus.

21.6.1 Sources of Important Minerals

Here is a list of good food sources for a number of important minerals that are an essential part of good nutrition.

Calcium

Calcium is important to bone growth and formation, blood clotting, nerve and muscle functioning.

a) Sources: We get calcium from milk, cheese, egg yolk, beans, nuts, cabbage etc.

b) Deficiency: A deficiency may result in arm and leg muscles spasms, softening of bones, back and leg cramps, brittle bones, rickets, poor growth, osteoporosis, tooth decay and mental depression.

Iron

Iron is an essential mineral. Its major function is to combine with protein and copper in making hemoglobin, the component of the blood that carries oxygen from the lungs to the tissues throughout the body.

a) Sources: We get Iron from red meat, egg yolk, whole wheat, fish, spinach and mustard etc.

b) Deficiency: A deficiency may result in weakness, fatigue, paleness of the skin, constipation and anemia.

Phosphorus

Phosphorus is after calcium the second most abundant mineral in the body. It is a principal mineral of bones and teeth. Phosphorus is involved in most metabolic actions in the body, including kidney functioning, cell growth and the contraction of the heart muscle.

a) Sources: We get phosphorus from egg yolk, cheese, milk, cabbage etc.

b) Deficiency: A deficiency is unusual, but may have symptoms varying from painful bones, irregular breathing, fatigue, anxiety, numbness, skin sensitivity and changes in body weight.

Zinc

Zinc is vital to immune resistance, wound healing, digestion, reproduction, physical growth, diabetes control, taste and smell and maintaining normal Vitamin A levels and usage. Zinc can be found in almost every cell of the body and serves as part of more than 70 enzymes that control body processes.

a) Sources: We get zinc from Oyster, red meat, chicken, beans, nuts, dairy products and some sea foods.

b) Deficiency: A deficiency may result in poor growth, acne-like rash, hair loss, diarrhea, delayed sexual maturation, impotence, sterility, eye lesions, loss of appetite, reduced sense of taste and smell, skin lesions and inflammation, poor wound healing, reduced resistance to infections, mental confusion, poor learning ability, changes in hair and nails and anemia.

21.6.2. Biological Significance of Minerals

a) Importance / Significance of Iron:

The primary role of iron relates to the ability of red blood cells to adequately carry oxygen for use throughout the entire body. Some functions of iron are mentioned below.

Fatigue

To prevent fatigue, iron is needed by the body to make hemoglobin rich blood, which transports oxygen to the cells. It is also needed for adenosine triphosphate production (ATP), which is essential for cellular energy and proper cell function.

Exercise

Iron is lost through sweat and through bleeding of the digestive tract from the harsh motion of exercise. Studies indicate that 34% of female runners and 8% male runners are iron deficient.

Pregnancy

Iron is needed for proper placenta development and also for the prevention of pre-term and low birth weight babies. Studies estimate that up to 58% of pregnant women are iron deficient.

Pediatric

Iron is essential during the first eight months for brain growth and the effects of anemia may be associated with developmental delays in both motor and cognitive abilities.

Treatment Duration

Up to six months to restore low iron stores, its sufficient quantity must be used. When iron deficiency is left untreated, it can lead to conditions that are more serious.

Metabolic Processes

Iron plays an important part in the metabolic processes of the animals. The function of iron in the body is limited almost exclusively to the oxygen transport in the blood, through hemoglobin. It is present in some enzymes that catalyze reactions of cellular oxidation. In human body, the richest organs in iron are liver and spleen. In smaller amount, it is also present in bones, medulla, kidneys and intestines.

b) Importance / Significance of Calcium:

Calcium is the most common mineral in the human body, where it is present in almost the same relative abundance as in the earth's crust. There are six stable isotopes of calcium: calcium40 is the most common (97 %), and calcium46 the least abundant (0.003 %).

- The integrity of the system depends critically on vitamin D status; if there is a deficiency of vitamin D, the loss of its calcaemic action leads to a decrease in the ionised calcium and secondary hyperparathyroidism and hypophosphataemia. This is why experimental vitamin D deficiency results in rickets and osteomalacia whereas calcium deficiency gives rise to osteoporosis.
- Approximately 99% of total body calcium is in the skeleton and teeth and 1% in blood and soft tissues. Calcium has four major biological functions:
  a. Structural as stores in the skeleton
  b. Electrophysiological - carries charge during an action potential across membranes
  c. Intracellular regulator, and
  d. As a cofactor for extracellular enzymes and regulatory proteins.

c) Importance / Significance of Phosphorus

Phosphorus is present in plants and animals. There is over 1 lb (454 grams) of phosphorus in the human body. It is a component of adenosine triphosphate (ATP), a fundamental energy source in living things. It is found in complex organic compounds in the blood, muscles, and nerves, and in calcium phosphate, the principal material in bones and teeth. Phosphorus compounds are essential in the diet. Organic phosphates, ferric phosphate, and tricalcium phosphate are added to foods. Dicalcium phosphate is added to animal feeds.

1. The main function of phosphorus is in the formation of bones and teeth.
2. It plays an important role in the body's utilization of carbohydrates and fats and in the synthesis of protein for the growth, maintenance, and repair of cells and tissues.
3. It is also crucial for the production of ATP, a molecule the body uses to store energy.
4. Phosphorus works with the B vitamins.
5. It also assists in the contraction of muscles, in the functioning of kidneys,
6. In maintaining the regularity of the heartbeat, and
7. In nerve conduction.

d) Importance / Significance of Zinc

Zinc is the most important of all trace elements involved in human metabolism. More than a hundred specific enzymes require zinc for their catalytic function. If zinc is removed from the catalytic site, Activity is lost; replacement of zinc restores activity. Studies in individuals with acrodermatitis enteropathica, a genetic disorder with zinc malabsorption resulting in severe deficiency, have provided much insight into the functional outcomes of zinc deficiency. These include impairments of dermal, gastrointestinal, neurologic and immunologic systems.

Loss of zinc through gastrointestinal tract accounts for approximately half of all zinc eliminated from the body. Considerable amount of zinc is secreted through the biliary and intestinal secretions, but most of it is reabsorbed and this process is an important point of regulation of zinc balance. Other routes of zinc excretion include the urine and surface losses (desquamated skin, hair, sweat).

Quick Quiz

1. What is biological significance of mineral?
2. Define mineral. Give its percentage present in human body.
3. Minerals of which metals are required for assimilation of vitamins B, C and E?
4. What problems are caused by deficiency of calcium and Phosphorus?
5. Give importance of zinc mineral.
6. Give significance of (i) Keratin (ii) Myosin and fibrin Fibrous protein.
7. How much intake of manganese should be per day?
8. How hibernating animals obtain energy during hibernation?
9. Give few macro and micro minerals.
10. How much sodium and potassium should be taken per day?
11. What is insulin?

Society, Technology and Science

Glycogen – A store house

Glycogen is reserved food material that is stored in muscles and liver in animals and human. When body requires energy due to lack of glucose, the glycogen reconverted into glucose and provide energy to the body in the form of ATP.

Hibernating Animals and Reserve Food

Large amount of fat is stored in the body of some animals that hibernate during winter. In winter the metabolic activities slow down. They use this fat as reserved food material that produce ATP during oxidation.

Complex carbohydrates which Lubricate the Elbow and Knee:

Glucosamine, glucosaminoglycons or proteoglycan are the complex carbohydrates which provide lubrication to elbow and knee.

Glucosamine ($C_6H_{13}NO_5$) is an amino sugar. It is produced naturally in the body and plays a key role in building cartilage and lubricating joints. It is found in the fluid that is around joints. It is a prominent procurer for glycosaminoglycans and for glyeosaylated proteins and lipids.

Gluasamine has been shown to help keep our joints resilient and healthy by lubricationg and resting the connective tissue. It is a naturally occurring nutrient and is a glutamine derivative that retains an amine group and a sugar molecule (glucose).

Over time, every day wear and tear, less than perfect nutrition, injuries and aging can result in dry, brittle cartilage which is vulnerable to damage and stiffening. Research has shown that glucosamine may repair damaged or strained connective tissue.

Our joints are made up of two third of water yet are into able to attract and retain it. Glucosamine has shown to help keep cartilage resilient and healthy by attracting and holding water and nutrients within this matrix. Studies have even shown glucosamine may even help to regenerate new cartilage once it becomes damaged, thereby restoring joint function and mobility. Because of its ability to help to lubricate and restore elbow and knee joints, it is quite popular with weight trainers, sports enthusiasts etc.

Glucosaminoglycans (CAGs) are the most abundant hetropolysaccharides in the body. They are long unbranched molecules containing a repeating disaccharide unit. Usually one sugar is uronic acid and the other is either GlcNAc or CalNAc. GAGs have negative charge on them. GAGs are a major component of joint cartilage.

Chondroitin sulphate (D. glucuronate + CalNSc sulphate) is the most abundant GAG found in cartilage. Keratan sulphate (Gal + GlcNAc sulphate) is often aggregated with chondroitin sulphate.

GAGs have unique properties i.e. the ability to fill space, bind and retain water and repel negatively charged molecules. Because of high viscosity and low compressibility, they are ideal for a lubricating fluid in the joints especially in knee and elbow. On the other hand, their rigidity provides structural integrity to the cells.

Proteoglycans (mucoportiens) are formed of glycosamineglycaosn (GAGs) and core proteins, covalently bonded to each other. These are found in all connective tissues.

Proteoglycans can also be called joint grease. Proteoglycan appears to be a mecessary compound in synovial fluid for normal joint lubrication and function. (Synovial fluid is a clear pale yellow fluid, the main function of which is to serve as a lubricant in joints or tendon sheath.)

Aggrecan is one of the most important extra cellular proteoglycan. To each aggrecaon core protein, multiple chains of chondroitin sulphate and keratin sulphate are covalently attached through the trisaccharade linker. They play an important role in hydration of cartilage of joints. They give cartilage its gel like properties i.e. lubricate it and provide resistance to deformation.

Fibrous Proteins from hair and Silk:

Fibrous proteins consist of elongated molecules having one or more polypeptide chains he form of fibrils. They are insoluble in aqueous media, a property conferred by a high concentration of hydrophobic amino acid residues both in interior of the proteins and or its surface. They play structural or supporting role in the body. Examples are silk fiber, keratin (of nails, and hair), myosin (in muscle cells), fibrin of blood clot.

Insulin – A protein hormone whose deficiency leads to diabetes mellitus.

Insulin is a 51 amino acid peptide hormone that is produced exclusively by pancreatic beta cells. F. Sanger was the first scientist who determined the sequence of amino acids in insulin. After 10 years of careful work, he concluded that insulin is composed up of 51 amino acids in two chains, one alpha chain and one beta chain. The alpha chain contains 21 amino acids and the beta chain contains 30 amino acids. Both chains are held together by disulphide bridges. The molecule weight of insulin is 5808.

Insulin hormone is central in regulating carbohydrate and fat metabolism in the body. It causes the cells in liver, muscles and fat tissue to take up glucose from the blood. In the liver and skeletal muscles, glucose is stored as glycogen, while in adepocytes, it is stored as triglycerides.

Insulin stops the use of fat as energy source. When blood glucose level falls below a certain limit, the body begins to use stored sugar as an energy source through glycogenolysis. As a central metabolic control mechanism its status is also used as a control signal to other body systems (such as amino acids uptake by body cells.). in addition, it has several other anabolic effects throughout the body. Insulin is used meidically to treat some forms of diabebas patients.

Role of Minerals in the Body

- Minerals act as cofactors for the enzyme reactions. Enzymes don't work without minerals. All cells require enzymes to work and function. They give us our vitality.
- They maintain the pH balance with in the body.
- Minerals actually facilitate the transfer of nutrients across cell membranes.
- They maintain proper nerve conduction.
- Mineral help to contract and relax muscles.
- They help to regulate our bodies' tissue growth.
- Minerals provide structural support for the body.

These are two categories of mineral essential with in body, macro-minerals and micro-minerals. There is no one mineral deficiency; they all must be maintained in balance within body.

Macro-minerals

- Calcium
- Chloride
- Phosphorous
- Sodium
- Potassium
- Sulfur
- Magnesium

Micro-minerals (or Trace Minerals)

- Iron
- Boron
- Chromium
- Iodine
- Manganese
- Molybdenum
- Selenium
- Silicon
- Copper
- Cobalt
- Rubidium
- Germanium
- Lithium
- Zinc
- Vanadium

Structure and Function of Minerals

The term mineral is applied to chemical elements present in the ash of calcined tissue. Dietary minerals Amy are present in inorganic salts, or as part of carbon containing organic compounds. For example, magnesium is present in chlorophyll, the pigment that makes plants green. Six minerals are required by people in gram amount: sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), Phosphorous (P), and chlorine (Cl). Daily requirements range from 0.3 to 2.0 grams per day. Nine trace mineral are required by people in minute amounts: chromium (Cr), copper (Cu), iodine (I), iron (Fe), fluorine (F), manganese (Mn), molybdenum (Mo), selenium (Se), and zinc (Zn). There are additional requirements for cobalt (Co) but these are generally expressed in terms of the cobalt containing vitamin B12. All trace minerals are toxic at high levels.

Fluorine

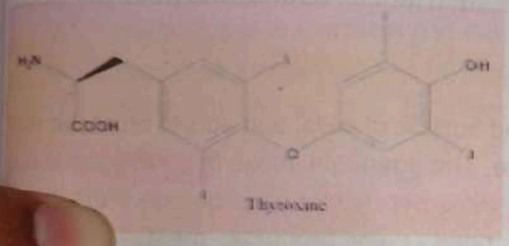


Fig 21.19

Most of the body's fluorine (F) is contained in bones and teeth. The main source of fluoride is drinking water. Fluorine hardens tooth enamel and effectively prevents dental caries. Excessive fluorine in drinking water can accumulate in teeth and bones, causing fluorosis. Permanent teeth that develop during high fluorine intake have irregularly distributed chalky patches on the surface of the enamel which become stained yellow or brown, producing a characteristics mottled appearance.

Iodine

Iodine (I) is primarily involved in the synthesis of two thyroid hormones, thyroxine and triiodothyronine. In adults about 80% of the iodide absorbed is trapped by the thyroid gland.

Most environmental iodine occurs in seawater. People living far from the sea are at particular risk of deficiency. Salt fortified with iodide (typically 70ug/g) helps ensure adequate intake (100ug/day). Deficiency is rare in areas where iodized salt is used but common world wide. Iodine deficiency develops when iodide intake is less than 20ug/day. In mild or moderate deficiency the thyroid gland hypertrophies to concentrate iodine in itself, resulting goiter which is an enlargement of the thyroid gland visible as a swelling of front the of neck. Excessive iodine consumption can lead to thyrotoxicosis, a condition resulting from high concentrations of thyroid hormones in the body which can result from eating foods that have high amounts of iodine, such as kombu-type kelp or seaweed.

Magnesium

Magnesium (Mg) has several important metabolic functions in the production and transport of energy. It is also important for the contraction and relaxation of muscles. Magnesium is involved in the synthesis of protein, and it assists in the functioning of some enzymes. Most dietary magnesium comes from nuts, cereals, and dark green, leafy vegetable which are rich in chlorophyll.

Manganese

Manganese (Mn) is necessary for healthy bone structure and is a component of several enzyme systems including manganese-specific glycosyltransferases and phosphoenolpyruvate carboxykinase. Manganese is found in cereal and nuts. The adequate intake of manganese is 2 to 5 mg / day.

Molybdenum

Molybdenum (Mo) is a component of coenzymes necessary for the activity of xanthine oxidase, sulfite oxidase, and aldehyde oxidase. Sulfite oxidase catalyses the transformation of sulfite to sulfate which is necessary for the metabolism of sulfur containing amino acids, such as cysteine. Legumes such lentils, beans, and peas are good sources of molybdenum.

Potassium

Potassium (K) maintains fluid volume inside and outside of cells, and acts to blunt the rise of blood pressure in response to excess sodium intake. The adequate intake of potassium is 4.5 grams per day for children 9 to 13 years old and 4.7 grams per day for older person. Potassium is generally found in fruits and vegetables, dried peas, dairy products, meats and nuts. Potassium from supplements or slat subtitles can result in hyperkalemia and possibly sudden death if excess is consumed by individuals with chromic renal insufficiency (kidney disease) or diabetes.

Selenium

Selenium (Se) is a part of the enzyme glutathione peroxides, which metabolizes hydroperoxides formed from polyunsaturated fatty acids. Selenium is also a part of the enzyme that deiodinate thyroid hormones. Generally, selenium acts as an antioxidant that works with vitamin E. deficiency of selenium causes Keshan disease which is a form of congestive chardiomyopathy. The RDA for selenium is 70 micrograms (mcg). The tolerable upper level of selenium is 400 mcg/day for adults based on the prevention of hair and nail brittleness and early signs of chronic selenium toxicity.

Sodium

Sodium (Na) is usually consumed as table salt (Sodium Chloride, NaCl). The adequate intake of 1.5 grams per day with an upper limit of 2.3 grams per day is calculated to meet the needs for sweet losses for individuals 8 years or older engaged in recommended levels of physical activity. Active people in humid climates who sweat excessively may need more than the adequate intake.

Key Points

- Carbohydrates are the most abundant macromolecule on earth. They are of three types i.e. Monosaccharides, disaccharides and polysaccharides.
- People eating a diet high in carbohydrates are less likely to accumulate body fat compared with those who follow a low carbohydrate /high-fat diet.
- Proteins are the most important class of bimolecules. They are major structural components of animals and human tissues. They are classified as a simple ά protein, conjugated proteins and derived proteins. They are actually the polymers of Amino acids.
- Nucleoproteins act as the carrier of heredity from one generation to the other.
- Hemoglobin is a protein and carrier of oxygen. Some of the proteins act as hormones.
- Enzymes are biocatalyst and catalyze chemical reactions in living organisms. They are quite specific in their function. Their Activity depends upon temperature, substrate concentration and pH. They are protein in nature and are used extensively in food, brewing, paper industries.
- All lipids are hydrophobic. Fats are solid while oils are liquid at room temperature. They are insoluble in water while soluble in organic solvents such as diethyl ether, acetone, benzene etc.
- Some lipids are essential for our diet and some are non-essential.
- Nucleic acids are present in every living cell as well as in viruses. They have ability to reproduce, store and transmit genetic information. They are of two types DNA and RNA. Nucleotide is the structural unit of DNA and consists of one sugar, one nitrogenous base and at least one phosphate.
- Minerals are the nutrients and are as necessary as oxygen for life. They are constituents of teeth, bones, tissues, blood, muscles and nerve tissues.
- Minerals are classified as major and trace minerals i.e. those required in appreciable quantity are major and those required in low quantity are trace.

Exercise

Q 1: Select the right answer from the choices given with each question.

i. Biochemistry covers the practical applications of:

a. Medicine b. Agriculture c. Nutrition [✓ d. All of these]

ii. Macromolecules are of how many types?

a. Three [✓ b. Four] c. Five d. Six

iii. The general formula for Carbohydrates is:

a. $N_n(H_2O)_n$ b. $P_n(H_2O)_n$ [✓ c. $C_n(H_2O)_n$] d. $H_n(CO_2)_n$

iv. Most organic matter on earth is made up of:

[✓ a. Carbohydrates] b. Lipids c. Olive Oils d. Proteins

v. The no. of Carbon atoms in Hexose is:

a. One b. Four [✓ c. Six] d. Ten

vi. The long chains of Amino Acids are called:

a. Oils [✓ b. Polypeptides] c. Proteins d. Monopeptides

vii. Proteins are used in both forms of:

a. Catabolism b. Anabolism c. Enzymes [✓ d. Metabolism]

viii. What is TRUE about enzymes?

a. They make biochemical reaction to proceed spontaneously

[✓ b. They lower the activation energy of a reaction]

c. They are not very specific in their choice of substrates

d. They are needed in large quantities

ix. To what category of molecules do enzymes belong?

a. Carbohadrates b. Lipids c. Nucleic acids [✓ d. Proteins]

x. What is TRUE about cofactors?

a. Break hydrogen bonds in proteins [✓ b. Help facilitate enzyme Activity]

c. Increase activation energy d. Are composed of proteins

xi. Prosthetic groups are:

a. Required by all enzyme b. Loosely attached with enzymes

c. Proteinsous nature [✓ d. Tightly bound to enzyme]

xii. Lipids are generally defined in terms of:

[✓ a. Solubility] b.Structure c. Molarity d.All of these

xiii. DNA and RNA are made up of:

a. Peptides [✓ b.Nucleotides] c. Neurons d.None of these

xiv. _____ of the human body weight is mineral matter?

[✓ a. 5 %] b.10 % c. 50 % d.100 %

xv. ___________ is needed for Vitamin C utilization.

a. Acid b. Iron c. Phosphorus [✓ d. Calcium]

xvi. The component of blood that carries oxygen in the body is:

a. Fats b. Myoglobin [✓ c. Hemoglobin] d. Amino Acids

xvii. Most RNA molecules are:

a. Independent b. Double Stranded [✓ c. Single Stranded] d. Multiple Stranded

xviii. ___________ are the major component of soap.

[✓ a. Fatty Acids] b. Palm Oils c. Proteins d. Saccharides

xix. The mineral, related with the formation of bones and teeth, is:

a. RNA [✓ b. Phosphorus] c. Iron d. Sulphur

Q 2: Give brief answers for the following questions.

i. What do you understand by the word 'Biochemistry'?
ii. Briefly state the functions of Carbohydrates.
iii. Name the classes and sub-classes of Proteins.
iv. In a range of 0-35^{0}C, the rate of reaction of an enzyme is proportional to temperature. Justify it.
v. How does pH affect enzyme Activity?
vi. Describe lock and key mechanism of enzyme action.
vii. What is the main use of enzymes in paper industry?
viii. Define cofactor and co-enzymes. ☆
ix. Shortly explain the only property that all the Lipids have in common.
x. Explain the structural components of DNA and RNA.
xi. Define Lipids and state the difference between fat and oil. ☆
xii. Briefly state how Vitamin D is formed in human body? ☆
xiii. State the differences between the chemical structures of DNA and RNA.
xiv. Briefly state why minerals are important for human life.
xv. Name different routes for the loss of Zinc from human body. ☆

3: Give detailed answers for the following questions.

i. Describe different classes of Carbohydrates.
ii. Explain the structure of Proteins.
iii. Briefly describe the factors that affect the Activity of enzymes.
iv. What is the nutritional importance of Lipids?
v. Explain the structures of Nucleic acids.
vi. Describe four important minerals and their sources.

Skilled Activities

1. Take beads and ribbon of different color and make different structures of protein. (Model)
2. Take / cut cards of different colors and try to construct / develop a model about "Enzyme Action".
3. Take a thermopore sheet and cut into pieces / small blocks of required size. Also use straw and construct / develop a models for "DNA, Purines and Pyrimidines".

22

INDUSTRIAL CHEMISTRY

After completing this lesson, you will be able to:

This is 10 days lesson (period including homework)

- Discuss the importance of the chemical industries in the economy of Pakistan.
- Describe the raw materials available in Pakistan for various chemical industries.
- Describe the chemical processes of addition and condensation polymerization.
- Interpret difference between petrochemical and chemical derived from them.
- Describe the fractional distillation and refining of petroleum.
- List the various raw materials for petrochemical industry.
- Identify the important fractions.
- Describe the basic building block processes in petrochemical technology.
- Describe the petrochemical process technology.
- List some major petrochemicals.
- Describe the formation and use of PVC and Nylon.
- Describe preparation and application of various cosmetics like nail varnish nail polish remover and lipsticks.
- Describe types and application of synthetic adhesives

Reading

Before we define industrial chemistry, it may be helpful to know that the development of industrial chemistry started when a need to know how various chemicals are produced in much more than the laboratory scale, arose. Chemistry knowledge was applied to furnish the rapidly expanding chemical industries with "recipes" which we now call chemical processes. Industrial chemistry keeps up with the progress in science and technology. It incorporates other emerging disciplines such as biotechnology, microelectronics, pharmacology and material science. The discipline is also concerned with economics and the need to protect the environment.

We define industrial chemistry ***as the branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity.***

Classical chemistry (organic, inorganic and physical chemistry) is very essential for advancing the science of chemistry by discovering and reporting new products, routes and techniques. On the other hand industrial chemistry helps us to close the gap between classical chemistry as it is taught in colleges and universities, and chemistry as it is practiced commercially. The scope of industrial chemistry therefore includes:

- The exploitation of materials and energy in appropriate scale
- Application of science and technology to enable humanity experiences the benefits of chemistry in areas such as **food production, health and hygiene, shelter, protection, decoration, recreation and entertainment.**

22.1(A) INTRODUCTION TO THE CHEMICAL INDUSTRY

The chemical industry can also be classified according to the type of main raw materials used and/or type of principal products made. We therefore have **industrial inorganic chemical industries** and **industrial organic chemical industries.** Industrial inorganic chemical Industries extract inorganic chemical substances, make composites of the same and also synthesize inorganic chemicals.

Heavy industrial organic chemical industries produce petroleum fuels, polymers, petrochemicals and other synthetic materials, mostly from petroleum.

Light organic industries produce specialty chemicals which include pharmaceuticals, dyes, pigments and paints, pesticides, soaps and detergents, cosmetic products and miscellaneous products.

The Structure of the Global Chemical Industry

We normally put a value to something according to how much it has cost us. Some things are of high value while others are of low value. For low valued products, you need to produce them in large volumes to make significant profit. This means that the raw materials are cheap and easily accessible. There is also an existing, relatively simple, and easily accessible processing technology. To sell a large volume of product, there must be a large market. This brings stiff competition which also makes the price to remain low.

We are now ready to describe the structure of the global chemical industry

Commodity Chemicals:

The global chemical industry is founded on basic inorganic chemicals (BIC) and basic organic chemicals (BOC) and their intermediates. Because they are produced directly from natural resources or immediate derivatives of natural resources, they are produced in large quantities.

In the top ten BIC, almost all the time, sulphuric acid, nitrogen, oxygen, ammonia, lime, sodium hydroxide, phosphoric acid and chlorine dominate. The reason sulphuric acid is always number one is because it is used in the manufacture of fertilizers, polymers, drugs, paints, detergents and paper. It is also used in petroleum refining, metallurgy and in many other processes. The top ranking of oxygen is to do with its use in the steel industry.

Ethylene and propylene are usually among the top ten BOC. They are used in the production of many organic chemicals including polymers.

BIC and BOC are referred to as commodity or industrial chemicals.

Commodity chemicals are therefore **defined** as low-valued products produced in large quantities mostly in continuous processes. They are of technical or general purpose grade.

Specialty Chemicals:

High-value adding involves the production of small quantities of chemical products for specific end uses. Such products are called specialty chemicals.

These are high value-added products produced in low volumes and sold on the basis of a specific function. They are judged by performance and efficiency. Enzymes and dyes are performance chemicals. Other examples of specialty chemicals include medicinal chemicals, agrochemicals, pigments, flavour and fragrances, personal care products, surfactants and adhesives.

Fine Chemicals:

The purified or refined chemicals are called fine chemicals. By **definition** they are high value-added pure organic chemical substances produced in relatively low volumes and sold on the basis of exact specifications of purity rather than functional characteristics.

The global market share for each type is roughly as follows:

Commodities	**80%**
Specialties	**18%**
Fine	**2%**

22.1. (B) RAW MATERIAL FOR THE CHEMICAL INDUSTRY

All chemicals are derived from raw materials available in nature. The price of chemicals depends on the availability of their raw materials. Major chemical industries have therefore developed around the most plentiful raw materials

The natural environment is the source of raw materials for the chemical industry.

Raw materials from the atmosphere

The atmosphere is the field above ground level. It is the source of air from which six industrial gases namely N_2, O_2, Ne, Ar, Kr and Xe are manufactured. The mass of the earth's atmosphere is approximately 5x 10^{15} tons and therefore the supply of the gases is virtually unlimited.

Raw materials from the hydrosphere

Ocean water which amounts to about 1.5x 10^{21} litres contains about 3.5 percent by mass dissolved material. Seawater is a good source of sodium chloride, magnesium and bromine.

Raw materials from the lithosphere

The vast majority of elements are obtained from the earth's crust in the form of mineral ores, carbon and hydrocarbons. Coal, natural gas and crude petroleum besides being energy sources are also converted to thousands of chemicals.

Raw materials from the biosphere

Vegetation and animals contribute raw materials to the so-called agro-based industries. Oils, fats, waxes, resins, sugar, natural fibres and leather are examples of thousands of natural products.

Quick Quiz

1. Name those disciplines which play important role in industrial chemistry.
2. Define industrial chemistry.
3. What is difference between organic and inorganic chemical industries?
4. What type of products obtain from heavy and light organic industries?
5. What raw material are obtained from atmosphere?
6. In which ratio dissolved materials are present?
7. Give few natural products.
8. Give examples of Basic organic chemicals. Ethylene
9. What do you mean by commodity chemicals?
10. What is meant by performance chemicals?
11. Give share of different types of chemicals in global market.

22.2. SAFETY CONSIDERATIONS IN PROCESS INDUSTRIES

Introduction

Process safety technology has played an important role in the chemical processing industries so that handling flammable and combustible liquids and gases could proceed without undesirable consequences. During the 1980s, the oil and gas industries, for example, recognized that process safety technology alone, without process safety management, would not prevent catastrophic incidents. With this in mind, a number of industry associations, such as, in the United States, the Centre for Chemical Process Safety (CCPS), the American Petroleum Institute (API) and the Chemical Manufacturers' Association (CMA), initiated programmes to develop and provide process safety management guidelines for use by their members.

Process Safety Management Requirements

Process safety management is an integral part of the overall chemical processing facility safety programme. An effective process safety management programme requires the leadership, support and involvement of top management, facility management, supervisors, employees, contractors and contractor employees.

Elements of the Process Safety Management Programme

There are a number of basic requirements which should be included in every chemical process safety management programme:

1) Process safety information

Process safety information is used by the process industry to define critical processes, materials and equipment. Process safety information includes all available written information concerning process technology, process equipment, raw materials and products and chemical hazards before conducting a process hazard analysis. Other critical process safety information is documentation relating to capital project reviews and design basis criteria.

2) Employee involvement

Process safety management programmes should include employee participation in the development and conduct of process safety analyses and other elements of the programme. Access to process safety information, incident investigation reports and process hazard analyses is usually provided to all employees and contractor employees working in the area. Most industrialized nations require that workers be systematically instructed in the identification, nature and safe-handling of all chemicals to which they may be exposed.

3) Process hazard analysis

After the process safety information is compiled, a thorough and systematic multi-disciplinary process hazard analysis, appropriate to the complexity of the process, is conducted in order to identify, evaluate and control the hazards of the process. Persons performing the process hazard analysis should be knowledgeable and experienced in relevant chemistry, engineering and process operations. Each analysis team normally includes at least one person who is thoroughly familiar with the process being analysed and one person who is competent in the hazard analysis methodology being used.

4) Management of change

Chemical process facilities should develop and implement programmes which provide for the revision of process safety information, procedures and practices as changes occur. Such programmes include a system of management authorization and written documentation for changes to materials, chemicals, technology, equipment, procedures, personnel and facilities that affect each process.

5) Operating procedures

Chemical processing facilities must develop and provide operating instructions and detailed procedures to workers. Operating instructions should be regularly reviewed for completeness and accuracy (and updated or amended as changes occur) and cover the process unit's operating limits.

6) Safe work practices

Chemical process facilities should implement hot-work and safe work permit and work order programmes to control work conducted in or near process areas. Supervisors, employees and contractor personnel must be familiar with the requirements of the various permit programmes, including permit issuance and expiration and appropriate safety, materials handling and fire protection and prevention measures.

7) Employee information and training

Chemical process facilities should use formal process safety training programmes to train and educate incumbent, reassigned and new supervisors and workers. The training provided for chemical process operating and maintenance supervisors and workers should be comprehensive.

Quick Quiz

1. What are requirement of process safety management?
2. How employees should be involved in safety management programme?
3. What is analysis team?
4. What is role of management of change in process industries?

22.3. DYES

imp

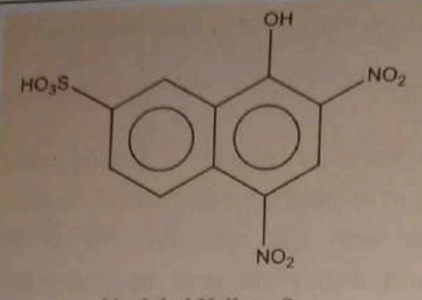
A dye is a coloured compound, normally used in solution, which is capable of being fixed to a fabric. The dye must be 'fast' or chemically stable so that the color will not wash with soap and water, or fade on exposure to sunlight (ultraviolet light).

A dye owes its color to the presence of a chromophore and its fixing property to the acidic or basic auxochromic groups such as OH, SO_3H, NH_2, NR_2, etc. The polarauxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure.

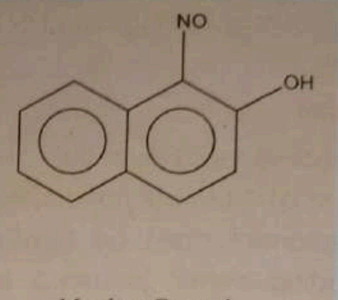
Classification of Dyes by structure

Dyes may be classified according to the type of chromophores present in their structures. This method of classification includes the following main types:

1) Nitro and Nitroso Dyes: The NO_2 and NO groups are chrmophores in this class of dyes. Examples are,



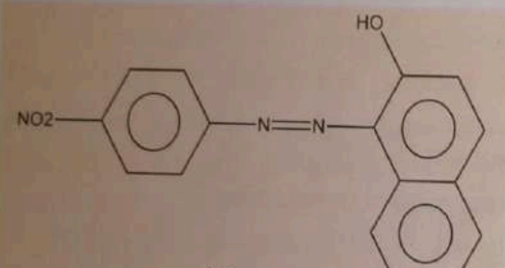
Naphthol Yellow S



Mordant Green 4

2) Azo Dyes: The azo dyes contain one or more azo groups, -N=N- as the primary chromophore. The common auxochromes are NH_2, NR_2, OH, SO_3H, etc.

Azo dyes form the largest and most important group of synthetic group of synthetic dyes. They are highly colored and can be prepared by diazotising an aromatic amine and subsequent in both the diazonium salt and the coupling compound series azo dyes can be produced with almost any color. Examples are,



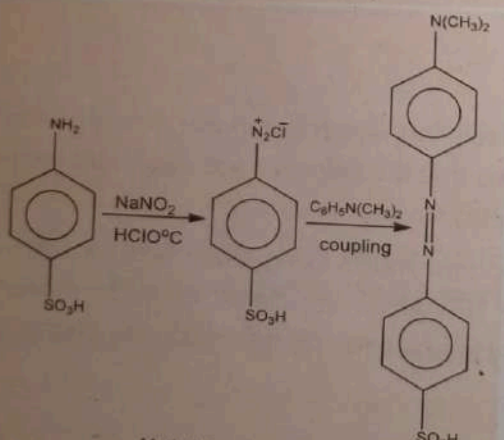
Azo

(a) Para Red

It was the first azo dye to be prepared. Para red is obtained by the reaction of diazotized p-nitroaniline with β–naphthol on fabric itself.

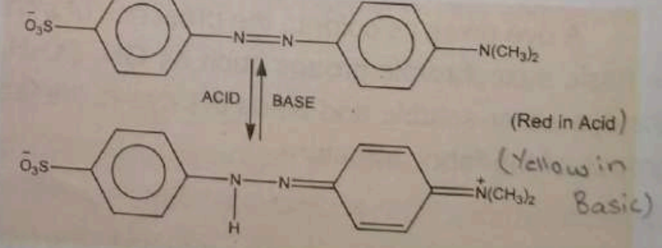
(b) Methyl Orange:

Methyl orange is obtained from sulphanilic acid by the following steps:



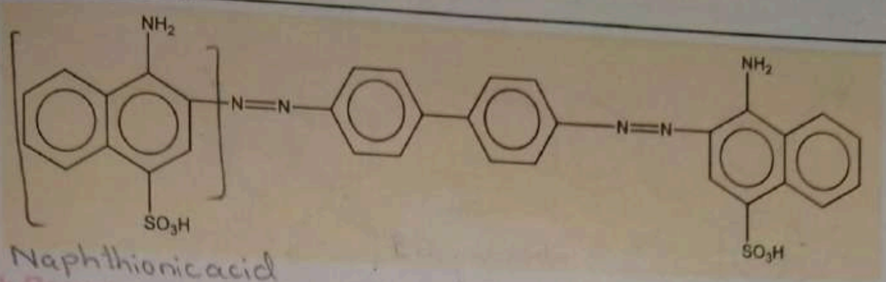
Methyl Orange

Methyl orange imparts orange color to wool and silk but the color is not fast to sunlight or washing. It is a valuable indicator for acid-base titrations because it gives yellow color in basic solution and red color in acid solution. The change in color is due to the change in the structure of the ions.



(c) Congo Red

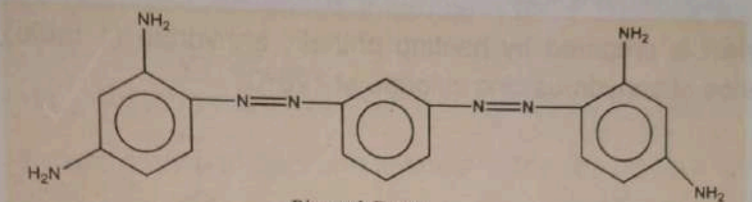
Congo red contains two azo groups. It is obtained by coupling tetrazotised benzidine with two molecules of naphthionic acid.



Naphthionicacid

(d) Bismarck Brown

It is obtained by coupling tetrazotised *m*-diaminobenzene with two molecules of *m*-diaminobenzene.

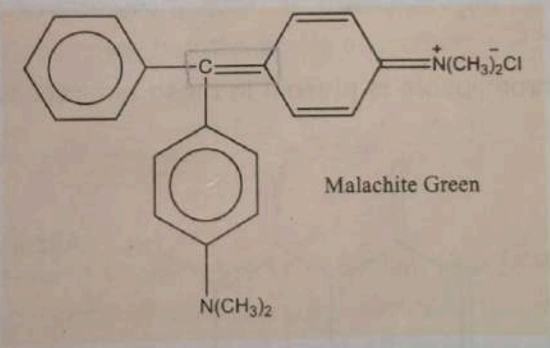


Bismarck Brown

Bismarck brown is a brown dye used in boot polishes and for dyeing wool and cotton.

3) Triarylmethane Dyes: In triarymlethane dyes, a central carbon is bonded to three aromatic rings one of which is in the quinoid form (the chromophore). The auxochromes are $-NH_2$, $-NR_2$ and $-OH$. Examples are:

(a) Malachite Green

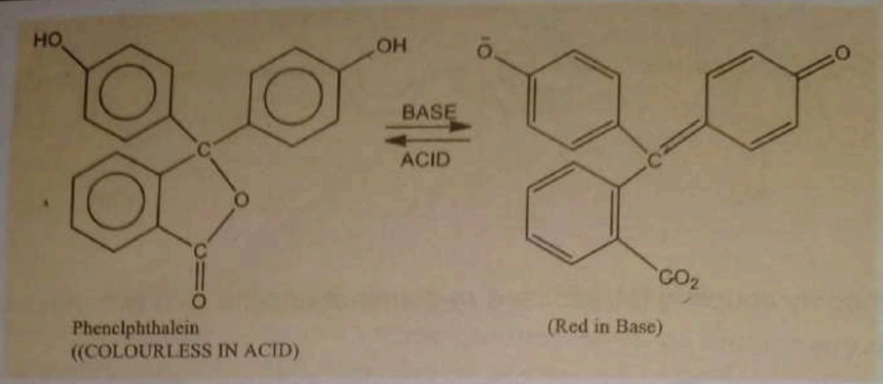


Malachite Green

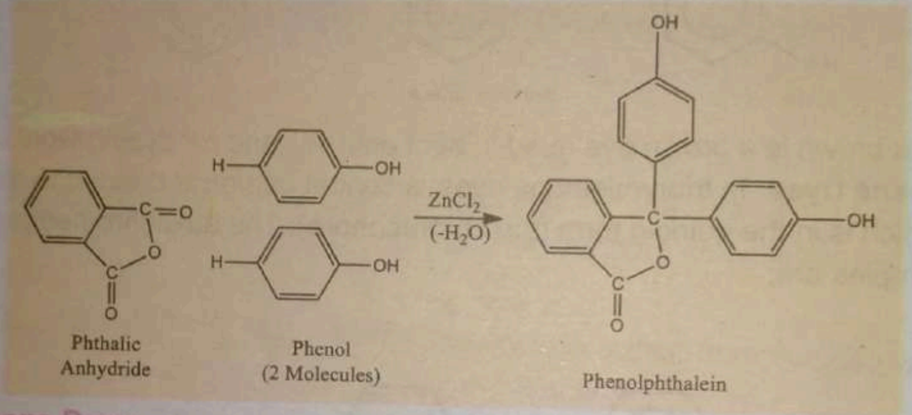
Malachite green has a deep green-blue color. Although the color fades in light, malachite green is used as a direct dye for wool and silk,

(b) Phenolphthalein:

It is also a triarmylmethane dye but it is better known as an acid-base indicator.

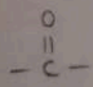


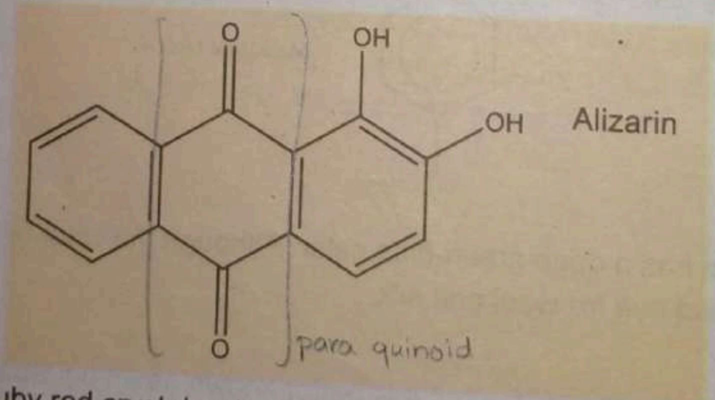
Phenolphthalein is prepared by heating phthalic anhydride (1 mole) and phenol (two moles) in the presence of anhydrous zinc chloride at 120^{0}C.



4) Anthraquinone Dyes:

The para quinoid chromophore is present in these anthracene-type dyes. Alizarin is a typical anthraquinone dye.

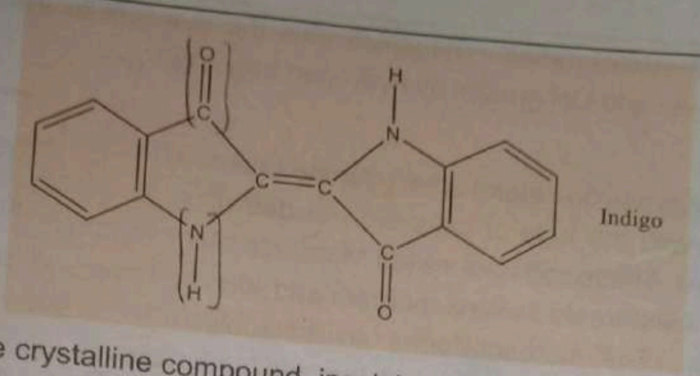




Alizarin forms ruby red crystals which dissolve in alkali to give purple solutions. It is used to dye wool and cotton.

5) Indigo Dyes:

Indigo is an example of the type of dyes which contain carbonyl chromophore.



It is a dark-blue crystalline compound, insoluble in water. It is used for dyeing cotton by the *Vat Process*. V. imp

CLASSIFICATION OF DYES BY METHODS OF APPLICATION

The chemical classification of dyes is of interest to the chemist but the dyer is concerned mainly with the application of dyes to fabrics. The method used for application in a particular case depends on the nature of both the dye and the fiber to be dyed. The dyes are often classified on the basis of technique employed for their application.

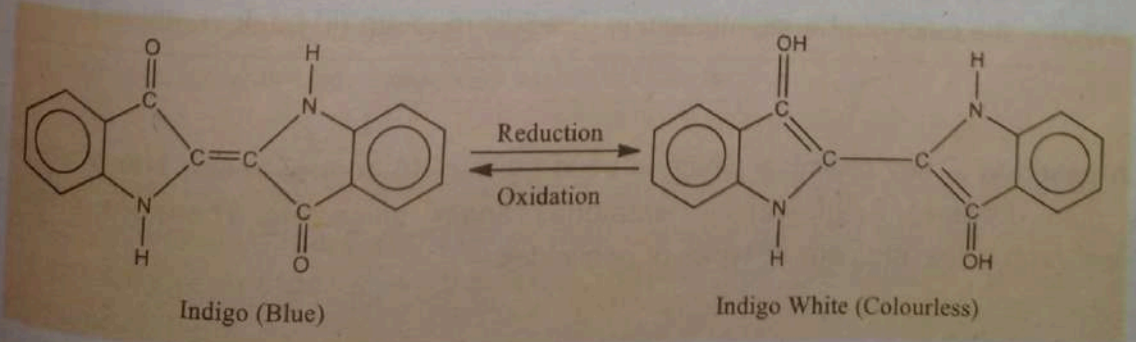
(1) Direct Dyes:

These can be applied to a fabric by direct immersion in a water solution of the dye. A direct dye contains acidic or basic auxochrome which combines with the opposite polar group present in the chemical structure of the fiber. Wool and silk are readily dyed by this method. Martius Yellow, a typical direct dye, has the acidic auxochrome –OH which interacts with the basic-NH_2 group of wool or silk.

$$\text{Fiber—NH} + \text{HO—Dye} \longrightarrow \text{Fiber—NH}_3 + \text{-----O—Dye}$$

(2) Vat Dyes: P

These dyes are insoluble in water but on reduction with sodium hydrosulphide in a vat form a colorless soluble compound which has a great affinity for cotton and other cellulose fibers. The cloth is soaked in the solution of a reduced dye and then hung in air, or treated with oxidants. As a result, the colorless compound is oxidized back to the insoluble dye which is now bound to the fabric. Indigo is a good example of a vat dye.



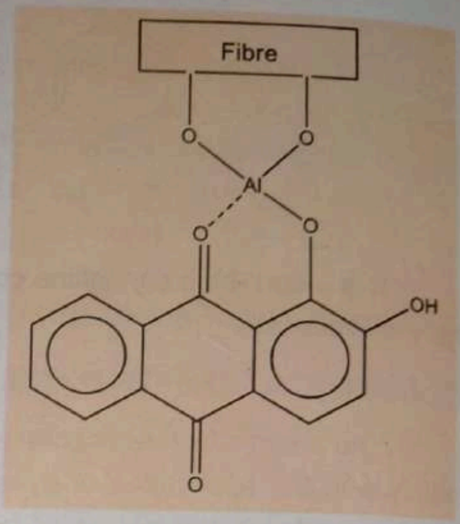
Indigo (Blue)

Indigo White (Colourless)

Indigo blue has auxochromes –OH which bind the dye fast to the cellulose fiber that contains ethereal oxygen and OH groups by hydrogen bonding.

(3) Mordant Dyes:

This class of dyes has no natural affinity for the fabric and are applied to it with the help of salts e.g., oxides of aluminum or chromium. These salts are called Mordants. A fiber such as cotton is first treated with a mordant and then with the dye solution. The mordant forms an insoluble coordination complex between the fiber and the dye and binds the two. The insoluble complex compound appears in the form of lakes that are fast to light and washing. The mordant dyeing is the most suitable for wool and nylon. Alizarin is an example of a mordant dye.



(4) Azoic Dyes (Ingrain Dyes).

In this method of dyeing, the water insoluble azo dye is produced in the fabric itself. The cloth is first soaked in the solution of a coupling reagent usually a phenol or naphthol. Then it is immersed in the solution of an auxochromes. The azoic dyeing is particularly suitable for cotton and other cellulosic fiber but may also be used for nylon.

(5) Disperse Dyes:

These dyes are insoluble in water but can be dispersed in a colloidal form in water. The fabric is immersed in the colloidal dispersion of the dye. The fine dye particles are absorbed into the crystal structure of the fabric. Disperse dyes are used with modern synthetic fabrics such as nylon, orlon, polyester and cellulose acetate.

Quick Quiz

1. Which one is first azo dye?
2. What is the color of Methyl orange: (i) in acidic medium (ii) in basic medium?
3. Which dye is used in boot polish and in dyeing wool and cotton?
4. What is the color of phenolphthalein in (i) acidic medium (ii) basic medium?

22.4. PESTICIDES

imp
5mark

A pesticide is any chemical which is used by man to control pests. The pests may be insects, plant diseases, fungi, weeds, nematodes, snails, slugs, etc. Therefore, insecticides, fungicides, herbicides, etc., are all types of pesticides.

Types of Pesticides

1- Insecticides

Insecticides are chemicals used to control insects. Often the word "insecticide" is confused with the word "pesticide." It is, however, just one of many types of pesticides. An insecticide may kill the insect by touching it or it may have to be swallowed to be effective. Some insecticides kill both by touch and by swallowing. Insecticides called **Systemics** may be absorbed, injected, or fed into the plant or animal to be protected. When the insect feeds on this plant or animal, it ingests the systemic chemical and is killed.

2- Miticides

Miticides (or Acaricides) are chemicals used to control mites (tiny Insecticides spider-like animals) **and ticks**. The chemicals usually must contact the mites or ticks to be effective. These animals are so numerous and small, that great care must be used to completely cover the area on which the mites live. Miticides are very similar in action to insecticides and often the same pesticide kills both insects and mites.

3- Fungicides

Fungicides are chemicals used to control the fungi which cause molds, rots, and plant diseases. All fungicides work by coming in contact with the fungus, because fungi do not "swallow" in the normal sense.

Herbicides

Herbicides are chemicals used to control unwanted plants. These chemicals are a bit different from other pesticides because they are used to kill or slow the growth of some plants, rather than to protect them. Some herbicides kill every plant they contact, while others kill only certain plants. It is of following types:

Nonselective herbicides are toxic to all plants. These are often used when no plants are wanted in an area. For example, nonselective herbicides could be used for clearing under guardrails or for total control of weeds in industrial areas.

Selective herbicides kill some plants with little or no injury to other plants. Usually selective types will kill either broadleaved plants or grassy plants. These are useful for lawns, golf courses or in areas with desirable trees. Some very selective herbicides may kill only certain plants in a group; for example, crabgrass killers on lawns.

5- Rodenticides

Rodenticides are chemicals used to control rats, mice, bats and other rodents. Chemicals which control other mammals, birds, and fish are also grouped in this category by regulatory agencies. Most rodenticides are stomach poisons and are often applied as baits.

6- Nematicides

Nematicides are chemicals used to control nematodes. Nematodes are tiny hair-like worms, many of which live in the soil and feed on plant roots. Very few of these worms live above ground. Usually, soil fumigants are used to control nematodes in the soil.

7- Molluscicides

Molluscicides are chemicals used to control snails and slugs. Usually the chemicals must be eaten by the pest to work. Baits are often used to attract and kill snails or slugs in an area.

8- Repellent

A repellent is a pesticide that makes a site or food unattractive to a target pest. They are registered in the same way other pesticides are and must be used according to the label. Insect repellents are available as aerosols and lotions and can be applied to skin, clothing, or plants to repel biting and nuisance insects. They can be sprayed or painted on nursery crops, ornamental plantings, orchards, vineyards, vegetables, and seeds. Repelling deer, dogs, birds, raccoons, and others can protect sites from damage.

Quick Quiz

1- Differentiate between (i) Pesticides and Insecticides (ii) Fungicides and herbicides
2- What do you understand by systemics?
3- How do herbicides different from other pesticides?
4- Give different types of repellents.
5- What are molluscicides

22.5. PETROCHEMICAL

The prefix "petro-" is an arbitrary abbreviation of the word "petroleum"; since "petro-" is Ancient Greek for "rock" and "oleum" means "oil". Therefore, the etymologically correct term would be "oleochemicals". However, the term oleochemical is used to describe chemicals derived from plant and animal fats.

Petrochemical Plant in the Kingdom of Saudi Arabia

Meanings:

Petrochemicals are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.

Types/Classes of Petrochemical Raw materials (Building Blocks):

Petrochemical classes are:-

a) Olefins including ethylene and propylene,

b) Aromatics

c) Synthesis Gas

Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents, and adhesives.

Primary petrochemicals are divided into three groups depending on their chemical structure:

a) Olefins includes ethylene, propylene, and butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels. At oil refineries olefins are produces mainly from hydrocarbons by chemical cracking such as steam cracking and by catalytic reforming.

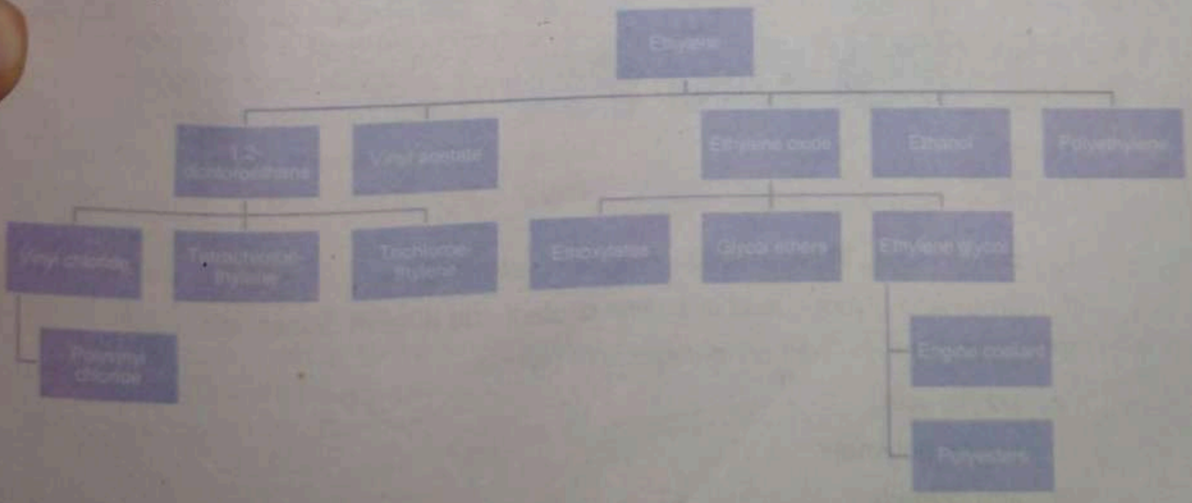
b) Aromatics includes benzene, toluene, and xylenes. At oil refineries, aromatic hydrocarbons are mainly produced by catalytic reforming or similar processes.

c) Synthetic gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer-urea and methanol is used as a solvent and chemical intermediate.

World production of ethylene is around 110 million tons per annum and that of propylene 65 million tons and of aromatic raw materials 70 million tons. The largest petrochemicals industries are to be found in the USA and Western Europe, though the major growth in new production capacity is in the Middle East and Asia. There is a substantial inter-regional trade in petrochemicals of all kinds.

List of significant petrochemicals and their derivatives

The following is a partial list of the major commercial petrochemicals and their derivatives:



Chemicals produced from Ethylene

Ethylene- the simplest olefin; used as a chemical feedstock and ripening hormone

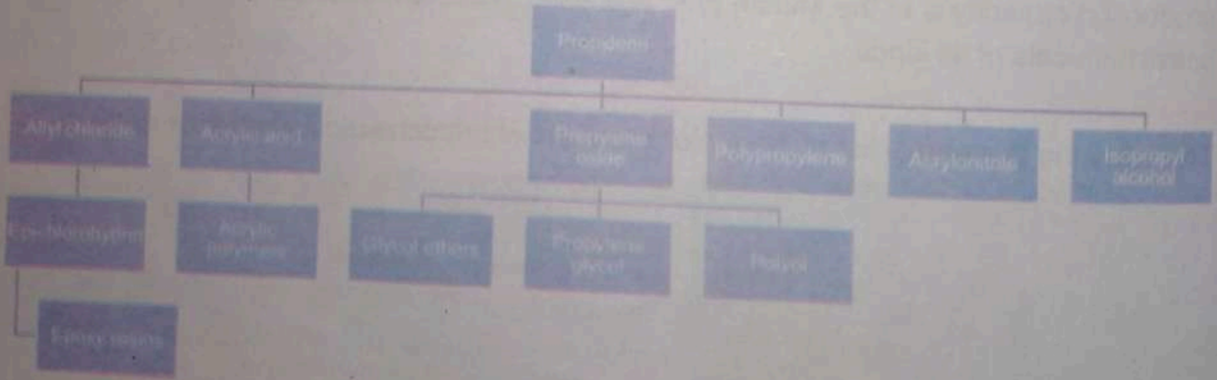
i. polyethylene - polymerized ethylene
ii. ethanol - via ethylene hydration (chemical reaction adding water) of ethylene
iii. ethylene oxide - via ethylene oxidation
    a) ethylene glycol - via ethylene oxide hydration
    b) engine coolant - ethylene glycol, water and inhibitor mixture
    c) polyesters - any of several polymers with ester linkages in the backbone chain
    d) glycol ethers - via glycol condensation
    e) ethoxylates
iv. vinyl acetate
v. 1,2-dichloroethane
    b) trichloroethylene
    c) tetrachloroethylene - also called perchloroethylene; used as a dry cleaning solvent and degreaser.
i) vinyl chloride - monomer for polyvinyl chloride

polyvinyl chloride (PVC) - type of plastic used for piping, tubing, other things

Chemicals produced from propylene

propylene - used as a monomer and a chemical feedstock

a. isopropyl alcohol - 2-propanol; often used as a solvent
b. acrylonitrile - useful as a monomer in forming Orlon.
c. polypropylene - polymerized propylene
d. propylene oxide



i. polyol - used in the production of polyurethanes
ii. propylene glycol - used in engine coolant and aircraft deicer fluid
iii. glycol ethers - from condensation of glycols
e. acrylic acid
f. acrylic polymers
g. allyl chloride - $\underbrace{CH_2=CH-CH_2}_{\text{Allyl}}-Cl$

h. epichlorohydrin - chloro-oxirane; used in epoxy resin formation

i. epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine

Chemicals produced from benzene

a) Benzene - the simplest aromatic hydrocarbon

i. ethylbenzene - made from benzene and ethylene

ii styrene made by dehydrogenation of ethylbenzene; used as a monomer

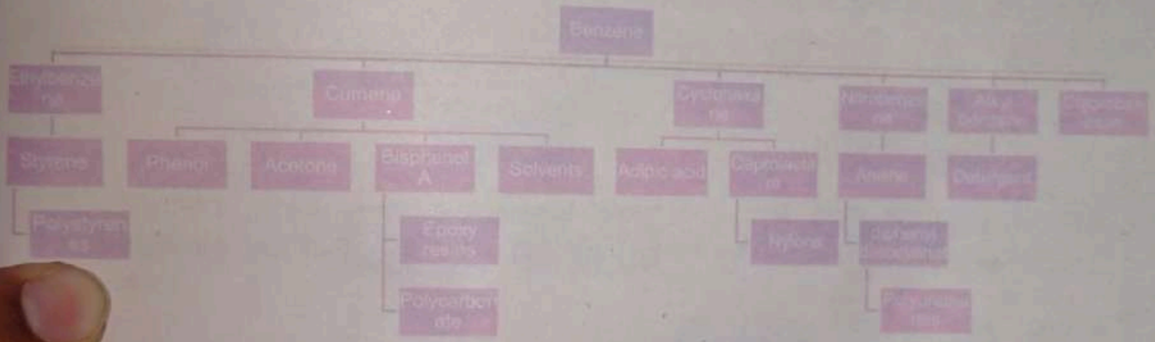
- polystyrenes - polymers with styrene as a monomer

b) cumene - isopropylbenzene; a feedstock in the cumene process

i) phenol - hydroxybenzene; often made by the cumene process

ii) acetone - dimethyl ketone; also often made by the cumene process

iii) bisphenol A - a type of "double" phenol used in polymerization in epoxy resins



c) cyclohexane - a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent

i) adipic acid - a 6-carbon dicarboxylic acid which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.

- nylons - types of polyamides.

ii) caprolactam - a 6-carbon cyclic amide

d) nitrobenzene - can be made by single nitration of benzene

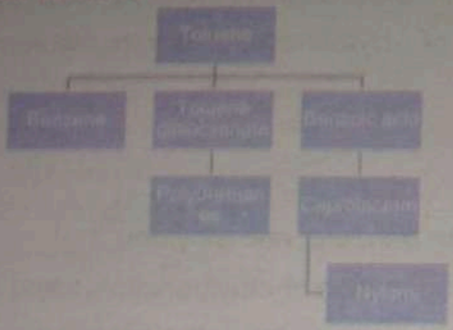
i) aniline - aminobenzene

e) alkylbenzene - a general type of aromatic hydrocarbon which can be used as a presursor for a sulfonatesurfactant (detergent)

i) detergents - often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates

f) chlorobenzene

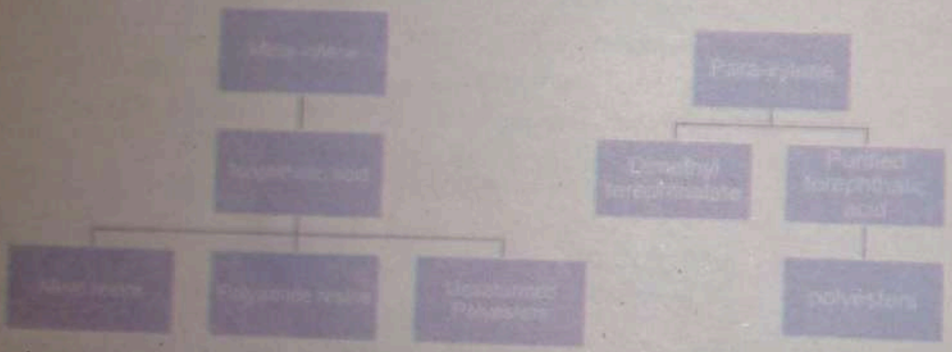
Chemicals produced from toluene



a) toluene - methylbenzene; can be a solvent or precursor for other chemicals
  a) benzene
  b) toluene diisocyanate (TDI) - used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
 i) polyurethanes - a polymer formed from diisocyanates and diols or polyols
  c) benzoic acid - carboxybenzene
 i) caprolactam

- nylon

b) Chemicals produced from xylenes



a) mixed xylenes - any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals
  a) *ortho*-xylene - both methyl groups can be oxidized to form (*ortho*-)phthalic acid
 i) phthalic anhydride
  b) *para*-xylene - both methyl groups can be oxidized to form terephthalic acid
 i) dimethyl terephthalate - can be copolymerized to form certain polyesters

- polyesters - although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.

ii) purified terephthalic acid - often copolymerized to form polyethylene terephthalate

- polyesters

c) *meta*-xylene
 i) isophthalic acid

- alkyd resins

- Unsaturated Polyesters

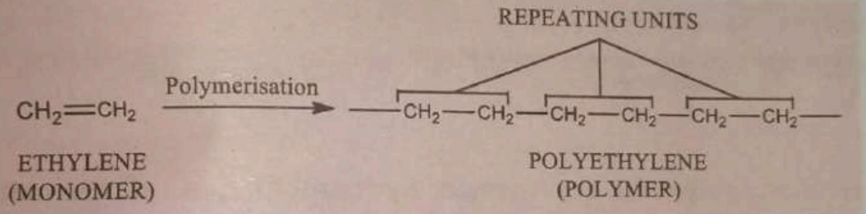
Quick Quiz

1. What do you mean by petrochemicals?
2. What are classes of petrochemical raw materials?
3. What are important fractions of petroleum?
4. How does refining of petroleum carried out in Pakistan?

22.6. SYNTHETIC POLYMERS

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerization.

The formation of polyethylene from ethylene is an example of polymerisation reaction.



Polymers which are synthesized from only one kind of monomer are called **homopolymers.** Polymers which are prepared from more than one kind of monomer are called **copolymers.**

Classification of Polymers

There are two main types of polymers: Addition polymers and Condensation polymers.

I) Addition Polymers (*Chain-Growth Polymers*)

imp (short)

Addition polymers are formed by combination of alkenes monomers to produce a single huge molecule only. These reactions are catalyzed by peroxides or acids. The reactions require pressures of 1000 atmospheres at 2000°C. Much lower temperatures and pressures can be used with so called **Ziegler Catalysts** which consist of a trialkyl aluminum and titanium tetrachloride in an inert solvent.

$(CH_3)_3Al$

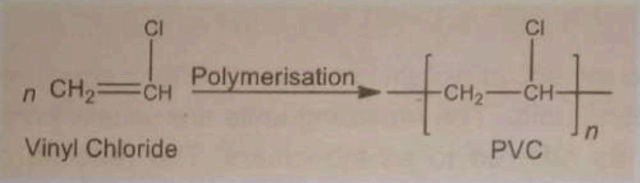
1) Polyethylene (Polythene). It is obtained by polymerizing ethylene. Polyethylene has been produced commercially since 1943. It is used in the manufacture of houseware such as buckets and dustbins, carpet backing, packing materials, and cable insulation.

$$n\ CH_2{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2—CH_2 \right]_n$$

ETHYLENE POLYETHYLENE

Notice that the monomer (ethylene) contains a double bond and the polymer does not. The electrons of the monomer *pi* bond have moved and are used to link one monomer unit to another by *sigma* bonds as indicated by extended lines in abbreviated polymer formula. The backbone of the polymer consists of the carbon atoms that originally formed the double bonds. Nothing is lost. The monomers simply add to each other.

2) Polyvinyl Chloride (PVC). It is obtained by polymerizing vinyl chloride. PVC is used in the manufacture of imitation leather, floor covering, corrugated roofing material and gramophone records.



$$n\,CH_2{=}\underset{}{\overset{Cl}{CH}} \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{Cl}{CH} \right]_n$$

Vinyl Chloride PVC

Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of $HgCl_2$.

$$HC\equiv CH + HCl \xrightarrow{HgCl_2} CH_2{=}CH-Cl$$

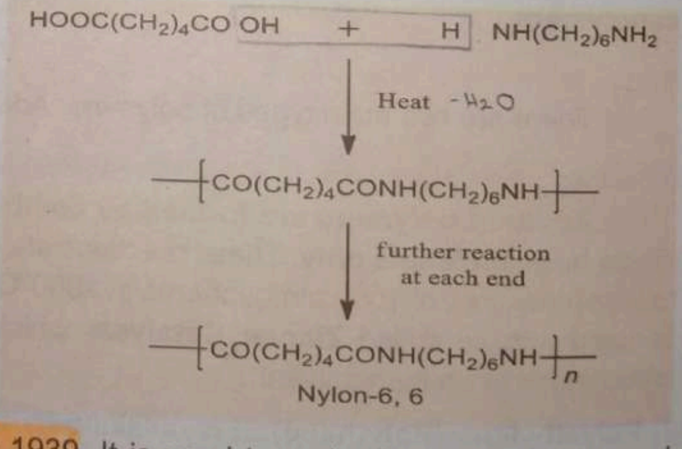
Acetylene Vinyl chloride

II) Condensation Polymers (*step-growth polymers*)

[illegible] (short)

Condensation polymers are formed by combination of monomers with the elimination of simple molecules such as H_2O or CH_3OH. There are two main types of condensation polymers: Polyesters or Polyamides. The most common example is:

Nylon-6,6 is the most important polyamide. It is obtained by heating adipic acid with hexamethylene diamine under nitrogen at 2000C. Nylon-6,6 derives its name from its starting materials, adipic acid and hexamethylene diamine, both of which have six carbons.



Nylon-6, 6

Nylon-6,6 was developed as a synthetic fiber for the production of stocking and other wearing apparel. It was introduced to the public at the New York World's Fair in 1939. It is used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes, and molded objects such as gears and bearings.

Thermoplastic and Thermosetting Polymers

A thermoplastic polymer is one which softens on heating and becomes hard on cooling.

A thermosetting polymer is one which becomes hard on heating it can not be softened by heating.

Quick Quiz

1. What are uses of (i) PVC (ii) Nylon-6,6?
2. What is the difference between addition and condensation Polymers?
3. Give differnce between thermoplastic and thermoselting plastic
4. How vinyl chlorid is prepared from acetylene?
5. Write forumula of (i) adipic acid (ii) hexmethylene diamine.
6. Give the use of Nylon-6,6

22.7. COSMETIC CHEMISTRY

Introduction

The global market for skincare and color cosmetics exceeded 53 billion dollars in 2002. The number of new products brought to market continues to expand exponentially. Cosmetic chemists are always looking for interesting and exotic ingredients that improve skin's appearance and health. A vast array of compounds is required to supply these products. The latest edition of the Cosmetics Toiletries and Fragrance Association (CTFA) Dictionary lists more than 10,000 raw materials. Every year hundreds of new ingredients are added to the list of those that have been used for centuries.

This particular topic is very vast but we will restrict ourselves in the following topics and discuss them one by one with a sufficient detail in each case:

1. Nail Polish
2. Nail Polish Remover
3. Lipstick
4. Hair dyes

22.7.1. Nail Polish

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Background

Unlike many other cosmetics that have a history of hundreds or even thousands of years, nail polish (or enamel) is almost completely an invention of twentieth century technology. Nail coverings were not unknown in ancient times—the upper classes of ancient Egypt probably used henna to dye both hair and fingernails—but essentially, its composition, manufacture and handling reflect developments in modern chemical technology.

Modern nail polish is sold in liquid form in small bottles and is applied with a tiny brush. Within a few minutes after application, the substance hardens and forms a shiny coating on the fingernail that is both water- and chip-resistant. Generally, a coating of nail polish may last several days before it begins to chip and fall off. Nail polish can also be removed manually by applying nail polish "remover," a substance designed to break down and dissolve the polish.

Raw Materials

There is no single formula for nail polish. There are, however, a number of ingredient types that are used. These basic components include:

1. **Film forming agents** e.g. Nitrocellulose
2. **Resins and plasticizers** e.g. castor oil, amyl and butyl stearate, and mixes of glycerol, fatty acids, and acetic acids
3. **Solvents** e.g. Butyl stearate and acetate compounds
4. **Coloring agents** e.g. "pearl" or "fish scale"

The manufactruing process includes following steps:

1. When properly and fully milled, the mixture is removed from the mill in sheet form and then broken up into small chips for mixing with the solvent. The mixing is performed in **stainless steel** kettles.
2. At the end of the process, the mixture is cooled slightly before the addition of such other materials as perfumes, moisturizers and cooling agents.
3. The mixture is then pumped into smaller, 55 gallon drums, and then trucked to a production line. The finished nail polish is pumped into explosion proof pumps, and then into smaller bottles suitable for the retail market.

22.7.2. Nail Polish Remover

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Nail polish remover base commonly contains a mixture of two organic solvents **acetone** and **ethyl acetate.**

Acetone belongs to a group of organic molecules called ketones or alkanones. The proper name acetone is propanone. It is also sometimes called 2-propanone.

Interesting Information
Acetone is an organic liquid that is colorless, flammable and is often used as a solvent as it is completely miscible with water and nearly all other organic liquids.

Ethyl acetate belongs to a group of organic molecules called esters or alkyl alkanoates. The proper name for ethyl acetate is ethyl ethanoate.

Quick Quiz

1. Give composition of nail polish
2. What is use of plasticizers in nail polish?
3. How can raw material of nail polish be mixed?
4. What is nail polish remover?
5. Give composition of nail polish remover

22.7.3. Lipstick and Chemical Composition

Lipsticks are simple in chemical composition, however complicated their application or effects. They are made up of three ingredients—a waxy or fatty base, a dye and a perfume. There is no danger in the use of lipstick. In fact, for sensitive mucous membranes they are protective. Anyone can eat a lipstick with no more harm than eating a pat of butter.

Raw Materials: The primary ingredients found in lipstick are wax (The wax used usually involves some combination of three types: beeswax, candelilla wax, or the more expensive carnauba) oil (such as mineral, caster, lanolin, or vegetable oil) alcohol, fragrance and pigment, Preservatives and antioxidants.

In general, wax and oil make up about 60 percent of the lipstick (by weight), with alcohol and pigment accounting for another 25 percent (by weight). Fragrance added to lipstick, accounts for one percent or less of the mixture.

The Manufacturing Process: The manufacturing process is the easiest to understand if it is viewed as three separate steps: melting and mixing the raw material; pouring the mixture into the tube; and packaging the product for sale.

Melting and mixing: First, the raw ingredients for the lipstick are melted and mixed—separately because of the different types of ingredients used. One mixture contains the solvents, a second contains the oils, and a third contains the fats and waxy materials.The solvent solution and liquid oils are then mixed with the color pigments. After the pigment mass is ground and mixed, it is added to the hot wax mass until a uniform color and consistency is obtained.

Molding: Once the lipstick mass is mixed and free of air, it is ready to be poured into the tube. A variety of machine setups are used, depending on the equipment that the manufacturer has. The melted mass is dispensed into a mold, "up-side down" so that the bottom of the tube is at the top of the mold. The lipstick is cooled and separated from the mold, and the bottom of the tube is sealed. The lipstick then passes through a flaming cabinet (or is flamed by hand) to seal pinholes and improve the finish.

Labeling and packaging: After the lipstick is retracted and the tube is capped, the lipstick is ready for labeling and packaging. Labels identify the batch and are applied as part of the automated operation. The final step in the manufacturing process is the packaging of the lipstick tube. There are a variety of packaging options available.

Quick Quiz

1. Give composition of lipstick
2. What type of wax is used as raw material of lipstick?
3. How many steps are involved in manufacturing of lipstick?
4. Give percentage of alcohol and pigments in lipstick

22.7.4. Hair dye

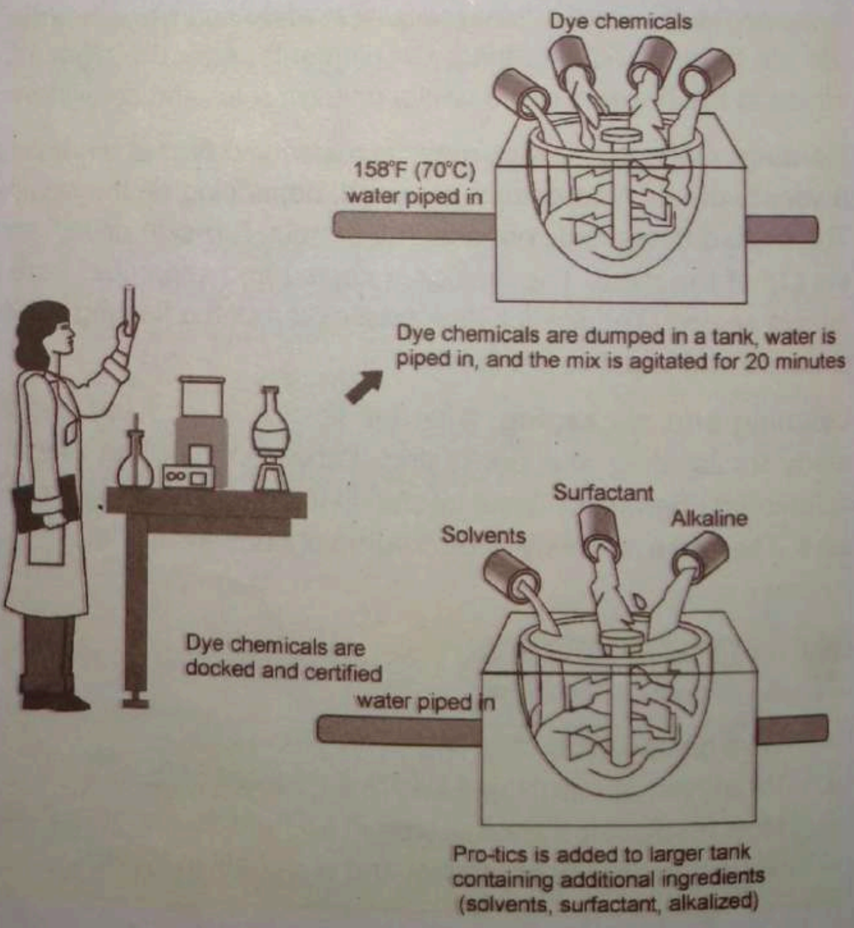
History:

1. Hair dye is one of the oldest known beauty preparations, and was used by ancient cultures in many parts of the world. Records of ancient Egyptians, Greeks, Hebrews, Persians, Chinese, and early Hindu peoples all mention the use of hair colorings.
2. Early hair dyes were made from plants, metallic compounds, or a mixture of the two.
3. Rock alum, quicklime, and wood ash were used for bleaching hair in Roman times. Henna was known in many parts of the world; it produces a reddish dye.
4. Many different plant extracts were used for hair dye in Europe and Asia before the advent of modern dyes.
5. Indigo, known primarily as a fabric dye (see section 22.3), could be combined with henna to make light brown to black shades of hair dye.
6. An extract of the flowers of the chamomile plant was long used to lighten hair, and this is still used in many modern hair preparations.
7. The bark, leaves, or nutshells of many trees were used for hair dyes.
8. Other dyes were produced from walnut leaves or nut husks.

Modern Age:

Preparations such as these were the only hair dyes available until the late nineteenth century. Hydrogen peroxide was discovered in 1818, but it was not until 1867 that it was exhibited at the Paris Exposition as an effective hair lightener. A London chemist and a Parisian hairdresser began marketing a 3% hydrogen peroxide formula at the Exposition as *eau de fontaine de jouvence golden* (golden fountain of youth water), and this was the first modern chemical hair colorant.

Advances in chemistry led to the production of more hair dyes in the late nineteenth century. The first synthetic organic hair dye developed was pyrogallol, a substance that occurs naturally in walnut shells.



Dye chemicals are dumped in a tank, water is piped in, and the mix is agitated for 20 minutes

Dye chemicals are docked and certified

Pro-tics is added to larger tank containing additional ingredients (solvents, surfactant, alkalized)

Raw Materials

In general, hair dyes include:

1. **Dyes** e.g. 4-amino-2-hydroxytoluene
2. **Modifiers** e.g. resorcinol
3. **Antioxidents** e.g. sodium sulfite
4. **Alkalizers** e.g. ammonium hydroxide

Beyond these basic chemicals, many different chemicals are used to impart special qualities. They may be shampoos, fragrances, chemicals that make the formula creamy, foamy, or thick, or contribute to the overall action of the formula.

Hair dyes are usually packaged with a developer, which is in a separate bottle. The developer is most often based on hydrogen peroxide, with the addition of small amounts of other chemicals depending on the manufacturer.

The Manufacturing Process

The manufacturing process includes the following steps

1. First of all chemicals must be tested to make sure they are what they are labeled. Then weigh the chemicals accurately.
2. Further these chemicals are mixed in preheated water or other solvents. The premix is agitated for about 20 minutes.
3. The pre mix is then added to a large tank, containing the other ingredients of the hair dye.
4. After getting proper consistency this mixture is delivered to a tank where it is filled in bottles labeled, caped, pack with developer and then distributed in the market.

22.8. ADHESIVES

imp

Meanings:

Adhesives are meant to stick things together. An adhesive is a compound that adheres or bonds two items together. Adhesives may come from either natural or synthetic sources. Adhesives are natural product; it is also manufactured in factories. Some modern adhesives are extremely strong, and are becoming increasingly important in modern construction and industry.

Types:

a) **Natural adhesives:** are made from inorganic mineral sources, or biological sources such as vegetable matter, starch (dextrin), natural resins, animal skin. They are often referred to as bioadhesives.

b) **Synthetic adhesives:** Elastomers, thermoplastic, and thermosetting adhesives are examples of synthetic adhesives.

c) **Drying adhesives:** These adhesives are a combination of ingredients suspended in a solvent. White glue and rubber cements are members of the drying adhesive family. As the solvent evaporates, the adhesive hardens.

d) **Contact adhesives:** Contact adhesives must be applied to both surfaces and allowed some time to dry before the two surfaces are pushed together. Some contact adhesives require as long as 24 hours to dry before the surfaces are to be held together.

e) **Hot Glue:** Also known as "hot melt" adhesives, these adhesives are thermoplastics; they are applied hot and simply allowed to harden as they cool. These adhesives have become popular for crafts because of their ease of use and the wide range of common materials to which they can adhere. The glue gun melts the solid adhesive and then allows the liquid to pass through the "barrel" of the gun onto the material where it solidifies.

f) **UV and light curing adhesives:** UV and light curing adhesives consist essentially of low or medium molecular weight resins.

Quick Quiz

1. Define adhesives
2. Give few examples of natural adhesives
3. Why and when drying adhesives harden?
4. How adhesives are used/applied?
5. How hot glue is applied?
6. Low molecular resins are present in which category or adhesive.

Society, Technology and Science

Development of synthetic fibers.

Nylon is the first synthetic fiber.

Synthetic fibers are made from synthesized polymers or small molecules. The compounds that are used to make these fibers come from raw materials such as petroleum based chemicals or petrochemicals. These materials are polymerized into a long, linear chemical that bond two adjacent carbon atoms. Different chemical compounds will be used to produce different types of fibers.

There are several methods of manufacturing synthetic fibers but the most common is the **Melt-Spinning Process**. It involves heating the fiber until it begins to melt, then drawing out the molten fiber with tweezers as quickly as possible. The next step is to draw the molecules by aligning them in a parallel arrangement. This brings the fibers closer together and allows them to crystallize and orient. Lastly, is Heat-Setting. This utilizes heat to permeate the shape and dimensions of the fabrics made from heat-sensitive fibers.

In general, synthetic fibers are created by forcing, usually through extrusion(the act or process of pushing or thrusting out to create objects of a fixed, cross-sectional profile) fiber, forming materials through holes (called spinnerets) into the air, forming a thread. Before synthetic fibers were developed, artificially manufactured fibers were made from cellulose.

Uses of synthetic fibres

Synthetic fibres are used for making

Clothes
Ropes
Nylon is used in making stockings, parachutes and other military equipment.
Fish nets

Carpets

Tents

Derclon is used in making rugs.

Glass fiber is used for:

- industrial, automotive, and home insulation (glass wool)
- reinforcement of composite materials (glass-reinforced plastic, glass fiber reinforced concrete)
- specialty papers in battery separators and filtration

Metallic fiber is used for:

- adding metallic properties to clothing for the purpose of fashion (usually made with composite plastic and metal foils)
- elimination and prevention of static charge build-up
- conducting electricity to transmit information
- conduction of heat

In the horticulture industry synthetics are often used in soils to help the plants grow better. Examples are:

- expanded polystyrene flakes
- urea-formaldehyde form resin

polyurethane form phenolic resin foam.

Key Points

- ❖ Classical chemistry (organic, inorganic and physical chemistry) is very essential for advancing the science of chemistry by discovering and reporting new products, routes and techniques.
- ❖ Capital-intensive industries are classified as heavy while labour intensive industries are classified as light industries.
- ❖ Light industries are easier to relocate than heavy industries and require less capital investment to build.
- ❖ Specialty chemicals are mainly used in the form of formulations. Purity is of vital importance in their formulation. This calls for organic synthesis of highly valued pure chemicals known as fine chemicals.
- ❖ The polarauxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure.
- ❖ Insecticides, fungicides, herbicides, etc., are all types of pesticides. Some pesticides must only contact (touch) the pest to be deadly. Others must be swallowed to be effective.
- ❖ Petrochemicals are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.

- Polymers which are synthesized from only one kind of monomer are called homopolymers. Polymers which are prepared from more than one kind of monomer are called copolymers.
- A thermoplastic polymer is one which softens on heating and becomes hard on cooling.
- A thermosetting polymer is one which becomes hard on heating it can not be softened by heating.
- Modern nail polish is sold in liquid form in small bottles and is applied with a tiny brush.
- Nail polish remover base commonly contains a mixture of two organic solvents **acetone** and **ethyl acetate.**
- Lipsticks are simple in chemical composition, however complicated their application or effects. They are made up of three ingredients-a waxy or fatty base, a dye and a perfume.
- Many different plant extracts were used for hair dye in Europe and Asia before the advent of modern dyes.
- Elastomers, thermoplastic, and thermosetting adhesives are examples of synthetic adhesives.

Exercise

Q 1: Select the right answer from the choices given with each question.

i. The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw material and their derivatives to products is called:
a. physical chemistry b. classical chemistry
c. industrial chemistry d. both b and c

ii. Which dye is used in boot polish
a. Azo dye b. Congo red c. Methyl orange d. Bismarck Brown

iii. Miticides are used to control
a. ticks and mites b. Fungi c. Unwanted plants d. mice and bats

iv. Aerosoles and lotions are used as
a. Fungicides b. Repellent c. Herbicides d. a and c

v. Petrochemicals are classified into how many classes?
a. One b. Two c. Three d. Four

vi. How many classes of polymers?
a. One b. Two c. Three d. Four

vii. Nylon is a polymer obtained by
a. Addition polymerization b. Condensation polymerization
c. Homopolymer d. None

viii. Which of following is not a raw material for nail polish?
a. Pearl b. Castor oil
c. Resorcinol d. Nitrocellulose

ix. A polymer which becomes hard on heating is:
a. Thermosetting b. Thermoplastic
c. Addition d. None

x. Nail Polish remover base commonly contains a mixture of two organic solvents as
a. Benzene and acetone
b. Ethyl acetate and CS_2
c. Benzene and CS_2
d. Acetone and ethyl acetate

xi. Which of following adhesives are also known as bioadhesives?
a. Drying adhesives
b. Synthetic adhesives
c. Natural adhesives
d. Hot glue

xii. A chemical compounds which is meant to stick things together
a. Nail polish
b. Lipstick
c. Hair dye
d. Adhesives

xiii. In early ages hair dyes were made from
a. Plants
b. Animals
c. Metallic compounds
d. Both a and c

xiv. Polymers which are prepared from more than one kind of monomer are
a. Homopolymer
b. Copolymer
c. Addition polymer
d. None

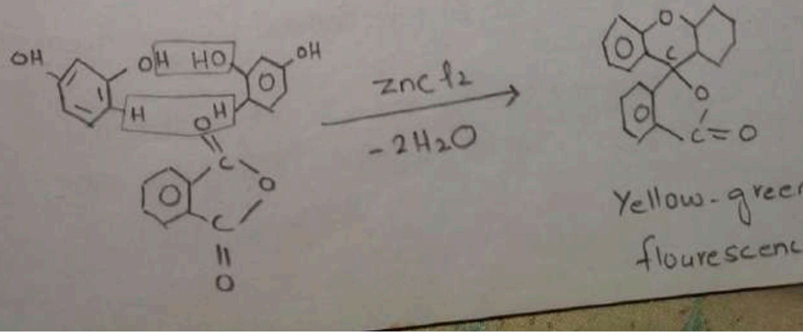
Q 2: Give brief answers for the following questions.

i. What is the difference between classical and industrial chemistry?
ii. How is methyl orange prepared?
iii. How is Bismarck Brown prepared?
iv. How is Fluorescein prepared?
v. Enlist different chemicals produced from ethylene.
vi. Write different chemicals produced from Toluene.
vii. Differentiate between homopolymer and Copolymer
viii. What is the difference between thermoplastic and thermosetting polymer?
ix. How will you synthesize Nylon 6,6 from 1,3-Butadiene?

Q3: Give detailed answers for the following questions.

i. What is chemical industry? Discuss different raw materials used in this industry.
ii. What are dyes? How are they classified on the basis of structure?
iii. What do you know about dyes? How are they classified on the basis of application?
iv. Write a note on:
(i) Vat Dyes (ii) Mordant Dyes
v. What is meant by Pesticides? Describe its types in detail.
vi. Describe the basic building block in petrochemicals technology.
vii. Describe raw materials and manufacturing process of Nail Polish.
viii. What are adhesives? Discuss its working and types.

(iv)



Yellow-green in alkaline Solution
flourescence

23

ENVIRONMENTAL CHEMISTRY

After completing this lesson, you will be able to:

This is 10 days lesson (period including homework)

- Recognize various chemical reactions occurring in the atmosphere.
- Recognize that the release of COx SOx NOx VOCs is associated with the combustion of hydrocarbon based fuels.
- Outline problem associated with release of pollutants including acid rain and the formation by free radical reaction of hazardous inorganic and organic compound e.g., PAN (Analyzing)
- Describe causes and impacts of urban smog.
- Explain greenhouse effect and global warming as resulting in climate change.
- Explain the buildup to and recognize the adverse effects of ozone in the troposphere.. (Applying)
- Describe the role of CFCs in destroying ozone in the stratosphere.
- Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth.
- List possible alternatives to the use of CFCs
- Recognize and describe various water pollutants.
- Explain the various parameters of water analysis.
- List some major products of the petrochemicals industry together with their uses. (Applying)

Reading

INTRODUCTION:

It is the branch of chemistry which deals with the chemicals and other pollutants in the environment resulting directly and indirectly from human activities.

In this we study the sources, chemical reactions, transportation of the chemicals and their adverse effects on human beings.

Components of the Environment:

1. Atmosphere → We will study it in detail
2. Hydrosphere → Concerned with all water bodies i.e. ocean, rivers, streams lakes, glaciers and ground water reservoirs.
3. Lithosphere → Concerned with hard and rigid rocky earth crust.
4. Biosphere → Area on earth which support life i.e. air, lakes, etc.

Atmosphere: Our surrounding on earth is called atmosphere. It consists of gases i.e. N_2, CO, He, Ne, Kr, Xe and water vapours. Its thickness is about 1000 km above the surface of earth.

The gases present in the atmosphere are very important in the following ways:

1) These gases absorb harmful radiations (cosmic rays and electromagnetic radiation) of Sun to protect life on earth. Otherwise these rays are very harmful to living things on earth.
2) N_2 is used by nitrogen fixing bacteria
3) O_2 is necessary for breathing in animals.
4) CO_2 is necessary for photosynthesis in plants and
5) Water vapours are responsible for sustaining life on earth.

Actually our atmosphere has been divided into four layers:

1- Troposphere 2- Stratosphere 3- Mesosphere
4- Thermosphere.

We are concerned here with only first two layer i.e. troposphere and stratosphere.

23.1. CHEMISTRY OF TROPOSPHERE

Troposphere is very close to earth in which we live. It extends up to 20km. It contains all those gases which are present in our atmosphere.

In this part of our atmosphere, we will discuss

1) Different pollutants (Their sources and effects and smog (development and chemistry))
2) Effects and chemical reactions which occur during acid rain, green house effect and global warming
3) Role of automobile in air pollution

23.1.1 Smog

imp

"It is a combination of smoke and fog i.e. 'sm' from smoke and 'og' from fog". The smog is of two types; one is reducing smog and second is oxidizing smog.

Reducing smog: This smog containes high contents of SO_2, it is chemically reducing in nature and ~~in~~ is known as reducing smog. For example, the smoke and SO_2 produced from the burning of coal can combine with fog to create industrial smog.

Oxidizing smog: Photochemical smog is termed as oxidizing smog which consists of higher concentration of oxidants like Ozone. It is a yellowish, brownish, grey haze which is formed in the present of water droplets and chemical reaction of pollutants in the air. It has unpleasant odor because of its gaseous components.

Major Chemical Pollutants in Photochemical Smog:
(Sources and Environmental Effects)

Objective

Table 23.1

Toxic Chemical	Sources (Natural and Human)	Environmental Effects	Additional Notes
Nitrogen Oxides (NO and NO_2)	- Combustion of oil, coal, gas in both automobiles and industry. - bacterial action in soil - forest fires - volcanic action - lightning	- Decreased visibility due to yellowish color of NO_2 - NO_2 contributes to heart and lung problems - NO_2 can suppress plant growth. - decreased resistance to infection - may encourage the spread of cancer	- All combustion processes account for only 5 % of NO_2 in the atmosphere, most is formed from reactions involving NO -concentrations likely to rise in the future
Volatile Organic Compounds (VOCs)	- evaporation of solvents - evaporation of fuels - incomplete combustion of fossil fuels - naturally occurring compounds like terpenes from trees	- eye irritation - respiratory irritation - some are carcinogenic - decreased visibility due to blue-brown haze	- the effects of VOCs are dependent on the type of chemical - samples show over 600 different VOCs in atmosphere - concentrations likely to continue to rise in future
Ozone (O_3)	- formed from photolysis of NO_2 - sometimes results from stratospheric ozone intrusions	- bronchial constriction - coughing, Sneezing - respiratory irritation - eye irritation - decreased crop yields - retards plant growth - damages plastics - breaks down rubber - harsh odor	- concentrations of 0.1 parts per million can reduce photosynthesis by 50 % - people with asthma and respiratory problems are influenced the most - can only be formed during daylight hours
Peroxyacetyl Nitrates (PAN)	- formed by the reaction of NO_2 with VOCs (can be formed naturally in some environments)	- eye irritation - high toxicity to plants - respiratory irritation - damaging to proteins	- was not detected until recognized in smog - higher toxicity to plants than ozone
	- Incomplete combustion of carbon containing fuels. (CO)	- Causes	

Carbon Oxide (CO and CO_2)	- Incomplete combustion of agricultural of slush matter, (CO) - During the reaction in blast furnace (CO) - Cigarette smoke (CO) - Burning of fossil fuels produce CO_2 - Cultivation of Soil (CO_2) - Eruption of Volcanoes (CO_2) - Respiration of living organism. (CO_2)	Anoxia (Oxygen Starvation) result suffocation - Causes Green house and Global Warming results climatic changes - Respiratory irritation	
Oxides of Sulphur (SO_2, SO_3)	- Volcanic Eruption - Burnt of oil & coal. - Sulphide ores are roasted	- Causes acid rain - Respiratory irritation. - Loss of green color in plants Fading in color of Fabrics, leathers, paper and paints.	

b) Chemistry of Photochemical Smog (Chemical Reactions in the Atmosphere)

The previous section suggested that the development of photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions. To begin the chemical process of photochemical smog development the following conditions must occur: imp

- **Sunlight**.
- The production of oxides of nitrogen (NOx).
- The production of volatile organic compounds (VOCs).
- Temperatures greater than 18 degrees Celsius.

If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog. The following discussion outlines the processes required for the formation of two most dominant toxic components: ozone (O_3) and peroxyacetyl nitrate (PAN). Which is primarily created from volatile organic compounds. Other oxidizing agents are H_2O_2, HNO_3 etc. PAN is an eye irritant and is also toxic through plants.

Quick Quiz

1. What is environmental chemistry?
2. What is smog? What are its types?
3. What are different sources and environmental effects of:
   (i) Ozone (ii) Carbon oxides (iii) Sulphur oxides?
4. For the development of photochemical smog, what conditions are necessary?

23.1.2. Acid Rain

We know that air contains SO_2, NO_2 and CO_2.

1) SO_2 present in air undergoes photolytic and catalytic oxidation to form SO_3 which reacts with rainy water or moisture to form H_2SO_4 i.e.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

2) NO_2 reacts with rainy water or moisture in the presence of O_2 and O_3 and produces HNO_3 i.e.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

3) CO_2 reacts with rainy water or moisture to form H_2CO_3 i.e.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

4) In some countries due to release of HCl by volcanic eruption, there is temporary acid rain.

H_2SO_4, HNO_3 and H_2CO_3 formed as above come down the atmosphere as acid rain or acid snow. As far as H_2CO_3 is concerned, it has no severe effects on animals, plants or any other things.

Q **Impacts:** imp

1) It makes the lakes so acidic that they can no longer support fish life.
2) The yield of agricultural crops is also reduced.
3) HNO_3 acid rain gradually eats up lime stone and marble of the buildings and corrodes metals.
4) It fades the color of fabrics (e.g. cotton, nylon and rayon), leather and paper
5) Causes extensive leaf-drop in plants.
6) It is very corrosive and attacks skin.
7) Acidification of soil and rocks can leach metals like Al, Hg, Pb and Ca and discharge them into water bodies. Then these heavy metals are eaten by fishes which proves very much dangerous for those animals and birds which eat these fishes.
8) It also damages steel, paint, plastic, cement, masonry work and sculptural materials.

Quick Quiz

1. What is acid rain?
2. Write down different effects of acid rain?
3. List out those acid present in acid rain.
4. Name those heavy metals which leach due to acidification of soil.

23.1.3 Green House Effect and Global Warming

The greenhose effect is the warming that happened when cetain gases in earth atmosphere trap it. These gases lets in light but keep heat from escaping, like the glass walls of a greenhouse.

Greenhouse Effect

The heat causes the atoms in the earth's suface to viberate and radiate heat and infrared radiation. Neither O_2 nor N_2 apsorbs b infrared radiatin radiation, however, other substances in the atmosphere, especislly CO_2 and H_2O, do absorb infrared radiation. This absorbtion warms the atmosphere, which then radiates the infrared rays. The effect is to trap the sun's warmth. Thus, som e of the heat the earth must lose in order to be in equilibrium is traped in the atmosphere, and thew temperature eises raises which produce a war effect on the earth. Two gases CO_2 and water vapours in the air, by absorbing infrared radition radiation, act as an insolating blanket to prevent heat from escaping, this is often reffered to as a greenhouse effect. The traping of heat on the surface of earth by CO_2 and water vapour in the atmosphere is known as greenhouse effect.

Global Warming

In the atmosphere, water vapour absorbs more infrared radioation than CO_2 because its consultration is higher. The concentration of CO_2 in the atmosphere is low (about 330 ~~PBM~~ PPM) but is known to be increasing. Concentration of CO_2 is increased up to 400 ~~PBM~~ PPM than temperature should rise as much as 1°C. The main global temperature at Earth's surface is about 15°C. This temperature is determind by a deligate balance between the energy which is absorbed by the Sun and the energy emitted back into space by the Earth. Any change in the amount of energy absorbed or emitted by the Earth could upset this balance, effecting our climate.

The ~~e~~ a verage global temperature and concentration of CO_2 have fluctuated on a cycle of hundreds of thousands of years as Earth's position relative to the sun has varied. As result, ice ages have come and gone.

Occasionally, other factors briefly influence global temperatures. Volcanic eruptions, for example, emit particles that temporarily cool Earth's surface. But these have no lasting effect beyond a few years. Other cycles, such as **E1Nino**, also work on fairly short and predictable cycles.

Now, human have increased the amont of CO_2 in the atmosphere by more than a third since the industrial revolution. Changes this large have historically taken thousands of years, but are now happening over the course of decades.

Scientists are already seeing some of the changes occurring more quickly than they had expected. According to the intergovernmental panel on climate change, eleven of the twelve hottest years since thermomerter readings became available occurred between 1995 and 2006.

Quick Quiz

1. Is CO_2 responsible for green house effect? If yes then how?
2. What is the importance of green house effect?
3. High concentration of CO_2 is responsible for climate changes. Comment.

23.1.4. Automobile (Pollutants and Converter) imp

In automobiles during incomplete combustion of petrol, we get smoke of different gases which pollute our atmosphere. The engine used in these motor vehicles are called internal combustion engines because the petrol which is used as a fuel is burnt inside the engine and contains CO, NO, NO_2, un-burnt carbon particles, some lead compounds, some alcohol and acids. All theses substances are poisonous and hence pollute air.

Production of Pollutants:

The pollutants produced in the internal combustion engine by the use of petrol (which mainly contain hydrocarbon) are CO, NO, NO_2.

Petrol burns very fast in a car engine. Due to short time available for burning, incomplete combustions of petrol takes place and some CO, un-burnt carbon particles, CO_2, water vapors, some alcohol and acids are produced. CO and carbon particles are emitted into the air and thus air is polluted.

When petrol burns in a car engine, a very high temperature is produced. At this high temperature, N_2 and O_2 present in air of the engine combine together and form NO and NO_2. These gases also pollute the air.

Control Measure:

In order to control the air pollution caused by hydrocarbons and CO etc the following methods are used. Q

1) **By adding lead tetraethyl $Pb(C_2H_5)_4$ to petrol:** $Pb(C_2H_5)_4$ is added to the petrol to slow down the rate of combustion of petrol. $Pb(C_2H_5)_4$ provides more time to the petrol for its combustion and hence enables it to burn more completely. Due to this the quantity of unburnt hydrocarbons and CO coming out of the engine, with exhaust gases is reduced and hence air pollution is also minimized.
2) **Catalytic oxidation / Converter:** The pollution of air caused by unburnt hydrocarbons and CO present in the exhaust gases of the vehicle's engine can also be reduced by

attaching gas device with the vehicle's engine, in which the exhaust gases can be mixed with more air and then burnt completely in the presence of platinum catalyst before they are discharged into the environment. Hydrocarbons and CO are oxidized by O_2 of the air in presence of platinum catalyst.

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2\ 18H_2^+O$$
$$2CO + O_2 \longrightarrow 2CO_2$$

Quick Quiz

1. What is the role of tetraethyl lead in minimizing the air pollution?
2. What is internal combustion engine?
3. Name those pollutants produced in automobile engines.
4. What gas is produced due to high temperature of engine?
5. What is drawback of tetraethyl lead used to control air pollution?

23.2. CHEMISTRY OF THE STRATOSPHERE

imp

This layer of atmosphere is present 20-40 km above the earth and ozone is present in this layer at a height of about 28 kilometers. The concentration of ozone in this layer is 10 ppm (10 parts per million) but it is present in small concentration through the atmosphere.

In this layer of atmosphere, we will discuss comprehensively about ozone.

a) Production of O_3 and its toxic effects

Some O_3 is produced during various combustion processes taking place in the air around us. Traces of O_3 in air do not harm but O_3 of concentration more than 0.1 ppm is toxic and harmful to human beings. O_3 also attacks rubber products. O_3 is also produced in the upper part of the atmosphere by the action of sunlight on O_2.

$$3O_2 \longrightarrow 2O_3$$

b) Protective action of ozone layer in the atmosphere

The thickest layer of O_3 exists at a height of 23 km from the surface of the earth. Since O_3 present in this layer absorbs harmful ultraviolet radiations coming from the sun. If these radiations reach the earth, they will cause skin cancer and will destroy the organic molecules necessary for life.

Thus, we see that O_3 does not allow the ultra-violet radiations to reach the earth and we are thus saved from the harmful effects caused by these radiations. If O_3 layer in the atmosphere disappears completely, then all the harmful ultra-violet radiations coming from the sun would reach the earth and would cause skin cancer in men and animals and will also damage the plants. All the life on earth would then gradually be destroyed.

c) Sources of destruction/destroying the ozone layer present in stratosphere.

In 1980 scientists showed that there is a hole in the O_3 layer. This hole was detected over the region of Antarctica. Due to the presence of O_3 layer, the ultraviolet rays coming from the sun can pass through the hole and thus can reach the earth's surface. The presence of O_3 in the atmosphere is due to the fact that the amount of O_3 present in stratosphere is getting reduced day by day and thus the ozone layer is becoming thinner and thinner. The depletion of the ozone layer is due to the following sources. Q

1) Oxides of Nitrogen: The oxides of nitrogen present in the atmosphere decompose O_3 into O_2 and are themselves regenerated.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO + O \longrightarrow NO_2$$

Thus we see that the presence of nitrogen oxides in the atmosphere destroys the ozone layer. These oxides destroy about 70% of O_3 found in the stratosphere. Greater is the amount of the oxides in the atmosphere greater is the percentage of O_3 which is destroyed.

2) Nuclear Tests: Nuclear tests being conducted in the world generate high temperature. At high temperature, atmospheric nitrogen is favorably oxidized to NO. NO thus formed destroys ozone layer, as shown above at (1) Q

imp Q

3) Role of Flouro-Chloro Carbons is destroying ozone: Fluoro-chloro-carbons are the fluoro-chloro methanes like, Freon-1 ($CFCl_3$) and Freon12 (CF_2Cl_2). These are stable compounds. These are chemically inert and hence do not react with the substances. These are used as aerosol spray propellants, refrigerants, firefighting reagent and solvents for cleaning electronic components. When they enter stratosphere, they absorb ultraviolet solar radiations and get broken down into free atomic chlorine. This atomic chlorine decomposes O_3 into O_2 (NO also breaks O_3 into O_2).

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O_3 \longrightarrow Cl + 2O_2$$

d) How to protect the ozone layer:

Scientists are worried over the gradual destruction of ozone layer by the oxides of nitrogen and fluoro-chloro carbons. In order to save the destruction of O_3 layer by fluoro-chloro carbons, their use should be banned or some new types of substances should be discovered which may be used as aerosol spray propellants and should not react with O_3 layer, so that it may be saved.

imp Q

Some Alternatives to Chloro-Fluoro Carbons (ClFCs):

The first ClFC substitutes to be introduced were HClFCs such as CF_3CHCl_2 and CHF_2Cl compounds that have fewer chlorine atoms than other ClFCs. HCFCs break down more readily in the atmosphere than ClFCs and thus are less likely to reach the stratosphere.

Much better substitutes for CIFCs are hydrofluoro carbons which contain no chlorine. One them CF_3CH_2F has been used successfully as a refrigerant and since 1994 has replaced reon in nearly all car air conditioners. In electronic industries, soapy water followed by rinsing nd air drying is now used instead of CIFCs to clean micro circuits.

Quick Quiz

1. Ozone is acts both useful as well as harmful. Justify the statement.
2. Enlist the possible alternatives to the use of CFCs.
3. How O_3 is decomposed by oxides of nitrogen?
4. How ozone is produced?

23.3. WATER POLLUTION AND WATER TREATMENT

The contamination of water with the substances which have adverse effects on human beings, animal and plants is called water pollution and the substances whose presence in the water makes it polluted are called pollutants.

23.3.1. Types of Water Pollutants

Water is essencial for life on Earth. 2/3 of the population of the world is devoid of clean drinking water. In spite of abandons of water on the earth, clean and fresh water is vital for survival of all human being and recently WHO has raised the slogan of clean water for all. Clean, drunkable water is called portable water as against unportable water.

These are of following types:

(A) Suspended Solid and Sediments: imp

These are wastes which are not completely soluble but suspended in the water. These wastes include:

1) Oil spillage
2) Live-stock waste
3) Industrial wastes and
4) Leather tanneries

1) Oil Spillage:

Petroleum is a complex mixture of many compounds which are mainly hydrocarbons. It is transported from one place to another through sea.

We know that petroleum products are used as:

1) Fuel
2) Lubricants
3) Plastics
4) Electrical appliances
5) Synthetic rubber ethyne

6) Detergents
7) Manufacture of petrochemicals

In order to prepare such a large varieties of substances, petroleum is handled on large scale in the world. So the oil spillage can take place and it creates serious problems.

Pollution of water by petroleum:

Water gets polluted by:

1) accidental oil spills
2) leakage from cargo oil tankers in sea
3) tanker trucks
4) pipelines leakage during offshore exploration
5) leakage of under ground storage tanks

Oil Spillage and animal life:

Many petroleum products are poisonous and create serious health problems to:

1) Humans
2) Animals
3) Aquatic life

Polycyclic hydrocarbons are carcinogenic even at very low concentration. Marine animals are seriously affected by soluble aromatic fractions of oil. The spilled oil damages the feather of the birds or fur of animals and sometimes causes their death.

Petroleum and under water plants:

When oil is spilled on the surface of sea then the light transmission is affected. The process of photosynthesis of plants does not remain much efficient moreover, the concentration of oxygen in water is decreased.

2) Live-Stock Waste:

Livestock waste is damped on open land. Sometimes it is discharged into sewage, canals or rivers. This practice pollutes the surface and ground water. In this way serious problem are created for the population.

5m8 (2021) ✓ Bacteria are present in the livestock waste. It contaminates the surface and ground water. This causes the diseases like:

a) Dysentery
b) Typhoid
c) Hepatitis

3) Industrial Wastes:

Sources:

Industries which produce large quantities of industrial effluents are leather/tanneries, fertilizers, oil refineries, petrochemicals, textiles, foods, sugar, paper/pulp, paper board, rubber products etc. the waste products may be waste heat, smoke, solid or water effluent.

Pollutants:

The industrial pollutants are highly toxic organic compounds and heavy metals like Pb, Cd, Cr, Hg, As, Sb etc. Oil greases, Mineral acids are also released in small quantities. These pollutants result in contamination of water and make it unsuitable for irrigation and drinking purposes.

Effects of Industrial pollutants:

Heavy metal particles are highly toxic and do not have any safe limits. When they are continuously ingested through food or water they get accumulated in the organisms and cause serious health problems like anemia, kidney diseases, nervous disorder, high blood pressure etc.

4) Leather Tanneries: imp (Short)

There are many leather tanning units working in Pakistan. Their sizes vary from cottage scale to big industrial units.

Leather industries use chromium salts which have +6 oxidation state of chromium. Only a few industries have the facility of waste treatment. This can be done by reducing Cr^{+6} oxidation states to Cr^{+3} oxidation state. Cr^{+3} is precipitated as $Cr(OH)_3$. Cr^{+6} salts are highly toxic and cause cancer.

(B) Dissolved Solids

These are wastes which are dissolved/soluble in water completely. These wastes include:

1) Detergents
2) Pesticides
3) Chemical fertilizers

1) Detergents:

Detergents are used in homes and industries for washing. After washing these detergents are thrown into water reservoirs. The amount of detergents in reservoirs is increasing day by day. This waste water containing detergents goes into rivers and finally reaches the ocean; which is harmful for life in seas. The detergents bound heavy metal ions like Pb, Cd and Hg and transport it from sediments into water. These metals particles are very toxic.

2) Pesticides:

The pesticides are both toxic and persistent. Analysis of polluted water has shown that it contains pesticides which are toxic to fish. **Endrin**, even in traces, is reported to be toxic for catfish and other varieties of fish. **D.D.T.** affects the central nervous system of fish and toxaphene has been reported to cause bone degeneration in fish.

3) Chemical Fertilizers:

Nitrate/phosphate salts are generally used as fertilizers, to increase the yield of the crops. When these fertilizers are used in excess, some of their unused quantity is washed away from the agriculture lands into the ponds, lakes and river with rain water and thus pollute the water. This water is polluted, since it contains unused nitrate/phosphate salts. Similarly the waste water coming from the fertilizer industries also contains nitrogenous/phosphatic fertilizers which, when washed away into the lakes and river with rain water, make the water polluted. The presence of nitrogenous/ phosphatic fertilizers in water is harmful to the aquatic life and human beings in the following ways:

a) The presence of the fertilizers in the polluted water increases the growth of algae and other aquatic plants which, later on undergo decomposition and produce disagreeable odor. These plants also deplete the amount of O_2 dissolved in water and hence the survival of aquatic life becomes difficult or impossible.

b) After a long period the lakes and slow moving waters which contains plant nutrients are converted into swamps (A swamp is an area of very wet land with wild plants growing in it) and marshes (A marsh is an area of land which is very wet and muddy).

c) The water containing nitrate salt is not fit for drinking by human beings. Moreover, this polluted water cannot be purified for drinking purposes.

(C) Thermal Pollution

Thermal pollution takes place because many electric generating companies use water in the process of cooling their generator. This heated water is then released into the system by causing a warming trend of the surface water. Thermal pollution results when the heated effluent is released into poorly flushed system. In these cases permanent temperature increase often result, which tend to decrease the solubility of dissolved oxygen. In lakes it also becomes possible to bring about nutrient redistributions and prolong summer stagnation periods.

When heated water gets released into large, well-flushed marine systems there is little if any permanent temperature rise. There are however problems related to the operation of plants utilizing marine water in the cooling process. Evidence reveals that seawater tends to corrode the cooling pipes, which are generally constructed of a copper nickel alloy termed monel. These metals readily dissolved in the heated seawater and are then released into the marine environment together with the heated effluent. This adds to the nickel and copper concentrations of these systems. In addition the screens covering the water intake pipes rapidly foul with marine organism, which decrease the flow of water into the plant. The screens have been commonly cleaned by using a concentrated detergent solution or copper sulfate. These cleaning materials have been then released into the contaminated waters in the surrounding.

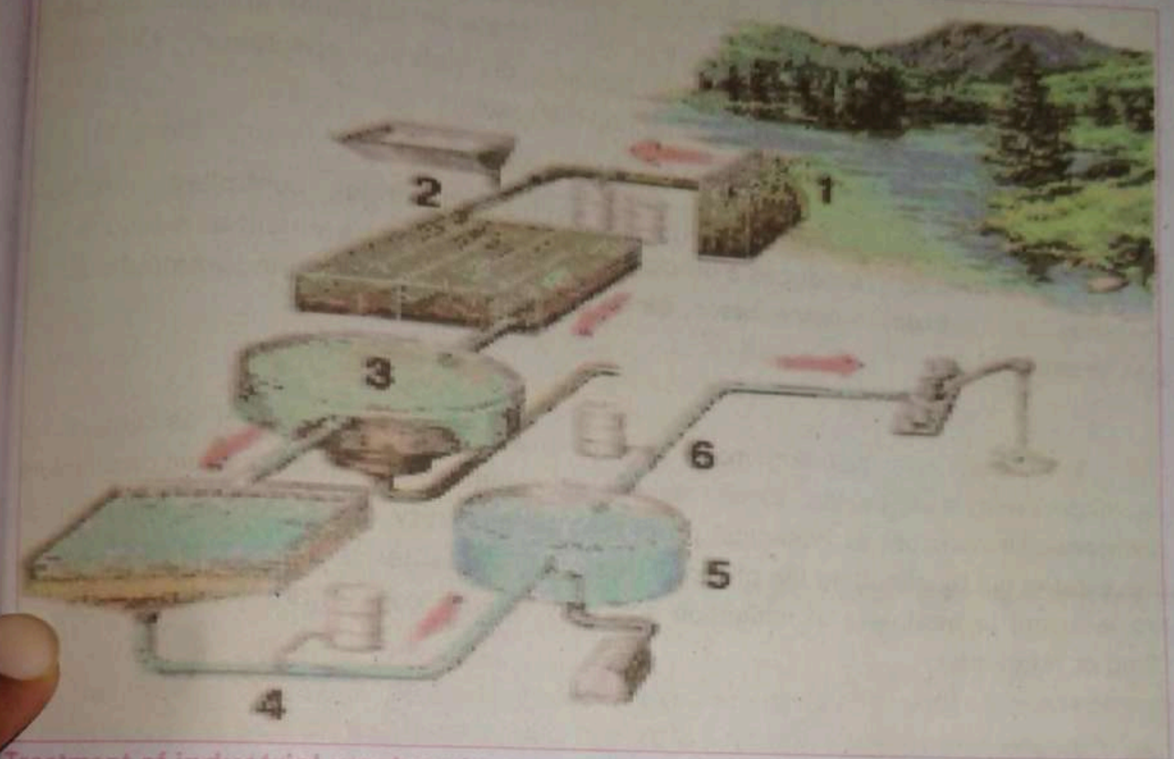
23.3.2. Waste Water Treatment

imp

i) Analysis/Purification of Water

Industrial wastewater treatment covers the mechanisms and processes used to treat waters that have been contaminated in some way by man's industrial or commercial activities prior to its release into the environment or its re-use.

Most industries produce some wet waste although recent trends in the developed world have been to minimize such production or recycle such waste within the production process. However, many industries remain dependent on processes that produce water based waste stream.



Treatment of industrial wastewater

The different types of contamination of wastewater require a variety of strategies to remove the contamination.

1) Solids removal

Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge.

2) Oils and greases

Many oils can be recovered from open water surfaces by skimming devices. However, hydraulic oils and the majority of oils that have degraded to any extent will also have a soluble or emulsified component that will require further treatment to eliminate.

3) Soft organics

Organic material of plant or animal origin is usually possible to treat using extended conventional waste water treatment processes. Problems can arise if the wastewater is excessively diluted with washing. The presence of cleaning agents, disinfectants, pesticides, or antibiotics can have detrimental impacts on treatment processes.

4) Hard organics

Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, cooking products etc can be very difficult to treat. Treatment methods are often specific to the material being treated. Methods include distillation, adsorption, nitrification, incineration, chemical immobilization or landfill disposal.

heat at high temperature

5) Acids and alkalis

Acids and alkalis can usually be neutralized under controlled conditions. Neutralization frequently produces a precipitate that will require treatment as a solid residue that may also be toxic. In some cases, gases may be evolved requiring treatment for the gas stream.

6) Toxic materials

Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by land filling or recycling.

Quick Quiz

1. Briefly describe about oil spillage as a source of water pollution and its effects on environment.
2. Enlist the diseases caused by live stock.
3. How industrial wastes pollute water?
4. How chemicals fertilizers pollute water?
5. How solubility of oxygen in water is reduced by thermal pollution?
6. What is swamp?

Various Parameters of Water Analysis

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Following table will help us to determine the water quality.
Table: Water quality Indicators

Parameters	Signficance	Level
DO (Dessolved Oxygen)	General indicator of water quality; source of O_2 for respiration	Minimum acceptable level, 4-5 mg/liter; 10-15 mg/liter for reproduction of desirable fish

Total suspended solids	Clog fish gills, bury eggs, reduce light penetration, increase heat absorption	Dependent on location
Total dissolved solids	Represents total mineral content which may or may not be toxic	A maximum of 400 mg/liter for diverse fish populations
BOD (Biological Oxygen Demand)	Amount of dissolved oxygen removed during decomposition of organic matter in a given time; a general indicator of contamination due to biodegradable organics.	BOD Water status 1 mg/liter very clean 2 mg /liter Clean 3 mg/liter Fairly clean 5 mg/liter Doubtful 10 mg/liter Contaminated
COD (Chemical Oxygen Demand)	Indicates the concentration of materials oxidizable by chemical reaction	0-5 mg/liter indicates very clean streams
pH	Indicates the addition of acids of bases	pH depends on actual system
Iron	Excessive amounts can clog fish gills; indicates drainage from iron-bearing sediments, mines, industrial processes	A maximum of 1 mg/liter is a common criterion for stream quality
Copper	Indicates drainage from copper-bearing sediment, mines, plating, or other industrial sources	A maximum of 0.02.10 mg/liter is a common criterion for stream quality.
Zinc	Indicates mine drainage or industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Hg, Cd, Pb, Ni, Cr, Ag, etc.	Indicates industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Nitrate	A major plant nutrient; in high-concentrations it can promote excessive plant growth; major sources are fertilizers, sludge, and sewage	
Phosphate	A major plant nutrient; major sources are detergents, fertilizers, sewage	A maximum of 0.03-0.04 mg/liter total inorganic phosphate is a common criterion

23.4. GREEN CHEMISTRY

The term *green chemistry*, coined in 1991, is defined as "the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances."

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or the environment. It has been applied to a wide range of industrial and consumer goods, including paints, dyes, fertilizers, pesticides, plastics, medicines, electronics, dry cleaning, energy generation, and water purification.

Why Green Chemistry?

Green chemistry is effective in reducing the impact of chemicals on human health and the environment. In addition, many companies have found that it can be cheaper and even profitable to meet environmental goals. Profits derive from higher efficiency, less waste, better product quality, and reduced liability. Many environmental laws and regulations target hazardous chemicals, and following all these requirements can be complicated. But green chemistry allows companies to comply with the law in much simpler and cheaper ways. Finally, green chemistry is a fundamental science-based approach. Addressing the problem of hazard at the molecular level, it can be applied to all kinds of environmental issues.

Since 1991, there have been many advances in green chemistry, in both academic research and industrial implementation. For example, **Spinosad**, an insecticide manufactured by fermenting a naturally occurring soil organism, was registered by the EPA as a reduced-risk insecticide in 1997. Spinosad does not leach, bioaccumulate, volatilize, or persist in the environment and in field tests left 70 to 90 percent of beneficial insects unharmed. It has a relatively low toxicity to mammals and birds and is slightly to moderately toxic to aquatic organisms, but is toxic to bees until it dries.

The Twelve Principles of Green Chemistry

The aim of green chemistry is to reduce chemical related impact on human health and virtually eliminate contamination of the environment through dedicated, sustainable prevention programs. Green chemistry searches for alternative, environmentally friendly reaction media and at the same time strives to increase reaction rates and lower reaction temperatures. The green chemistry concept applies innovative scientific solutions to solve environmental issues posed in the laboratory. **Paul T. Anastas**, an organic chemist working in the office of pollution prevention and toxins at the EPA, and **John C. Warner** developed the Twelve Principles of Green Chemistry in 1991. These principles can be grouped into "Reducing Risk" and "Minimizing the Environmental Footprint."

I - Reducing Risk in the Laboratory

Sigma-Aldrich is dedicated to providing alternative products designed with the health and safety of its employees, customers, and the public in mind.

- **Use Safer Chemicals** – Utilize performance chemicals that have the lowest levels of toxicity.

- **Design Less Hazardous Synthesis Methods** – Where feasible, make use of synthetic or biosynthetic methods that pose little or no toxicity to human health and the environment.
- **Use Safer Solvents and Reaction Conditions** – Search for the most up-to-date information on green solvents that will optimize your process and provide a safer working environment.
- **Accident Prevention** – Select substances that minimize the potential for explosions, fires and chemical releases into the environment.

II - Minimizing the Environmental Footprint

The 12 Principles focus on reducing the volumes of chemicals used and pollution prevention.

- **Waste Minimization and Prevention** – Develop chemical synthesis techniques, which reduce or prevent waste. It is better to prevent waste than to clean it up after its creation.
- **Use of Catalysts Instead of Stoichiometric Quantities** – Catalytic reactions inherently use smaller quantities of chemicals to carry out a specified transformation.
- **Reduce the Use of Chemical Derivatives** – The use of protecting groups or other forms of temporary modification of a functionality adds to the total waste incurred in a synthetic route.
- **Synthetic Efficiency (Atom Economy)** – An efficient chemical process ensures the maximum amount of your starting materials is used in the final product so that no atom is wasted.
- **Taking Advantage of Chemicals Designed for Degradation** – Reduce the effect on the environment by using chemicals that are designed to be biodegradable.
- **Establishment of In Process Controls for Pollution Prevention** – To avoid the formation of hazardous substances, adopt real-time analysis and in process monitoring during synthesis.
- **Use of Renewable Feedstocks** – Use raw materials or renewable feedstocks (waste from other processes or products derived from agricultural streams) whenever technically or economically feasible.
- **Encourage Energy Efficiency** – The realization of the economical and environmental impact of energy use in a chemical process and the development of alternative means to reduce the impact.

Quick Quiz

1. What is green chemistry?
2. Give importance of green chemistry.
3. What is depletion of ozone?
4. Give principle of green chemistry.
5. What is synthetic efficiency?
6. Give use of renewable Feed stocks.

Society, Technology and Science

Radiation Pollution

What is radioactive pollution?

Radioactive substances and nuclear radiations produced during nuclear reaction affect our environment adversely and thus radioactive pollution created.

Sources of radioactive pollution and its effects

1. Low level radioactive liquid wastes, radioactive gaseous wastes, and dusts are released during nuclear explosions. The radioactive gaseous wastes are injected into the upper layer of atmosphere where, due to cooling they condense to fine dust particles and thus radioactive cloud is formed. This cloud moves in the direction of the wind, settles down slowly to the surface of the earth and thus pollutes air, water and soil.
2. The radioactive substances produce energy which is so strong that the living cells are damaged or destroyed.
3. People working with radioactive elements develop tumors.
4. Radioactive element like strontium 90 affects our soil and through this human beings and animals are also affected adversely.
5. Nuclear explosions which are operated in sea make sea water polluted. This affects the aquatic life.
6. Among the radioactive radiations, gamma radiations are the most dangerous, since they have high energy and big penetrating power. These radiations can, therefore, pass freely in the human body, where they lose energy, which destroys the living cells by converting them into charged particles (ions). These charged particles are chemically very reactive and hence disrupt cell membrane, reduce the effectiveness of enzymes and even damage genes and chromosomes. All this results in diseases like leakaemania and cancer.
7. We know that in a nuclear reactor U_{235} is used as a nuclear fuel, which undergoes nuclear fission and energy is produced. Nuclear radiations are produced in the

processes viz mining and enrichment of U_{235} taking place in the nuclear reactor. These radiations can leak from the reactor and therefore, damage the health of the human beings and animals.

Control measures for minimizing radioactive pollution

The waste material produced in the mining, enrichment and fission of U_{235} inside the eactor are collectively called nuclear wastes. At present most of the nuclear wastes are being sorted in strong leak proof containers. These will be disposed off whenever a safe method of their disposal is found out.

Using catalytic Converters

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A catalytic converter removes pollutant gases from the exhaust by oxidizing or reducing them. The exhaust gases pass through a converter containing a precious metal catalyst, usually an alloy of platinum and rhodium. Several reactions may take place. NO_x and CO may take part in a redox reaction which neatly removes both of them at the same time: NO_x oxidizes CO to CO_2 and is reduced to harmless nitrogen gas.

$$2NO + 2CO \longrightarrow N_2 + 2CO_2$$

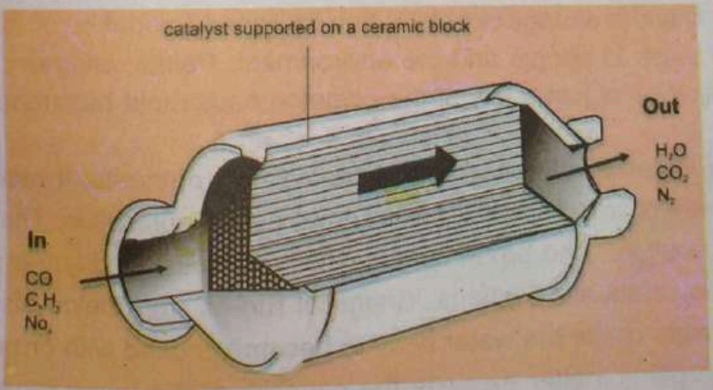
CO and C_xH_x are oxidized by air;

$$2CO + O_2 \longrightarrow 2CO_2$$

$$C_7H_{16} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$$

(Using C_7H_{16} to represent a typical hydrocarbon.)

For all three of these reactions happen, it is necessary to use a three way converter and to have an oxygen monitor fitted to the engine, this checks the quantity of oxygen going into the engine to make sure there is enough to carry out the oxidation reactions.



The overall result of passing exhaust gases through this kind of catalyst system is to convert CO, NO_x and C_xH_y to relatively harmless N_2, CO_2 and H_2O.

The catalytic reactions do not start working until the catalyst has reached a temperature of about 200°C so they are not effective until the engine has warmed up.

Catalyst systems of this type cost several hundred pounds, mainly because of the high cost of the precious metal they contain. The catalyst is poisoned by lead, so unleaded fuel must always be used.

Waste water from household and industries without treatment to river is dangerous

When we think about river pollution, we might assume it comes from places like factories, farms and industry. Waste water from manufacturing or chemical processes in industries contributes to water pollution.. Industrial waste water usually contains specific and readily identifiable chemical compounds yet, in many cases the pollution in our rivers comes from a much less obvious source - our homes. Incorrect plumbing could mean that waste water from dishwashers, washing machines, sinks, baths and even toilets.other impurities includes organic materials and plant nutrients that tend to rot. The main organic materials are food and vegetable waste, plant nutrient come from chemical soaps, washing powders, etc.these flushed directly into a local river. These 'misconnected' pipes are a common cause of pollution to rivers and streams, especially in towns and cities.

There are normally two forms of drainage -surface water and foul water.

Surface water drains, or 'storm drains' carry rainwater from road surfaces and rooftops into local rivers and streams and flows into the river untreated.

Foul water drains carry waste water from toilets, sinks, baths and household appliances to the sewage treatment works. This water is treated before it can safely flow back into river and streams.

Today, many people dump their garbage into streams, lakes, rivers, and seas, thus making water bodies the final resting place of cans, bottles, plastics, and other household products. The various substances that we use for keeping our houses clean add to water pollution as they contain harmful chemicals.

Americans generate 1.6 million tons of household hazardous waste per year. The average home can accumulate as much as 100 pounds of household hazardous waste in the basement or garage and in storage closets. When improperly disposed of, household hazardous waste can create a risk to people and the environment. Paints, cleaners, oils, batteries, and pesticides are examples of just a few of the common household hazardous wastes that need special disposal.

When fresh water is artificially supplemented with nutrients, it results in an abnormal increase in the growth of water plants. This is known as eutrophication. The discharge of waste from industries, agriculture, and urban communities into water bodies generally stretches the biological capacities of aquatic systems. Chemical run-off from fields also adds nutrients to water. Excess nutrients cause the water body to become choked with organic substances and organisms. When organic matter exceeds the capacity of the micro-organisms in water that break down and recycle the organic matter, it encourages rapid growth, or blooms, of algae. When they die, the remains of the algae add to the organic wastes already in the water; eventually, the water becomes deficient in oxygen. Anaerobic organisms (those that do not require oxygen to live) then attack the organic wastes, releasing gases such as methane and hydrogen sulphide, which are harmful to the oxygen-requiring (aerobic) forms of life. The result is a foul-smelling, waste-filled body of water.Untreated sewage effluent in the water causes oxygen levels to drop drastically, sewage fungus covers the bed of the watercourse like a blanket and in more severe cases the river can no longer support fish, insects and animals that live in and around the water.

Polluted water is unsuitable for drinking, recreation, agriculture, and industry. It diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution.

Once an aquifer is contaminated, it may be unusable for decades. The residence time, as noted earlier, can be anywhere from two weeks or 10 000 years.

Alternatives to ozone-depleting halocarbons

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are alternative halocarbons being used to replace ODS (ozone-depleting substances) in industrial and commercial applications and their use is becoming more widespread. Other alternatives to ODS include ammonia, carbon dioxide and hydrocarbons.

The relationship between ozone-depleting substances and their halocarbon alternatives and global warming

Ozone-depleting substances (ODS) and their halocarbon alternatives have a direct global warming potential and contribute to climate change. The production of some ozone depleting substances (e.g. ClFCs) has been ceased worldwide resulting in emission reductions of ozone-depleting substances into the atmosphere. However, emissions of other ODS (e.g. hydrochlorofluorocarbons [HClFCs]) and ODS alternatives (e.g. hydrofluorocarbons [HFCs]) is expected to continue to increase.

HFCs are ODS refrigerants alternatives and their use is becoming more widespread. Although HFCs have no ozone-depletion potential they do have high global-warming potential and are thousands times more potent greenhouse gases than carbon dioxide.

Regulations that prevent or minimize ODS and other halocarbons emissions serve a dual environmental benefit of lowering emissions that destroy the ozone layer and contribute to climate change.

Are ozone-depleting substances still an important environmental concern?

Although the production and use of many ODS has been phased out, the control of ODS emissions continues to be an important environmental issue, as the destruction of the earth's protective stratospheric ozone layer causes increased health risks and environmental impacts, such as cataracts, skin cancer and climate change.

Air Pollution

1. In past there was bull cart, donkey carts animals were used but now a days Aeroplane, cars, buses and trains are used for transportation. These vehicles need energy for their

working in the formal petrol or gas to provide energy for motion of vehicle. The end product of this burning include energy plus different gasses include hydrocarbons, Nitrogen oxides carbon monoxide, sulphur, heavy metals and particles. These gases enter into air and pollute in, when human breath in such polluted environment it causes asthma, coughing nausea, chest pain, bronchitis diseases etc.

2. It is estimated that usually 24000 deaths occur due to air pollution because pollution damage central nervous system.
3. Automobiles are responsible for depletion of ozone in stratosphere sheet because of source of ClFCs entering the atmosphere which is escape from vehicles, air conditions (ACs)

   Vehicles are responsible for 80% pollution in metropolitan region three fold increases in per capita energy consumption for global warming as burning of fuel produces CO_2.
4. Ways to improve impacts of car like uses of small cars, clearer cars, efficient engine catalytic, converters are compulsory and use of biocheral.

   A. Fuel cell cause only water comes out as its exhaust electrical vehicle pose problem because of range of batteries and sepe. Hybrid electric petrol they are providing solution for this pollution they cut down the fuel wastage and effect the high energy fuel on board.

   B. Restricts occurs to the cities or part of cities e.g. Chester York, oxford have driven the apparently to pack ad ride they have given free space for parking at the edge of town.

   C. Improve information about road condition and public transport. Polluter pay is another solution where the pollution emitted by the car is measured and the driver is changed on the buses of level multiplies the distance travel.

Technological changes to reduce cooling zone of engine wall and reduce hydrocarbon and carbon monoxide emission. Computer control at IC engine.

Catalytic converter technology (CCT) emission

Trap oxidizers ad ceramic filter an diesel vehicles

Direct injection fuel efficient diesel

Ozone

Ozone layer is found in the stratosphere approximately 20-40 Km above the earth surface. Ozone molecules have three atoms of oxygen instead of the normal two. The ozone layer protects us from the harmful effects of certain wave lengths of ultra violet (UV) light coming from the sun, especially UV. Any significant decrease in ozone in the atmosphere would result in an increase of UV-radiation reaching the earth surface. Increase in levels at UV- radiation can result in the increase in skin cancer; suppress the immune system, eye disorder including catavart and effect plants, animals and plastic materials.

Ozone Depletion

In 1985, scientists discovered that there is severe ozone depletion in the Antarctic region, which was confirmed by American Satellite observations.

Chlorofluorocarbons (ClFCs) were invented in 1928 found many used in foams, refrigeration, air conditioners, solvent, fire extinguishers etc. these ClFCs are long lied and their emissions reach stratosphere and cause ozone depletion. This has been dramatically confirmed through Antarctic ozone hole.

The United Nations Environment Programme (UNEP) has been addressing the issue of depletion of the ozone layer since 1977 and in 1981 UNEPs Governing Council set up a working group to prepare nine global framework conventions for protection of ozone layer.

By reducing the use of ClFCs we can protect ozone layer for saving the environment from harmful effects.

Montreal protocol on substances the deplete the ozone layer was finally agree upon on 16th September 1987 and adopted by the Government in this protocol ozone depleting substances are banned.

Natural Water Purification Methods

There are several, natural ways that you can purify water.

In the event of an emergency it may become necessary to purify the water that you drink to avoid getting sick. Though many people think purifying water is difficult, there are a number of simple, natural means of purifying water that can easily be used in an emergency.

Sand

- One of the most common ways that water is purified is by passing it through sand and soil. If contaminated water is poured onto fine sand, the water is going to travel down until it reaches the saturation level. The other chemicals that are mixed with the water, though, will be held back by the sand until only the water is left. This is the same method of water purification used in many sewage treatment facilities as a big part of separating water out of the waste that goes through the plant.

Boiling

- Water can be boiled to make it more pure. Boiling water kills bacteria and other germs in the water, which makes it safer to drink. Or, build a water still that functions off boiling. Water is poured into a sealed pot, with a tube leading out of it. The water turns into steam, and the steam escapes through the tube. The tube transports the steam to another container, where the steam condenses back into water. This process can eliminate more contaminants from water (such as salt), but it's also more complicated.

Cloth Filtration

- Cloth filters can be used to help keep larger contaminants out of water. This process is very simple; pour the water through a cloth, or through several layers of cloth, and the cloths' weave will strain the water and hold back impurities. This is the same process that happens when a coffee filter is used, except that the filter is paper rather than cloth. Paper can work as well, and if you have coffee filters or similar devices you can easily use those instead of a clean cloth to strain your water.

How rain water seepage through hazardous waste dumpsites can dissolve in drinking water supplies

Hazardous waste:

Hazardous waste is waste that is dangerous or potentially harmful to our health or the environment. Hazardous wastes can be liquids, solids, gases, or sludges. They can be discarded commercial products, like cleaning fluids or pesticides, or the by-products of manufacturing processes. It is very important to dispose off hazardous waste carefully otherwis it contaminate the air, water, and soil.

Groundwater:

Groundwater is rain water or water from surface water bodies, like lakes or streams, that soaks into the soil and bedrock and is stored underground in the tiny spaces between rocks and particles of soil.

Groundwater contaminants come from two categories of sources: point sources and distributed, or non-point sources. Landfills, leaking gasoline storage tanks, leaking septic tanks, and accidental spills are examples of point sources. Infiltration from farm land treated with pesticides and fertilizers is an example of a non-point source.

- Among the more significant point sources are municipal landfills and industrial waste disposal sites. When either of these occur in or near sand and gravel aquifers, the potential for widespread contamination is the greatest.
- Leaks of petroleum products have been increasing over the last two decades because underground steel tanks installed in large numbers in the 1950s and 1960s have become corroded. Before 1980, most underground tanks were made of steel. Without adequate corrosion protection, up to half of them leak by the time they are 15 years old.
- Groundwater dissolves many different compounds, and most of these substances have the potential to contaminate large quantities of water. For example, one litre of gasoline can contaminate 1 000 000 litres of groundwater. This problem is particularly severe in the Atlantic provinces where there is a high usage of groundwater. In many cases, the problem is noticed long after the aquifer is contaminated, for example, when consumers start tasting or smelling gasoline.

- Groundwater can become contaminated in many ways. Chemicals from hazardous wastes buried in unsecured landfills If rain water or surface water comes into contact with contaminated soil while seeping into the ground, it can become polluted and can carry the pollution from the soil to the groundwater. From here, contaminants can spread to wells or surface water, making it unsafe to drink.
- Groundwater can also become contaminated when liquid hazardous substances themselves soak down through the soil or rock into the groundwater. Some liquid hazardous substances do not mix with the groundwater but remain pooled within the soil or bedrock. These pooled substances can act as long-term sources of groundwater contamination as the groundwater flows through the soil or rock and comes into contact with them.Groundwater contamination is extremely difficult, and sometimes impossible, to clean up.
- Apart from chemical pollutants the major culprits are Bacteria and Viruses which cause most of the commonly found water borne diseases.

  Bacterial diseases: Gastro-enteritis, Typhoid, Cholera, Paratyphoid, Dysentery and Diarrhea.

  Viral diseases: Polio, Dysentery, Gastro-enteritis, Diarrhea and Jaundice (Hepatitis)

Replacing CFC

Few compounds have CFCs combination of non-flammability, non-toxicity and inertness, and for uses such as refrigeration and aerosols, it is necessary to find compounds with exactly the right boiling point.

Some of the important replacements for these uses are the hydrofluorocarbons, HFCs (also known as hydrofluoroalkanes or HFAs.). An example is 1,1,1,2-tetrafluoroethane, CF_3CH_2F, which is used as a refrigerant. HFCs have the advantage that they contain no Cl atoms, so they do not release damaging Cl radicals in the stratosphere. Moreover, their molecules include C-H bonds, which are relatively reactive, which means that these compounds break down in the atmosphere more quickly than CFCs so they do not persist for so long.

Key Points

- Actually our atmosphere has been divided into four layers:
- 1- Troposphere 2- Stratosphere 3- Mesosphere 4- Thermosphere.
- Photochemical smog is formed only when the atmosphere contains soot particles, hydrocarbons and oxides of nitrogen (mainly NO_2).

- H_2SO_4, HNO_3 and H_2CO_3 formed in air come down the atmosphere as acid rain or acid snow.
- In automobiles during incomplete combustion of petrol, we get smoke of different gases which pollute our atmosphere. The engines used in these motor vehicles are called internal combustion engines.
- When petrol burns in a car engine, a very high temperature is produced. At this high temperature, N_2 and O_2 present in air of the engine combine together and form NO and NO_2. These gases pollute the air.
- Nuclear tests being conducted in the world generate high temperature. At high temperature, atmospheric nitrogen is favorably oxidized to NO. NO thus formed destroys ozone layer.
- By keeping the vehicle properly tuned for the optimum ignition of fuels. This method also prevents air pollution caused by CO and hydrocarbons present in the exhaust fumes of the vehicles.
- Use of fluoro-chloro carbons (e.g. Freon-1 and Freon-12) as aerosol spray propellant destroys the O_3 layer, as oxides of nitrogen do.
- Water gets polluted by: accidental oil spills, leakage from cargo oil tankers in sea, tanker trucks, pipelines leakage during offshore exploration, leakage of under ground storage tanks
- Polycyclic hydrocarbons are carcinogenic even at very low concentration. Marine animals are seriously affected by soluble aromatic fractions of oil. The spilled oil damages the feather of the birds or fur of animals and sometimes causes their death.
- Surfactants are organic compounds having polar or hydrophilic groups such as $-COOH$, $-SO_3H_2$, NH_4^+ or non-polar or lyophilic groups soluble in water.
- The waste heat from electrical generating stations is transferred to cooling water obtained from local water bodies such as a river, lake, or ocean.
- Water purification is a process of removing harmful substances and odor from a raw water source.

Exercise - 1

1: Select the right answer from the choices given with each question.

i. Air is polluted by:

a. Toxic materials b. Hydrocarbons c. Harmful gases [✓ d. All of above]

ii. Which of following gas is not pollution?

a. SO_2 b. CO [✓ c. CO_2] d. NO_2

iii. Oxides of sulfur and nitrogen react with oxygen to form:

a. Bases [✓ b. Acids] c. Salts d. All of above

iv. Oxidizing smog consists of high concentration of:

a. SO_2 [✓ b. Ozone] c. NO_2 d. Cl_2

v. Thickness of ozone is:

[✓ a. 20-25KM] b. 25-28Km c. 30-32Km d. 20-30Km

vi. Ozone is destroyed by:

a. SO_2 b. NO_2 [✓ c. Chlorofluorocarbons] d. None of above

vii. In leather industry:

[✓ a. Chromium (IV) is used] b. Chromium (III) is used c. Nickel is used
d. Aluminum is used

viii. Water is purified:

a. Aeration b. Coagulation c. Disinfection [✓ d. All of above]

ix. The Ecosystem is the smaller unit of:

[✓ a. Biosphere] b. Lithosphere c. Atmosphere d. Hydrosphere

x. When chlorine is passed through water then the disinfection is done due to the production?

a. HCl [✓ b. HOCl] c. NOCl d. $HClO_4$

xi. Peroxyacetylnitrate (PAN) is an irritant to human beings and it affects

[✓ a. eyes] b. ears c. stomach d. nose

xii. Fungicides are the pesticides which

[✓ a. control the growth of fungus] b. kill insects c. kill plants d. kill herbs

2: Give brief answers for the following questions.

i. What are the components of Environment?

ii. Briefly discuss the role of atmosphere in our environment..

iii. What are the sources of air pollution?

iv. What are the important air pollutants?

v. What are the sources of CO emission? Discuss its effects.

vi. Differentiate between:

  (i) Industrial and Photochemical Smog.

  (ii) Primary and Secondary Pollutants.

vii. How does photochemical smog differ from reducing smog?

viii. What is global warming?

ix. What are the latest predictions about global warming?

x. What gases are responsible for greenhouse effect?

xi. Briefly discuss the effects of acid rains.

xii. What are different sources and Environment effects of:

  (i) VOCs (ii) PAN

xiv. What are the effects of excess of CO_2 present in the atmosphere.

xv. Discuss the sources and typical effects of SO_2 as pollutant.

xvi. Briefly discuss the sources and typical effects of oxides of nitrogen (NO_x).

xvii. What is ozone? How does it work as safeguard?

xviii. How ozone is formed in stratosphere?

xix. What do you know about "ozone hole"?

xx. How is ozone layer depleting?

xxi. What are the effects of ozone layer depletion?

xxii. What should we do to save ozone?

xxiii. What is water pollution? Write different types of water pollutants.

xxiv. Briefly discuss the effects of water pollution.

xxv. How preliminary treatment of waste water is done?

xxvi. What is primary treatment of waste water?

xxvii. What is secondary treatment of waste water?

xxviii. How would you avoid from thermal pollution?

Give detailed answers for the following questions.

i. Describe different chemical reaction occurring in our atmosphere.

ii. Write a comprehensive note on acid rain.

iii. How would you control air pollution? Describe different methods.

iv. What is Thermal Pollution? Discuss its sources and environmental effects.

v. What is waste water treatment? Discuss different methods of it.

vi. Write a note on Green Chemistry.

24

ANALYTICAL CHEMISTRY

After completing this lesson, you will be able to:

This is 16 days lesson (period including homework)

- Compare the classical method of analysis with modern methods.
- Discuss the procedure of combustion analysis
- Define spectroscopy and discuss its application in analytical chemistry
- State the regions of electromagnetic spectrum used in IR and UV/vis spectroscopy
- Explain the origin of IR absorption of simple molecules.
- Determine structure of phenol toluene, acetone and ethanol from its IR spectrum. (Analyzing)
- Predict whether a given molecule will absorb in the UV/visible region. (Analyzing)
- Predict the color of a transition metal complex from its UV/visible spectrum. (Analyzing)
- Outline in simple terms the principles of proton NMR spectroscopy.
- Explain how chemical environment of a Proton affects the magnetic filed. It experiences and hence the absorption of energy at resonance frequency
- Describe standard scales used in proton NMR
- Explain instrumentation and working of MS.
- Outline the use of MS in determination of relative isotopic masses and isotopic abundance
- Define and explain atomic emission and atomic absorption spectrum.

Reading

INTRODUCTION

Analytical chemistry is the branch of chemistry that deals with separation and analysis of a sample to identify its components. The separation is carried out prior to qualitative and quantitative analysis. **Qualitative analysis** provides the identity of a substance (composition of chemical species). On the other hand, **Quantitative analysis** determines the amount of each components present in the sample. Hence, in this branch different techniques and instruments used for analysis are studied. The scope of this branch covers food, water, environmental and clinical analysis.

24.1 CLASSICAL METHOD OF ANALYSIS

I - Combustion Analysis and determination of Molecular Formula

Empirical and molecular formulas for compounds that contain only carbon and hydrogen (C_aH_b) or carbon, hydrogen, and oxygen ($C_aH_bO_c$) can be determined with a process called combustion analysis. The sole products will be CO_2 and H_2O and these two products of combustion are separately collected.

Procedure:

The steps for this procedure are:

- Weigh a sample of the compound to be analyzed and place it in the apparatus shown in the image below.
- Burn the compound completely. The only products of the combustion of a compound that contains only carbon and hydrogen (C_aH_b) or carbon, hydrogen, and oxygen ($C_aH_bO_c$) are water and carbon dioxide.
- The H_2O and CO_2 are drawn through two tubes. One tube contains a substance that absorbs water, and the other contains a substance that absorbs carbon dioxide. Weigh each of these tubes before and after the combustion. The increase in mass in the first tube is the mass of H_2O that formed in the combustion, and the increase in mass for the second tube is the mass of CO_2 formed.
- Assume that all of the hydrogen in the compound has been converted to H_2O and trapped in the first tube. Calculate the mass of hydrogen in the compound from the mass of hydrogen in the measured mass of water.
- Assume that all the carbon in the compound has been converted to CO_2 and trapped in the second tube. Calculate the mass of carbon in the compound from the mass of carbon in the measured mass of CO_2 formed.
- If the compound contains oxygen as well as carbon and hydrogen, calculate the mass of the oxygen by subtracting the mass of carbon and hydrogen from the total mass of the original sample of compound.
- Use this data to determine the empirical and molecular formulas in the usual way.

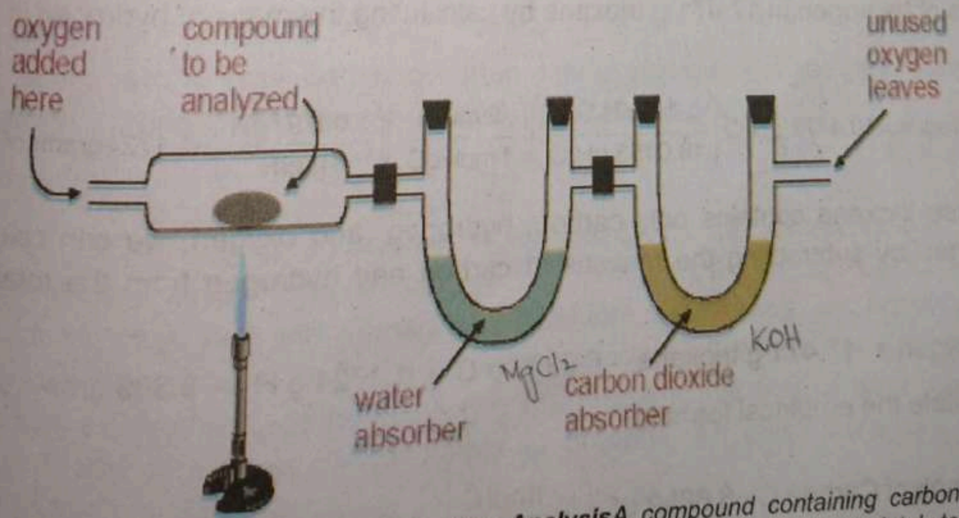


Fig 24.1 Apparatus for Combustion Analysis *A compound containing carbon and hydrogen (C_aH_b) or carbon, hydrogen, and oxygen ($C_aH_bO_c$) is burned completely to form H_2O and CO_2. The products are drawn through two tubes. The first tube absorbs water, and the second tube absorbs carbon dioxide.*

To illustrate how empirical and molecular formulas can be determined from data derived from combustion analysis, lets consider a substance called trioxane. Formaldehyde, CH_2O, is unstable as a pure gas, readily forming a mixture of a substance called trioxane and a polymer called paraformaldehyde. That is why formaldehyde is dissolved in a solvent, like water, before it is sold and used. The molecular formula of trioxane, which contains carbon, hydrogen, and oxygen, can be determined using the data from two different experiments. In the first experiment, 17.471 g of trioxane is burned in the apparatus shown above, and 10.477 g H_2O and 25.612 g CO_2 are formed. In the second experiment, the molecular mass of trioxane is found to be 90.079.

We can get the molecular formula of a compound from its empirical formula and its molecular mass. To get the empirical formula, we need to determine the mass in grams of the carbon, hydrogen, and oxygen in 17.471 g of trioxane. Thus, we need to perform these general steps.

- First, convert from the data given to grams of carbon, hydrogen, and oxygen.
- Second, determine the empirical formula from the grams of carbon, hydrogen, and oxygen. 44g of CO_2 containC=12g
- Third, determine the molecular formula from the empirical formula and the given molecular mass.

Because we assume that all the carbon in trioxane has reacted to form CO_2, we can find the mass of carbon in 17.471 g trioxane by calculating the mass of carbon in 25.612 g CO_2.

$$\text{Weight of Carbon} = 25.612\ \cancel{gCO_2}\left(\frac{1\ \cancel{molCO_2}}{44.010\ \cancel{gCO_2}}\right)\left(\frac{1\ \cancel{molC}}{1\ \cancel{molCO_2}}\right)\left(\frac{12.011 gC}{1\ \cancel{molC}}\right) = 6.6899\ \text{grams of Carbon}$$

Because we assume that all of the hydrogen in trioxane has reacted to form H_2O, we can find the mass of hydrogen in 17.471 g trioxane by calculating the mass of hydrogen in 10.477 g H_2O.

$$\text{Weight of Hydrogen} = 10.4777\ \cancel{gH_2O}\left(\frac{1\ \cancel{molH_2O}}{18.0153\ \cancel{gH_2O}}\right)\left(\frac{2\ \cancel{molH}}{1\ \cancel{molH_2O}}\right)\left(\frac{1.00797\ gH}{1\ \cancel{molH}}\right) = 1.1724\ \text{grams of Hydrogen}$$

Because trioxane contains only carbon, hydrogen, and oxygen, we can calculate the mass of oxygen by subtracting the masses of carbon and hydrogen from the total mass of trioxane.

Weight of Oxygen = 17.471 g trioxane - 6.9899 g C - 1.1724 g H = 9.309 grams of Oxygen

We now calculate the empirical formula.

$$\text{No of mols of Carbon } C = 6.6899\ \cancel{gC}\left(\frac{1 molC}{12.011\ \cancel{gC}}\right) = 0.58196\ molC \div 05818 \cong 1 molC$$

$$\text{No of mols of Hydrogen } H = 1.1724\ \cancel{gH}\left(\frac{1\text{molH}}{1.00797\ \cancel{gH}}\right) = 1.1631\text{molH} \div 05818 \cong 2\text{molH}$$

$$\text{No of mols of Oxygen } O = 9.309\ \cancel{gO}\left(\frac{1\text{molO}}{15.9994\ \cancel{gO}}\right) = 0.5818\text{molC} \div 05818 \cong 1\text{molO}$$

The empirical formula is CH_2O, which can be used to calculate the molecular formula.

Empirical formula mass = 1(12.011) + 2(1.00794) + 1(15.9994) = 30.026

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079}{30.026} \cong 3$$

Molecular formula $C_3H_6O_3$

Drawback:

The classical method i.e. combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen. So there is a need of such methods which explain/find all types of atoms/elements present in an organic compounds. So now modern methods are used which are being discussed in next topic.

Quick Quiz

1. Give difference between qualitative and quantitative analysis.
2. Name the products obtained by complete combustion of hydrocarbon.
3. How mass of oxygen is calculated if it also present along with carbon and hydrogen?
4. Give general steps use to calculate empirical formula.
5. Give drawback of combustion analysis.

24.2. MODERN METHODS OF ANALYSIS

Spectroscopy involved using instruments to examine the radiation emitted or absorbed by chemicals giving information about their molecular structure.

Spectroscopy

Define and Name spectroscopy method (s)

The branch of science which describes the interactions of electromagnetic radiation with matter is known as spectroscopy. It means, it is the area of study that represents molecular structure with electromagnetic radiation. Electromagnetic radiation is the form of energy commonly known as radiation energy such as light energy. According to quantum mechanics, electromagnetic radiation has the properties of both a wave and a particle, like discrete packet of energy, called quanta or photons. An electromagnetic radiation can be characterized in different ways;

Wavelength: The distance between two successive crests or troughs of a wave in a beam of radiation is called wavelength and is denoted by ʎ (lambda). The units commonly used for wavelength are angstrom, nanometer, micrometer and meter (1m=106 µm = 109 nm = 1010 °A).

Frequency: The number of waves passing through a point on the path of a beam of radiation per second is called frequency and is denoted by V (nu). It is expressed in hertz (Hz) or cycles per second (cps). (1 Hz = 1 cps).

Wave number: It is the number of waves passing per centimeter. A common unit for v¯s is the reciprocal centimeter (cm^{-1}).

Energy: Electromagnetic radiation can be characterized in terms of energy possessed by each photon of radiation. The SI unit is joule (J). Each photon has an energy which is proportional to the frequency of light.

Cosmic rays, gamma rays, X-rays, ultraviolet, visible light, infrared rays, microwaves and radio waves, all are electromagnetic radiation. Electromagnetic spectrum covers a wide range of wavelengths and the radiations of different wavelengths have different characteristics. The whole electromagnetic spectrum can be conveniently divided into several regions, each region can be defined by the limits of any of the four parameters, i.e., wavelength, frequency, wave number or energy.

Table 24.1 Ranges of electromagnetic radiations in spectral region;

Spectrum region	Wavelength	Frequency (Hz)	Wavenumber (cm^{-1})	Energy (J)
Cosmic rays	10^{-4} ^{0}A	$3x10^{22}$	10^{12}	2×10^{-11}
	10^{-3} ^{0}A	$3x10^{21}$	10^{11}	2×10^{-12}
Gsmma rays	10^{-1} ^{0}A			2×10^{-14}
	10^{-4} ^{0}A	$3x10^{19}$	10^{9}	
X-rays	100 ^{0}A (10nm)	$3x10^{16}$	10^{6}	2×10^{-17}
Ultraviolet	400 nm	$7.5x10^{14}$	2.5×10^{4}	5×10^{-19}
Visible	800nm	$3.8x10^{14}$	1.3×10^{4}	2.5×10^{-19}
Infrared	10^{3} µm	$3x10^{11}$	10	2×10^{-22}
Microwave	10^{6} µm (1m)	$3x10^{8}$	10^{-2}	2×10^{-25}
Radiowave	10^{3} m	$3x10^{5}$	10^{-5}	2×10^{-28}

Principle of Spectroscopy:

All organic compounds interact with electromagnetic radiation, that is, they absorb energy. When a molecule absorbs energy, a transformation occurs. Lower energy radiation may cause a molecular radiation, or a bond vibration. Higher energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

Whether the transformation involves molecular rotation, bond vibration, or electronic transition, the molecule absorbs only the wavelength, of radiation with exactly the energy necessary for the transition. The absorption of wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule. By measuring the absorption spectra of known compounds we can correlate the wavelengths of energy absorbed with characteristic structure feature. This information is then used to determine the structure of unknown compounds.

Spectrophotometer:

The instrument used to measure the amount of electromagnetic radiation absorbed by a compound is called spectrophotometer or spectrometer. It consists of light source of radiatin, with a prism that can select the desired wavelengths which are passed through a sample of the compound being investigated. The radiation that is absorbed by the sample is detected and is recorded on a char against the wavelength or wave number. Absorption peaks are plotted as minima in infrared, and usually as maxima in ultraviolet spectroscopy.

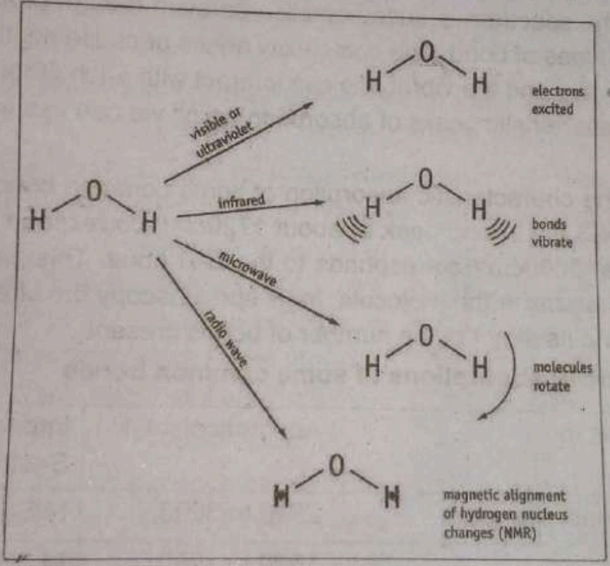


Fig. 24.2: Effect of different types of radiation on the water molecule

Infrared Spectroscopy (IR)

Wavelengths in IR region extends from 2.5 to 16 μm (4000 to 625 cm-1). Although this radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate. The molecular motion that is affected by the absorption of quanta of the infrared radiation is the vibrational motion. The studies of vibrational spectra of molecules lead to the information on the flexibility of the molecules. The small displacement of the constituent atoms from their equilibrium positions can be seen in term of vibrational motion of the atoms. Such changes in the bond-length produce a change in the dipole moment of a heteronuclear molecule and if the oscillating dipole couples with the electrical field of the radiation an exchange of energy takes place. For example in figure 24.3 shows the spectrum of propanone (CH_3COCH_3).

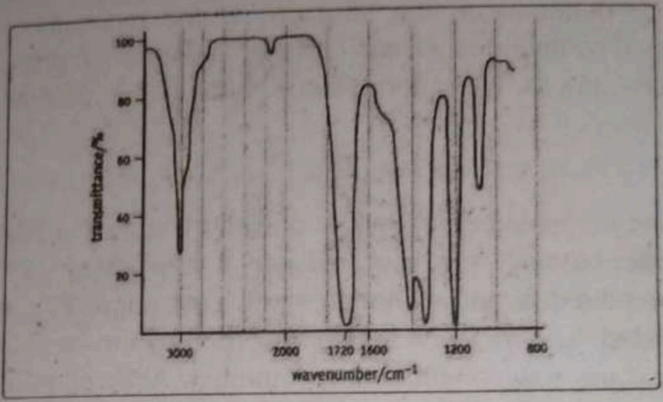


Figure 24.3: The infrared spectrum of propanone

You will see that the spectrum is quite complicated even though propanone is a simple molecule with only three types of bond. The complexity arises because each bonds can vibrate in a number of different ways and the vibrations can interact with each other. Nevertheless it is possible to see some characteristic peaks of absorption which we can use to identify functional groups in the molecule.

Table 24.2 gives the characteristic absorption of some common bonds. In the spectrum of propanone in figure 24.3 the strong peak at about 1720cm^{-1} corresponds to the C=O bond. The weaker absorption at 3000cm^{-1} corresponds to the C-H bond. This peak is weaker even though there are more H atoms in the molecule: in IR spectroscopy the strength of the peak is a characteristic of the bond itself not of the number of bonds present.

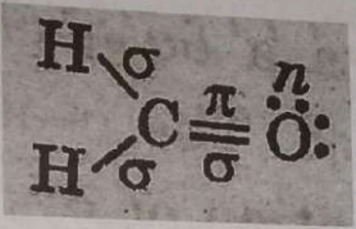
Table 24.2: Characteristic IR absorptions of some common bonds

Bond	Compound it is in	Absorption/cm-1	Intensity (M=medium, S=strong)
C—H	Alkanes, alkenes, arenes	2840 to 3095	M/S
C═C	alkenes	1610 to 1680	M
C═O	Aldehydes, ketones, acids, esters	1680 to 1750	S
C—O	Alcohols, ethers, esters	1000 to 1300	S
C≡N	nitriles	2200 to 2280	M
C—Cl	Chloro compound	700 to 800	S
O—H	free	3580 to 3670	S
	Hydrogen-bonded in alcohols, phenols	3230 to 3550	S (broad)

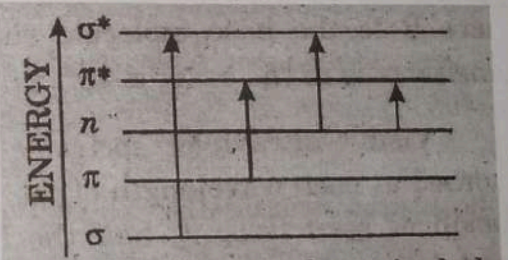
	Hydrogen-bonded in acids	2500 to 3300	M (broad)
N—H	Primary amines	3100 to 3500	S

Visible and Ultravoilet Spectroscopy (UV-VIS)

In ultraviolet-visible spectroscopy, the absorption of ultraviolet (200-400 nm) and visible (400-750 nm) radiation by molecules is associated with the extraction of loosely held electrons (such as unshared electrons or electrons in a π bond) from a lower-energy, occupied molecular orbital (MO) to a higher energy unoccupied molecular orbital (MO*). There are three kinds of electrons, these in δ bonds, these in π bonds and unshared electrons which are denoted by the letter for nonbonding e.g;



On absorbing energy any of these electrons can enter excited states, which are either anti-bonding δ^* or π^*. All molecules have δ and δ^* orbitals, but only those with π orbitals have π^* orbitals. Only the n $\quad\pi^*$, $\pi \quad \pi^*$, and more rarely the n $\quad\delta^*$ excitations occur in the near ultraviolet and visible regions, which are the available regions for ordinary spectrophotometers.



Relative energy changes involved in various electronic transitions

Figure no. 24.4:

The energy required for $\delta \quad \delta^*$ transition is very high and therefore, occurs it, in the vacuum UV region (below 200 nm) which is not usually accessible in most UV-Vis spectrophotometers. The relative energy for 3 electrons transitions detectable by UV spectrophotometer in order of increasing ΔE is n $\quad \pi^* < \pi \quad \pi^* <$ n $\quad \delta^*$. In fact, the absorption of UV-Vis radiation by a molecule results in the electronic transition from highest occupied MO to the lowest unoccupied MO (molecular orbital).

Interesting Information

Most of the compounds of transition elements are colored. The color of these compounds can often be related to incompletely filled d-orbitals in the transition metal ion.

In general, when light hits a substance, part is absorbed, part is transmitted (if the substance is transparent) and part may be reflected.

If all the incident radiation is absorbed then the substance look black. If all the incident radiation is reflected then the substance look white. On the other hand if only a very small proportion of the incident white light is absorbed and if all the radiation in the visible region of the spectrum are transmitted equally then the substance will appear colorless.

Quick Quiz

Look at the visible/UV spectrum of methylene blue in figure 24.5

1. What colors of visible light does methylene blue absorb?
2. Explain why methylene blue has a blue color.
3. How can we get information about a compound using UV/visible spectroscopy?
4. Give color of following wavelength (i) 600-620 (ii) 490-520

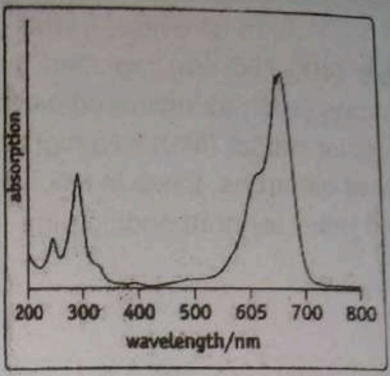


Figure 24.5: The visible/UV spectrum of methylene blue

Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR), as the name implies, is concerned with the magnetic properties of certain atomic nuclei. All nuclei carry a charge, and some of them also spin about their axes in a manner that is analogous to that in which electrons spin about their axis. The nuclei whose spin quantum number is zero, do not spin. The symbol '*I*' is used to denote the spin quantum number of a nucleus.

The Nuclear Magnet: A spinning charge, whether positive or negative, consisting a circular current which generates a magnetic dipole along the spin axis. Since all nuclei carry a charge, a spinning nucleus behaves as a tiny bar magnetic, called nuclear magnet, placed along the spin axis, and has a characteristic magnetic moment, μ. In the absence of an external magnetic field, the nuclear magnets are oriented in a random fashion. However, if they are placed under the influence of a uniform external magnetic field, they can take up different orientations with respect to the applied magnetic field in a quantized system. According to the quantum mechanics, the number of possible orientations of a nuclear magnet in an applied magnetic field in an applied magnetic field is determined by the spin quantum number of the nucleus and is given by $(2\ell + 1)$.

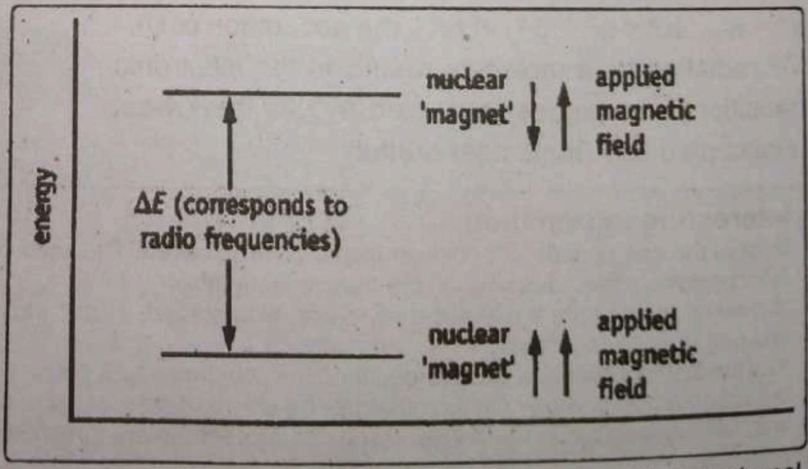


Figure 24.6 Two alignment of the nuclear magnet in an external magnet field. The energy difference between the two orientations is the basis of the technique of NMR

The absorption of electromagnetic radiation by a nucleus, to induced spin-flipping will take place when the frequency of the electromagnetic radiation is exactly equal to the processional frequency of the nucleus, i.e., the two frequencies are in resonance; hence the term nuclear magnetic resonance (NMR).

Instrumentation

There are two types of spectrophotometers which are commonly used for the NMR study:

(i) Continuous Wave (CW) NMR spectrophotometer

(ii) Fourier Transform (FT) NMR spectrometer

In CW-NMR spectrophotometer, the frequency of the electromagnetic radiation is kept constant and the strength of the applied magnetic field is gradually varied to sequentially bring the processional frequencies of all the nuclei in response with the frequency of the electromagnetic radiation. The spectrum is recorded directly as absorption verses frequency, and it takes several minutes to complete. In the FT-NMR spectrophotometer, the strength of the applied magnetic field is kept constant and the radio-frequency is applied as a single short-duration (microseconds) powerful pulse (a burst of radio-frequency energy) which effectively covers the whole frequency range to be studied. The signal detected in this case is recorded, digitized and stored in a computer as an array of numbers. Fourier Transformation (a mathematical treatment form as a CW spectrum. In the CW-NMR spectrophotometer, we measure the radiant energy which is absorbed, whereas in the FT-NMR spectrophotometer it is the energy emitted by the relaxing nuclei which is measured. Thus, the CW-NMR experiment provides an absorption spectrum, whereas the pulsed FT-NMR experiment provides an emission spectrum.

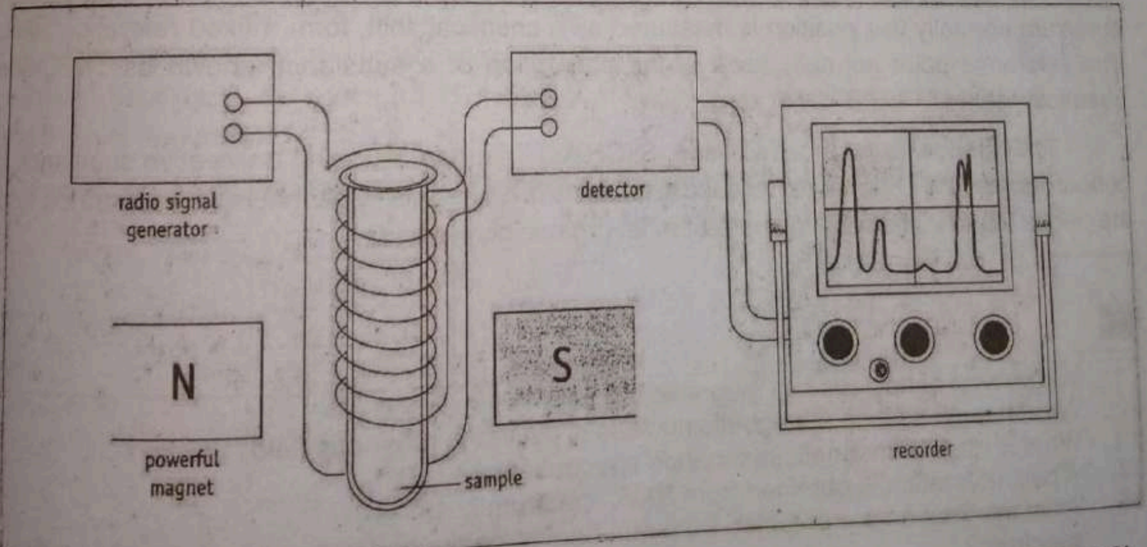


Figure 24.7. A simplified NMR spectrometer. The sample is dissolved in a solvent such as H_2O or CCl_4 which does not have nuclear magnetic properties.

The technique of NMR is particularly useful for identifying the number and type of hydrogen atoms (^1H) in a molecule. It is also used to find the position of carbon atoms. The common isotope of carbon, ^{12}C does not have a nuclear magnet but natural carbons contains 1% of the ^{13}C isotope which does show magnetic behavior and can be identified using NMR.

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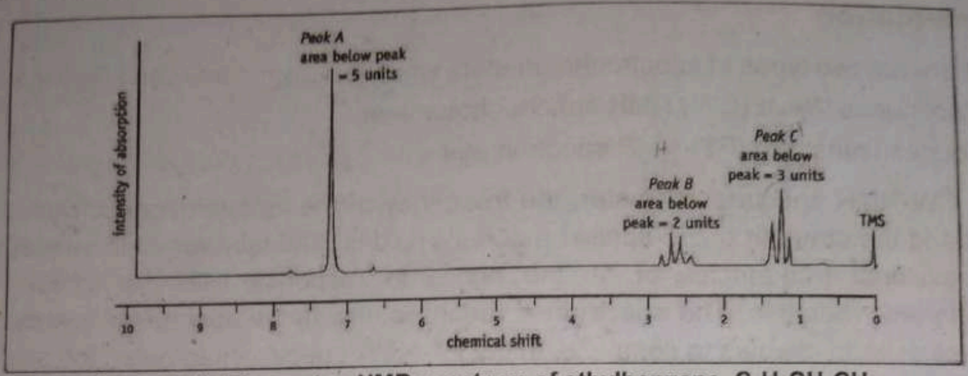

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Figure 24.8: The proton NMR spectrum of ethylbenzene, $C_6H_5CH_2CH_3$

Figure 24.8 shows the NMR spectrum of ethylebenzene $C_6H_5CH_2CH_3$. This is a proton NMR spectrum: the frequencies correspond to the absorption of energy by ^1H nuclei, which are protons. Notice that there are three major peaks of differing heights. Each peak corresponds to H atoms in a different molecular environment. This area under each peak is proportional to the number of that type of H atom in the molecule. The largest peak (A) corresponds to the 5 H atoms in C_6H_5, the benzene ring. The second largest (C) corresponds to the 3 H atoms in the –CH_3 group and the third peak (B) corresponds to the 2 H atoms in the CH_2 group.

The H atoms in a particular type of environment have similar positions in the NMR spectrum normally this position is measured as a chemical shift, form a fixed reference point. The reference point normally used is the absorption of a substance known as TMS. The chemicals shift of TMS is set at zero.

(P TMS stands for tetramethylsilane, $Si(CH_3)_4$. This non-toxic and uncreative substance is chosen as the NMR reference because its protons give a single peak that is well separated from the peaks found in the NMR spectra of most organic compounds.

Quick Quiz

1. Which type of nucleus has magnetic field?
2. What happens when a magnetic nucleus is placed in magnetic field?
3. What is nuclear magnetic resonance spectroscopy?
4. What information is obtained from NMR spectrum?
5. What information are obtained from numbers of peaks and area under peaks in NMR spectrum?
6. What is NMR reference?
7. Why does splitting of peaks occur?

(A) Atomic Emission Spectroscopy

Atomic emission spectroscopy pertains to electronic transitions in atoms which use ~~and~~ an excitation source like flames sparks. Emission spectroscopy is related to atoms. Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.

Principle

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy, E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy $h\nu$ is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

Types of Spectrum;

Spectrum may be classified as;

1. Continuous Emission Spectrum.
2. Line or Atomic Emission Spectrum.

1. Continuous Emission Spectrum

When a narrow beam of white light is passed through a prism, it spreads out into a band of seven colours on the screen. The seven colours diffuse into each other. The boundary lines between the colours cannot be marked. This type of spectrum is called a Continuous Emission Spectrum.

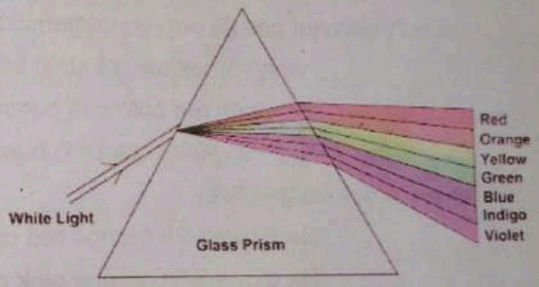

Table 24.3: The approximate wavelengths of visible radiation of different colours.

Colour	Approximate wavelength/nm
Infrared	Above 700
Red	620-700
Orange	600-620
Yellow	580-600
Green	520-580
Blue-green	490-520
Green-blue	440-490
Indigo	420-440

Violet	400-420
Ultraviolet	Below 400

2. Atomic or Line Emission Spectrum:

When an element is vaporized in a flame, or in an electric arc or in a discharge tube, it emits a light of characteristic colour. The resolution of ray of this light produces coloured lines separated by dark spaces. This type of separation is called a line emission spectrum.

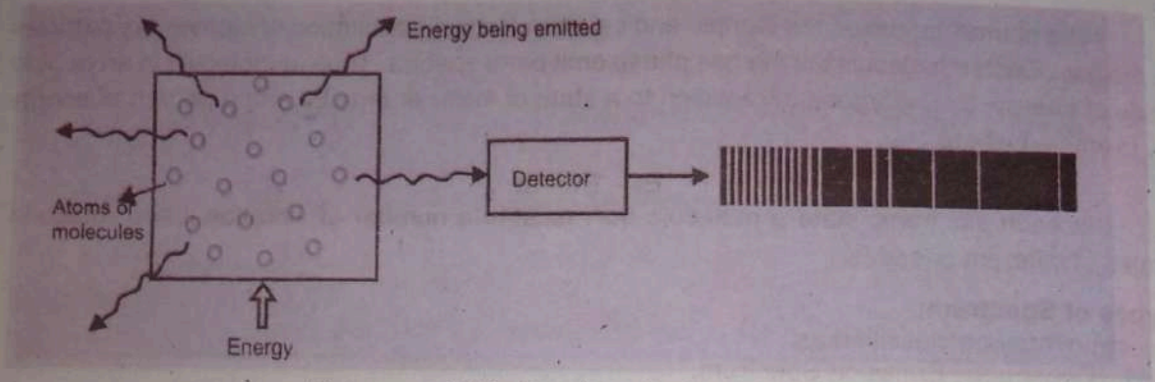

Figure no. 24.9: Atomic emission spectrum

Each element has its own characteristic colour by which it can be identified i. e.,

Na gives yellow colour in bunsen flame.

Sr gives red colour in bunsen flame.

K gives violet colour in bunsen flame.

Similarly in a discharged tube;

Ne glows with orange red colour.

He glows with orange pink colour.

H_2 glows with orange red and blue colour.

Cl_2 glows with orange green colour.

The lines in the spectrum of an element are not haphazardly distributed but they occur in groups or series. In series the separation between them decreases regularly as their wave length decreases. At a certain limiting value, the spectrum becomes continuous.

Advantages of Emission Spectroscopy

Emission method is extremely important in analysis

1) This technique is highly specific
2) This method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration.
3) Even metalloids have been identified by this technique.
4) This analysis can be performed either in solid or liquid state with almost equal convenience.

5) This technique requires minimum sample preparation as a sample can be directly introduced in to the spark.

6) The technique provides results very rapidly. If automated, time required is just 30 sec to one minute.

7) This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, environmental and biological samples.

Disadvantages of Emission Spectroscopy

1) The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.
2) Recording is done on a photographic plate which takes some time to develop, print and interpret the results.
3) Radiation intensities are not always be reproducible.
4) Relative error exceeds 1 to 2 %.
5) The accuracy and precision are not high.

Applications:

1) Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes.
2) Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analyzed.
3) Lubricants oils have been analyzed for Ni, Fe, Cr, Mn, Si, Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and tear need for engine overhaul.
4) In petroleum industry oil is analyzed for V, Ni, Fe the presence of which makes fuel poor.
5) Solid samples and animal tissues have been analyzed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc.
6) Emission spectroscopy has been used to detect 40 elements in plants and soil. Thus metal deficiency in pants and oil can be diagnosed.
7) The following materials have been analysed by emission spectroscopy:
    - i. Trace and major constituents in ceramics.
    - ii. Traces of Co, Ni, Mo and V in Graphite.
    - iii. Trace metal impurities in analytical regents.
    - iv. Trace of Ca, Cu, Zn in blood.
    - v. Zinc in pancreatic tissues.

Quick Quiz

1. Define atomic emission spectroscopy.
2. What is meant by excitation of molecule?
3. Name those elements which can analyze by emission spectroscopy.
4. How emission spectroscopy apply in metallurgy?

(b) Atomic Absorption Spectroscopy (AAS):

The technique has been particularly useful in the determination of trace metals in liquids. The versatility of AAS can be realized from the fact that 60-70 elements have been analyzed by this method in concentration as low as 1 ppm. The greatest advantage of AAS is the analysis of one metal in the presence of another metal, thus saving time and eliminating error.

Principle:

When white light is allowed to pass a sample of a substance, it may absorb radiation of a particular wave length. There will be a dark space in the continuous spectrum of white light for that particular wave length. This spectrum is called a line or atomic absorption spectrum.

A substance which absorbed a particular radiation in normal state will emit the radiation in excited state. The emission lines and absorption lines will be exactly at the same place in the spectrum. For example H_2 gas gives red colour spectrum in excited state. In normal state it absorbs the red colour. Thus there will be a dark line in place of red colour in the continuous spectrum.

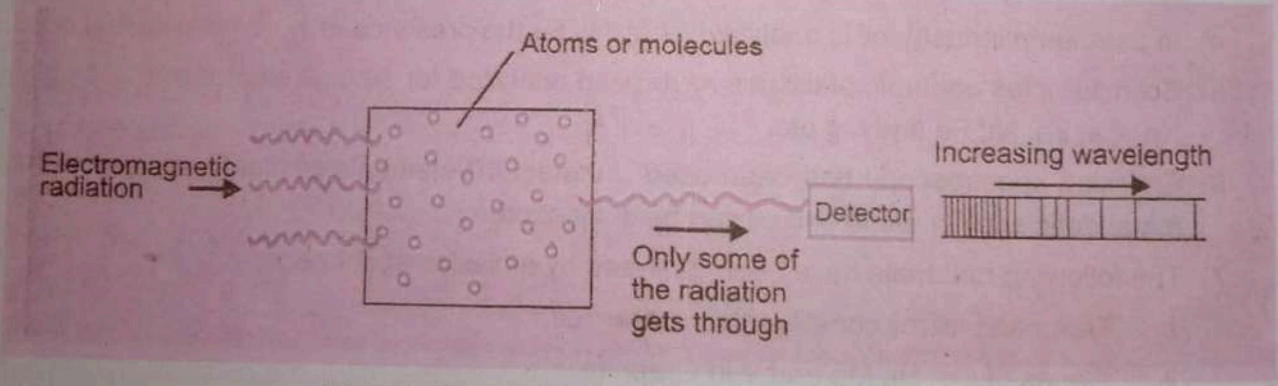

Figure 24.10: Atomic absorption spectrum

Applications of Atomic Absorption Spectroscopy (AAS)

1) The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration
2) It has several advantages over conventional absorption or emission spectroscopic methods.

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3) AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed.

4) The technique is firmly established in analytical chemistry ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

Quick Quiz

1. Give principle of atomic absorption spectroscopy.
2. Give few application of atomic absorption spectroscopy.

Mass Spectrometry (MS)

v.imp

The mass spectrometer is an instrument which turns atoms and molecules into ions and measure their mass.

In 1919, Aston invented the mass spectrometer. This gave chemists a reliable and accurate method of comparing the relative masses of atoms. At one time, the relative masses of atoms were known as atomic weights, but nowadays we refer to them as relative atoms masses.

Mass spectrometry is an analytical technique which involves the production of gaseous ions from the substance under investigation, their separation according to their mass-to-charge ratio (m/e) and the measurement of the relative abundance of these ions. In this technique, no absòrption of light is involved. This is why it is commonly called spectrometry instead of spectroscopy. It is called spectroscopy because the ultimate result is obtained in the form of a 'spectrum' as in the case of other spectroscopic techniques.

Basic Principle:

In mass spectrometry, as organic molecule under high vacuum is bombarded with an electron of energy greater than the ionization energy of the molecule; the ionization energy of most of organic molecules is around 10 eV (964 kj/mole). As a result of this, one of the electron of the molecule is dislodge and a singly charged molecular ion is produced. The molecular ion which is produced in this primary process is a radical cation, i.e., it has an unpaired electron and is positively charged.

$$M + e \xrightarrow{\qquad\qquad} M.^{+} + 2e$$

The sample in vapour state is usually subjected to a beam of electrons of 70 eV energy. These highly energetic electrons not only ionize the organic molecules but also impart a large amount of energy to the molecular ions. A molecular ions generally dissociates into fragments ions called fragment ions.

$$M^{+}\!: \xrightarrow{\qquad\qquad} (m_1^{+}. + m_2) \text{ or } (m_1^{+} + m_2)$$

The positively charged ions are separated by deflection in a variable magnetic field. The ions are directed into an analyzer tube surrounded by a magnet. The magnet deflects the ions from their original path causing them to adopt a circular path the radius of which depends on the mass-to-charge ratio (m/z) of the ions. The ion beam of a particular m/z can be selectively focused through a narrow slit on to an ion collector where it generates a current proportional to the relative abundance of the ions in the beam, which is recorded as a spectrum. The mass spectrum in fact, is a plot of the relative intensity of the ions against their dimensionless m/z value. The doubly charged ions are deflected much more than the singly charged ions and appear in the mass spectrum at half the m/z value (m/2z) of the singly charged ions of the same mass. For example, a doubly charged ion of mass 90 give rise to a peak at m/z 45.

Instrumentation and working

The basic idea of a mass spectrometer can be demonstrated using the apparatus in figure 24.11. Wooden balls of different sizes but with identical iron cores, roll down a sloping plain. At the bottom of the slope a powerful magnet attracts the iron cores and the moving balls are deflected.

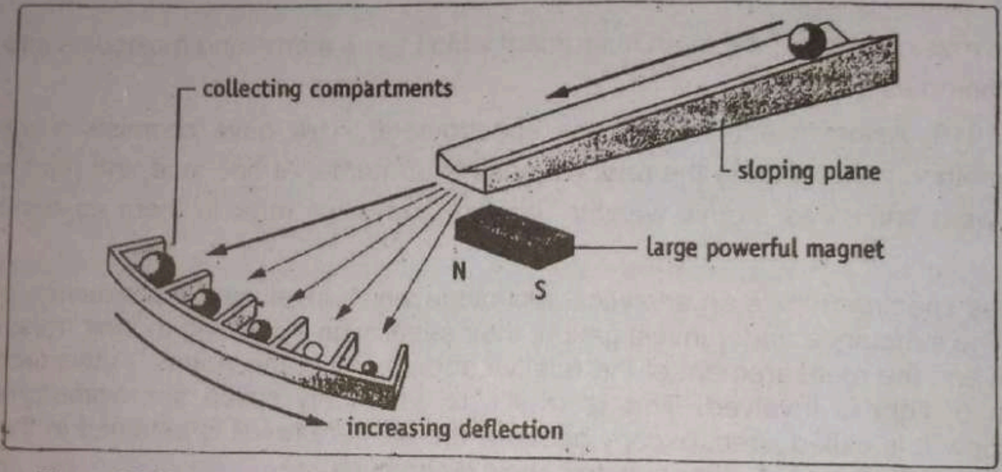


Figure 24.11 A simple model to illustrate the working of a mass spectrometer.

As the balls have identical iron cores, they are all attracted equally by the magnet. But the smaller balls are lighter and therefore they are deflected the most. The balls collect in different compartments depending on their mass. All balls of the same mass collect in the same compartment. Using this simple apparatus, it is possible to separate the different sized balls according to their mass and to find the relative numbers of each present.

Quick Quiz

1. Why does the magnet have the same attraction for all the balls?
2. Which size of ball will be deflected the most? Why?

A real mass spectrometer works in a similar fashion to this simple model. It separates atoms according to their mass and shows the relative numbers of the different atoms present. Before the atoms can be deflected and separated, they must be converted to positively charged ions.

Figure 24.12 shows a simple mass spectrometer. There are five main stages.

1. Vaporization – the sample of elements is vaporized.
2. Ionization – positive ions are obtained from the vapor.
3. Acceleration – the positive ions are accelerated by an electric field.
4. Detection – the ions are detected and a record is made.

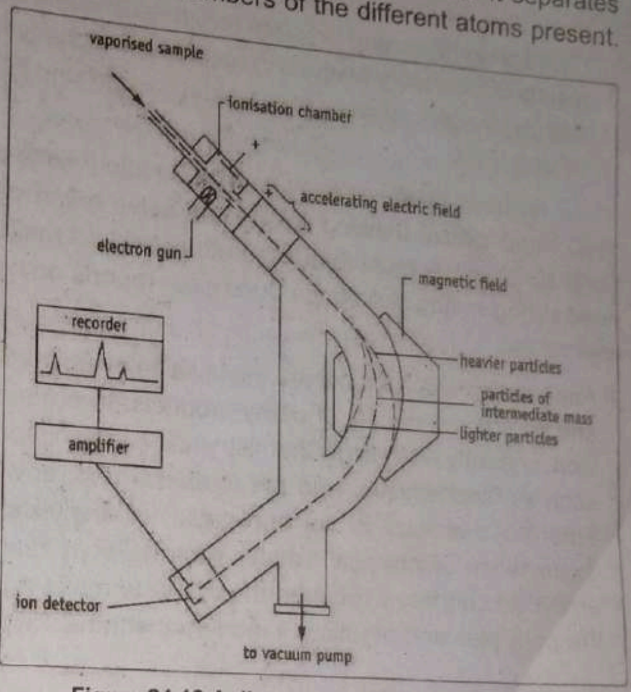


Figure 24.12 A diagram of a mass spectrometer.

Quick Quiz

Look closely at figure 24.13

1. How many different ions are detected in the mass spectrum of naturally occurring magnesium?
2. What are the relative masses of these different ions?
3. What are the relative proportions of these different ions?

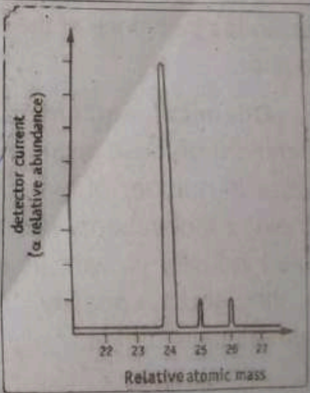


Figure 24.13 A mass spectrometer trace for naturally occurring magnesium

Society, Technology and Science

1. Forensic chemistry is the application of chemistry to criminal investigation. This major is recommended for individuals who wish to pursue a career in criminal investigation, in the laboratory analysis of forensic evidence, or pursue graduate study in forensic science. This course of study would also develop the analytical skills required for careers in other areas of

civil law such as environmental pollution, accident investigation and product liability. Due to the nature of forensic investigations, the forensic chemist requires a strong background in chemical analysis and problem solving skill and must be able to effectively communicate the results of laboratory analysis in reports and in the courtroom. So a forensic chemist must have a strong theoretical and experimental background in analytical chemistry as well as in problem solving skills.

Forensic chemists must have good attention to detail and superior problem-solving skills. They need critical thinking abilities to solve crime puzzles based on fragmentary evidence. Forensic chemists must take accurate notes and make accurate records of their findings. They need strong writing skills to produce clear reports on highly technical subjects so that others can understand.

2. Analytical measurements are essential to everyday life, required to determine the composition and control the quality of many products, to protect the environment and to monitor health. Consequently Analytical Chemistry has a major impact, not only in chemistry, but also in fields such as biochemistry, and the forensic, food, environmental and pharmaceutical sciences. Forensic chemistry is the application of analytical chemistry to the law and involves the examination of physical traces, such as body fluids, bones, fibres and drugs. Success in analytical chemistry requires the ability to make rigorous measurements, an appreciation of the principles and practice of modern instrumentation, and a problem-solving approach.

3. Chemical Instrumentation and Technology

Chemical instrumentsare used extensively in research and development activities, laboratories being one of the major users. Use of chemical instruments for disease diagnosis is on a rise.

Chemical equipment market is growing at a rapid rate due to the continuous requirement of these instruments in pharmaceutical and biotechnology industries. Besides, the increase in number of biotechnology firms worldwide, advances in life science research and technology innovations with human genome mapping, and emergence of proteomics have enabled industry growth; as such high-end research projects require quality instruments with high throughput capacity. All these factors are driving the life science and chemical instrumentation market.

The global life science and chemical instrumentation market was estimated to be $30.2 billion in the year 2011 and is expected to grow at a CAGR of 8.4% from 2011 to 2016 to reach $45.2 billion.

4. Connection between Chromatography and MS

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures and for the detection of small amounts of materials present in those mixtures. The mixture is dissolved in a fluid called the *mobile phase*, which carries it through a structure holding another material called the *stationary phase*. The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio of charged particles. It is used for determining masses of particles, for determining the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules, such as peptides and other chemical compounds. MS works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

Gas chromatography–mass spectrometry (**GC-MS**) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances, even present in small amounts, within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC-MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification. GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a *specific test*. A specific test positively identifies the actual presence of a particular substance in a given sample.

Liquid chromatography–mass spectrometry (**LC-MS**, or alternatively **HPLC-MS**) is a chemistry technique that combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry. LC-MS is a powerful technique used for many applications which has very high sensitivity and selectivity. Generally its application is oriented towards the general detection and potential identification of chemicals in the presence of other chemicals (in a complex mixture). Preparative LC-MS system can be used for fast and mass directed purification of natural-products extracts and new molecular entities important to food, pharmaceutical, agrochemical and other industries. The limitations of LC-MS in urine analysis drug screening is that it often fails to distinguish between specific metabolites, in particular with hydrocodone and its metabolites. LC-MS urine analysis testing is used to detect specific categories of drugs. However, gas chromatography (GC-MS) should be used when detection of a specific drug and its metabolites is required.

Key Points

- The empirical formula of an organic compound can be found by analysis of its combustion products
- The molecular formula of a compound can be found from the empirical formula once the relative molecular mass is unknown.
- The structural formula shows the precise arrangement of atoms. It can be found from a knowledge of some of the properties of the compound or by using instrumental methods, particularly mass spectrometry, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.
- The instrument that is used to measure the amount of electromagnetic radiation absorbed by an organic molecule is called Spectrophotometer or Spectrometer.
- Absorption of infrared radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to a higher vibrational energy level.
- Stronger bonds require greater energy to vibrate. Therefore such bonds absorb infrared radiation of shorter wavelengths.
- Different functional groups absorb infrared radiation at different wavelengths and their presence or absence in a molecule can be determined by examination of an IR spectrum.
- No two compounds have exactly identical infrared spectra.
- Absorption of ultraviolet visible radiation causes electrons within molecules to be promoted from one energy level to a higher electronic energy level.
- If an organic compound does not absorb UV-Vis radiation it means that the compound does not contain conjugated double bonds.
- If an organic compound absorbs UV-Vis radiation it means that the compound contains a carbonyl group or conjugated double bonds. For example, conjugated dienes, carbonyl compounds and aromatic compounds all absorb in the UV-Vis region.
- Absorption of radio waves in the presence of a magnetic field causes nuclei within molecules to be promoted from one spin energy level to a higher spin energy level.
- The number of signals in the NMR spectrum corresponds to the number of different types of protons in the molecules.
- The relative areas (Interrogation) under the signals give the ration of the numbers of each type of protons in the molecule. If the molecular formula is known, the actual number of each type of protons can be determined.

- The splitting pattern of each signal gives us the number of protons on neighboring carbons. The number of peaks into which a signal is split a signal is split is one more than the total number of protons on directly adjacent carbons.
- Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.
- Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible by neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame.
- Mass spectroscopy involves organic molecules being bombarded by a very high-energy electron beam.
- The peak of highest intensity in a mass spectrum is referred to as the base peak.
- Fragmentation processes can produce numerous fragments from which the structures of organic molecules can be deduced.
- When one electron is removed from a molecule, a molecular ion is produced. The *m/e* value of the molecular ion peak is the molecular weight of the compound being investigated. The molecular weights obtained by mass spectroscopy are extremely accurate.

Exercise

Q1: Select the right answer from the choices given with each question.

i. Which of the following techniques does not involve electromagnetic radiations?

a. Infrared spectroscopy
b. NMR spectroscopy
[✓ c. Mass spectroscopy]
d. All of these involve electromagnetic radiations

ii. Which region of the electromagnetic spectrum is involved in the electronic excitations?

a. Ultraviolet
b. Visible
[✓ c. Both of these]
d. None of these

iii. Which of the following techniques is different from the others as regards the basic principle?

a. Ultraviolet spectroscopy
b. Visible spectroscopy
[✓ c. Electronic spectroscopy]
d. None of these

iv. Which of the following is used as a source of visible radiations?

[✓ a. Tungsten filament lamp]
b. Hydrogen discharge lamp
c. Deuterium discharge lamp
d. All of these

v. What is the wavelength range of the ordinary infrared region?

a. 0.8-2.5 μm [✓ b. 2.5-16 μm]
c. 16-1000 μm d. 400-800 nm

vi. The position of an infrared absorption band is commonly expressed by:

a. Wavelength b. Wave number
[✓ c. Both of these] d. None of these

vii. Which of the following is not used as a source of infrared radiations?

a. Nernst filament [✓ b. Tungsten filament]
c. Globar d. None of these

viii. Which region of the electromagnetic spectrum is involved in mass spectrometry?

a. Visible b. Microwave
c. Radiowave [✓ d. None of these]

ix. Mass spectroscopy is an analytical technique which involves:

a. Production of gaseous ions from the sample
b. Separation of the gaseous ions
c. Measurement of the relative abundance of the gaseous ions
[✓ d. All of these]

x. Mass spectrometry can be used to determine:

[✓ a. Molecular weight] b. Molecular formula
c. Molecular structure d. All of these

xi. Which of the following species is detected in the mass spectrometer?

[✓ a. Positively charged species] b. Radicals
c. Neutral molecules [✓ d. All of these]

xii. Which of the following species is produced in the ionization chamber of a mass spectrometer?

[✓ a. Positively charges species] b. Radicals
c. Neutral molecules d. All of these

xiii. Which kind of information about a positively charged species obtained from a mass spectrum?

a. Molecular weight b. Relative abundance
[✓ c. Both of these] d. None of these

xiv. What kind of sample can be studied in a mass spectrometer?

a. A gas b. A liquid
c. A solid [✓ d. All of these]

xv. Near ultraviolet region of these electromagnetic spectrum generally lies between:

a. 10-200 nm
[✓ b.] 200-400 nm
c. 400-750 nm
d. 300-500 nm

xvi. Far ultraviolet or vacuum ultraviolet region generally lies between.

[✓ a.] 10-200 nm
b. 200-400 nm
c. 400-750 nm
d. 300-500 nm

xvii. Far infrared region of the electromagnetic radiation generally lies between:

a. 50-200 μm
b. 100-400 μm
[✓ c.] 50-1000 μm
d. 1-20 μm

Q2: Give brief answers for the following questions.

1. What is spectroscopy? Underline its principle.
2. What is meant by wavelength and frequency?
3. What is spectrometer? Briefly discuss its working.
4. How will you distinguish between (i) 1,3-Pentadiene and 1,4-Pentadiene (ii) Benzene and anthracene by UV-spectroscopy?
5. Two isomeric dienes (X) and (Y), having the molecular formula C_5H_8, absorb at λ_{max} 223nm and λ_{max} 178nm respectively. Write the structures of the two isomers.
6. Give significant application of Atomic Absorption Spectroscopy (AAS).
7. How will you distinguish between 2-Pantanone and 3-Pantanoe by using mass spectra?

Q3: Give detailed answers for the following questions.

1. What is combustion analysis? Describe its different steps.
2. An organic compound consists of carbon; hydrogen and oxygen was subjected to combustion analysis 0.5439g of the compound gave 1.039g of CO_2, 0.6369g of H_2O. Determine the empirical formula of the compounds. (Ans: C_2H_6O)
3. The combustion analysis shows that organic compounds contain 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is empirical formula? If the molecular mass of this compound is 110.15gmole^{-1} then calculate molecular formula of given organic compound. (Ans: C_3H_3O, $C_6H_6O_2$)
4. Write advantages and disadvatages of Emission Spectroscopy.
5. Discuss the general principle and instrumentation of Atomic Emission Spectroscopy.
6. What is the basic principle of Atomic Absorption Spectroscopy? Describe the instrumentation used.
7. What is the basic principle of Mass Spectrometer? How does it work?

Skilled Activities

1. Figure 24.14 shows the simplified NMR spectrum of 1- phenylbutan – 2- one

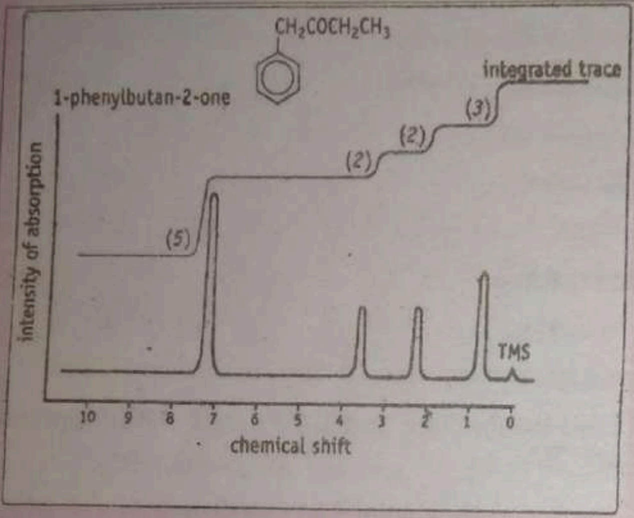


Table 24.4

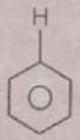
Types of proton	Chemical shift
R—CH_3	0.9
R—CH_2—R	1.3
$\text{R}-\overset{\text{R}}{\overset{\vert}{\text{CH}}}-\text{R}$	2.0
$-\underset{\underset{\text{O}}{\Vert}}{\text{C}}-CH_2-$	2.3
—O—CH_3	3.8
—O—CH_2—R	4.0
—O—H	5.0
	7.5

Fig 24.14. The simplified NMR spectrum of 1 – phenylbutan -2-one.

(a) Table 24.4 shows the chemical shifts for some types of protons (H atoms). Use the table to identify the protons responsible for the peaks at

(i) 7.2 Phenyl (ii) 2.3 carbonyl (iii) 0.9 alkyl

(b) Using your answer to (a), and a process of elimination, identify the protons responsible for the peak at 3.6. methoxy

2. Ethoxyethane, $CH_3CH_2OCH_2CH_3$, and butan -1- ol, $CH_3CH_2CH_2CH_2OH$ are isomers. Figure 24.15 shows the infrared spectra of these two compounds. The spectra are labelled A and B.

(a) Use table 24.2 (characteristic IR absorptions of some common bonds) to decide which spectrum belongs to which compound.

(b) Identify the bonds responsible for the peaks marked 1, 2 and 3 on figure 24.15.

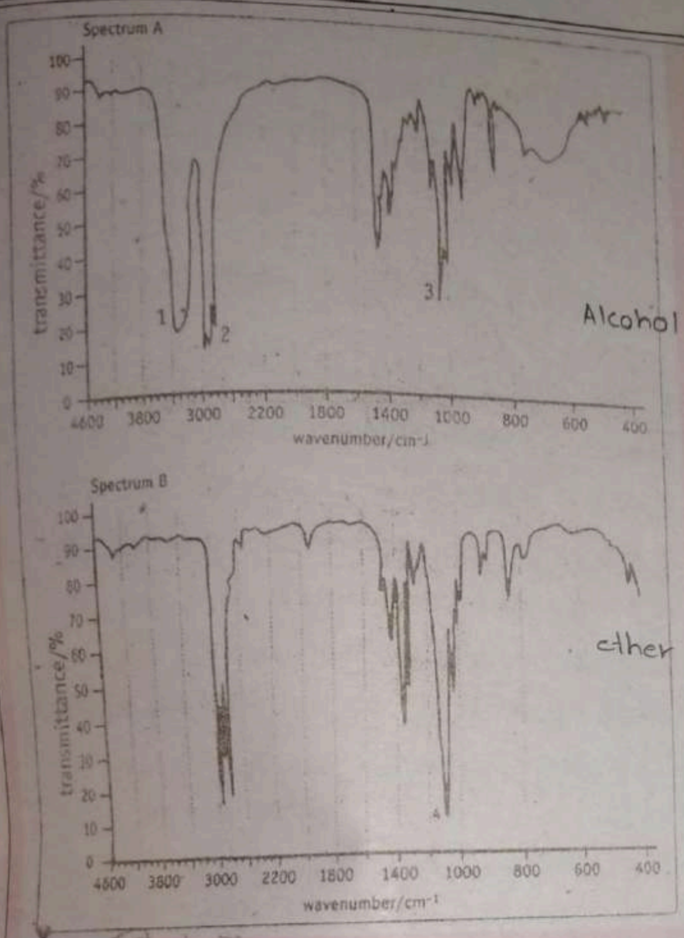


Figure 24.15: The IR spectra for ethoxyethane and butan-1-ol (not necessarily in that order).

3. Phenolphthalein is an organic chemical, molecular formula $C_{20}H_{14}O_3$ Figure 24.16 (a) shows the visible / ultraviolet absorption spectrum of phenolphthalein at pH 6. Figure 24.16 (b) shows the spectrum of the same chemical at pH 10. Table 24.3 gives the approximate wavelengths of visible radiation of different colours.

(a) Which colours does phenoplphthalein absorb at pH 6? ultravoilet

(b) What colour do you predict that a solution of phenolphthalein will be at pH6? colourless

(c) Which colours does phenolphthalein absorb at pH10? reddish orange

(d) What colour do you predict that a solution of phenolphthalein will be at pH 10? Pink (red + orange)

(e) Explain how you could use phenolphthalein in an acid base titration?

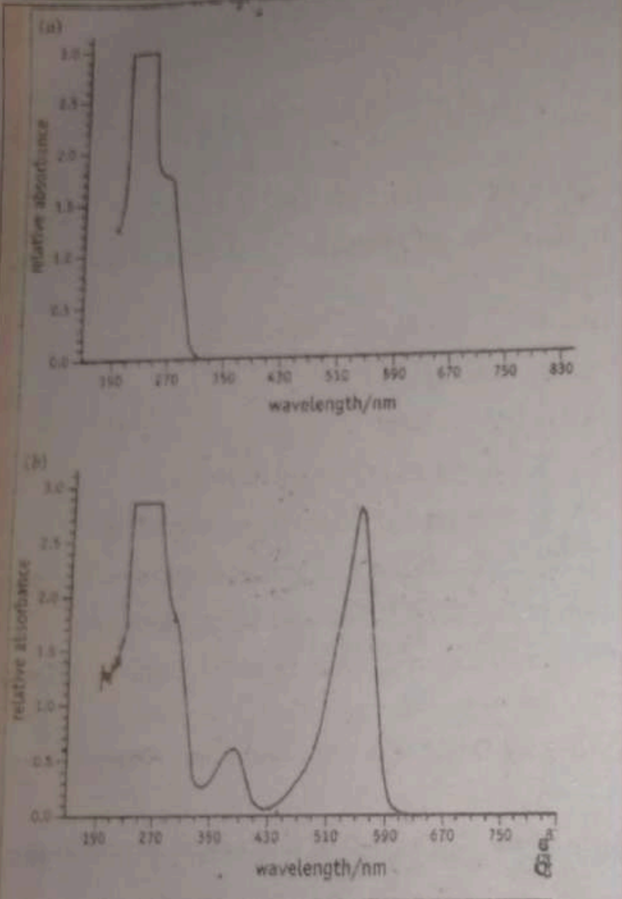


Figure 24.16: The visible/ultraviolet spectrum of phenolphthalein (a) at pH6, (b) at pH 10.

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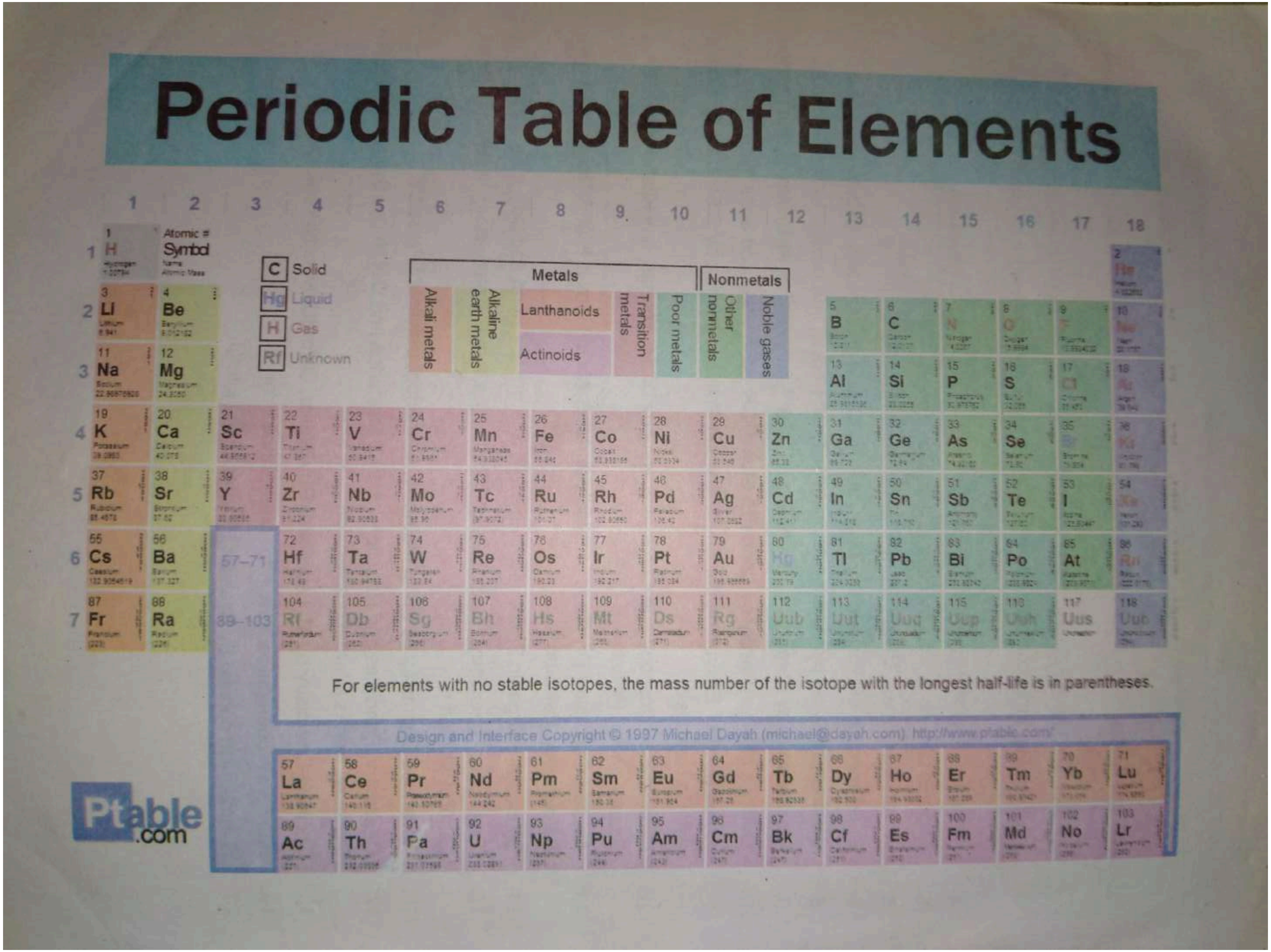

Periodic Table of Elements

Atomic #
Symbol
Name
Atomic Mass

C Solid
Hg Liquid
H Gas
Rf Unknown

Metals						Nonmetals	
Alkali metals	Alkaline earth metals	Lanthanoids Actinoids	Transition metals	Poor metals		Other nonmetals	Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57–71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89–103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

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

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57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Ptable.com

List of Elements with Their Symbols and Atomic Masses

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)	Meitnerium	Mt	109	(266)
Aluminum	Al	13	26.98	Mendelevium	Md	101	(256)
Americium	Am	95	(243)	Mercury	Hg	80	200.6
Antimony	Sb	51	121.8	Molybdenum	Mo	42	95.94
Argon	Ar	18	39.95	Neodymium	Nd	60	144.2
Arsenic	As	33	74.92	Neon	Ne	10	20.18
Astatine	At	85	(210)	Neptunium	Np	93	(237)
Barium	Ba	56	137.3	Nickel	Ni	28	58.69
Berkelium	Bk	97	(247)	Niobium	Nb	41	92.91
Beryllium	Be	4	9.012	Nitrogen	N	7	14.01
Bismuth	Bi	83	209.0	Nobelium	No	102	(253)
Bohrium	Bh	107	(262)	Osmium	Os	76	190.2
Boron	B	5	10.81	Oxygen	O	8	16.00
Bromine	Br	35	79.90	Palladium	Pd	46	106.4
Cadmium	Cd	48	112.4	Phosphorus	P	15	30.97
Calcium	Ca	20	40.08	Platinum	Pt	78	195.1
Californium	Cf	98	(249)	Plutonium	Pu	94	(242)
Carbon	C	6	12.01	Polonium	Po	84	(210)
Cerium	Ce	58	140.1	Potassium	K	19	39.10
Cesium	Cs	55	132.9	Praseodymium	Pr	59	140.9
Chlorine	Cl	17	35.45	Promethium	Pm	61	(147)
Chromium	Cr	24	52.00	Protactinium	Pa	91	(231)
Cobalt	Co	27	58.93	Radium	Ra	88	(226)
Copper	Cu	29	63.55	Radon	Rn	86	(222)
Curium	Cm	96	(247)	Rhenium	Re	75	186.2
Darmstadtium	Ds	110	(281)	Rhodium	Rh	45	102.9
Dubnium	Db	105	(260)	Rubidium	Rb	37	85.47
Dysprosium	Dy	66	162.5	Ruthenium	Ru	44	101.1
Einsteinium	Es	99	(254)	Rutherfordium	Rf	104	(257)
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	44.96
Fermium	Fm	100	(253)	Seaborgium	Sg	106	(263)
Fluorine	F	9	19.00	Selenium	Se	34	78.96
Francium	Fr	87	(223)	Silicon	Si	14	28.09
Gadolinium	Gd	64	157.3	Silver	Ag	47	107.9
Gallium	Ga	31	69.72	Sodium	Na	11	22.99
Germanium	Ge	32	72.59	Strontium	Sr	38	87.62
Gold	Au	79	197.0	Sulfur	S	16	32.07
Hafnium	Hf	72	178.5	Tantalum	Ta	73	180.9
Hassium	Hs	108	(265)	Technetium	Tc	43	(99)
Helium	He	2	4.003	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.008	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.85	Titanium	Ti	22	47.88
Krypton	Kr	36	83.80	Tungsten	W	74	183.9
Lanthanum	La	57	138.9	Uranium	U	92	238.0
Lawrencium	Lr	103	(257)	Vanadium	V	23	50.94
Lead	Pb	82	207.2	Xenon	Xe	54	131.3
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.0
Lutetium	Lu	71	175.0	Yttrium	Y	39	88.91
Magnesium	Mg	12	24.31	Zinc	Zn	30	65.39
Manganese	Mn	25	54.94	Zirconium	Zr	40	91.22

Electronic Configuration of Elements

Period Number	Elements with atomic number	K n=1	L n=2		M n=3			N n=4				O n=5				P n=6				Q n=7	
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
1	$\mathrm{H_1}$	1																			
	$\mathrm{He_2}$	2																			
2	$\mathrm{Li_3}$	2	1																		
	$\mathrm{Be_4}$	2	2	1																	
	$\mathrm{B_5}$	2	2	2																	
	$\mathrm{C_6}$	2	2	2																	
	$\mathrm{N_7}$	2	2	2																	
	$\mathrm{O_8}$	2	2	2																	
	$\mathrm{F_9}$	2	2	2																	
	$\mathrm{Ne_{10}}$	2	2	2																	
3	$\mathrm{Na_{11}}$	2	2	6	1																
	$\mathrm{Mg_{12}}$	2	2	6	2																
	$\mathrm{Al_{13}}$	2	2	6	2	1															
	$\mathrm{Si_{14}}$	2	2	6	2	2															
	$\mathrm{P_{15}}$	2	2	6	2	3															
	$\mathrm{S_{16}}$	2	2	6	2	4															
	$\mathrm{Cl_{17}}$	2	2	6	2	5															
	$\mathrm{Ar_{18}}$	2	2	6	2	6															
4	$\mathrm{K_{19}}$	2	2	6	2	6		1													
	$\mathrm{Ca_{20}}$	2	2	6	2	6		2													
	$\mathrm{Sc_{21}}$	2	2	6	2	6	1	2													
	$\mathrm{Ti_{22}}$	2	2	6	2	6	2	2													
	$\mathrm{V_{23}}$	2	2	6	2	6	3	2													
	$\mathrm{Cr_{24}}$	2	2	6	2	6	4	1													
	$\mathrm{Mb_{25}}$	2	2	6	2	6	5	2													
	$\mathrm{Fe_{26}}$	2	2	6	2	6	6	2													
	$\mathrm{Co_{27}}$	2	2	6	2	6	7	2													
	$\mathrm{Ni_{28}}$	2	2	6	2	6	8	2													
	$\mathrm{Cu_{29}}$	2	2	6	2	6	10	1													
	$\mathrm{Zn_{30}}$	2	2	6	2	6	10	2													
	$\mathrm{Ga_{31}}$	2	2	6	2	6	10	2	1												
	$\mathrm{Ge_{32}}$	2	2	6	2	6	10	2	2												
	$\mathrm{As_{33}}$	2	2	6	2	6	10	2	3												
	$\mathrm{Se_{34}}$	2	2	6	2	6	10	2	4												
	$\mathrm{Br_{35}}$	2	2	6	2	6	10	2	5												
	$\mathrm{Kr_{36}}$	2	2	6	2	6	10	2	6												
5	$\mathrm{Rb_{37}}$	2	2	6	2	6	10	2	6			1									
	$\mathrm{Sr_{38}}$	2	2	6	2	6	10	2	6			2									
	$\mathrm{Y_{39}}$	2	2	6	2	6	10	2	6	1		2									
	$\mathrm{Zr_{40}}$	2	2	6	2	6	10	2	6	2		2									
	$\mathrm{Nb_{41}}$	2	2	6	2	6	10	2	6	3		1									
	$\mathrm{Mo_{42}}$	2	2	6	2	6	10	2	6	4		1									
	$\mathrm{Te_{43}}$	2	2	6	2	6	10	2	6	5		2									
	$\mathrm{Ru_{44}}$	2	2	6	2	6	10	2	6	6		1									
	$\mathrm{Rh_{45}}$	2	2	6	2	6	10	2	6	7		1									
	$\mathrm{Pd_{46}}$	2	2	6	2	6	10	2	6	8		0									
	$\mathrm{Ag_{47}}$	2	2	6	2	6	10	2	6	10		1									
	$\mathrm{Cd_{48}}$	2	2	6	2	6	10	2	6	10		2									
	$\mathrm{In_{49}}$	2	2	6	2	6	10	2	6	10		2	1								
	$\mathrm{Sn_{50}}$	2	2	6	2	6	10	2	6	10		2	2								
	$\mathrm{Sb_{51}}$	2	2	6	2	6	10	2	6	10		2	3								
	$\mathrm{Te_{52}}$	2	2	6	2	6	10	2	6	10		2	4								
	$\mathrm{I_{53}}$	2	2	6	2	6	10	2	6	10		2	5								
	$\mathrm{Xe_{54}}$	2	2	6	2	6	10	2	6	10		2	6								
Period Number	Elements with atomic number	K n=1	L n=2		M n=3			N n=4				O n=4				P n=6				Q n=7	
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
6	$\mathrm{Cs_{55}}$	2	2	6	2	2	6	2	6	10		2	6			1					

	Ba$_{56}$		2	2	6	2	6	10	2	6	10		2	6			2			
	La$_{57}$		2	2	6	2	6	10	2	6	10		2	6	1		2			
	Ce$_{58}$		2	2	6	2	6	10	2	6	10	2	2	6	0		2			
	Pr$_{59}$		2	2	6	2	6	10	2	6	10	3	2	6	0		2			
	Nd$_{60}$		2	2	6	2	6	10	2	6	10	4	2	6	0		2			
	Pm$_{61}$		2	2	6	2	6	10	2	6	10	5	2	6	0		2			
	Sm$_{62}$		2	2	6	2	6	10	2	6	10	6	2	6	0		2			
	Eu$_{63}$		2	2	6	2	6	10	2	6	10	7	2	6	0		2			
	Gd$_{64}$		2	2	6	2	6	10	2	6	10	8	2	6	1		2			
	Tb$_{65}$		2	2	6	2	6	10	2	6	10	9	2	6	0		2			
	Dy$_{66}$		2	2	6	2	6	10	2	6	10	14	2	6	0		2			
	Ho$_{67}$		2	2	6	2	6	10	2	6	10	14	2	6	0		2			
	Er$_{68}$		2	2	6	2	6	10	2	6	10	14	2	6	0		2			
	Tm$_{69}$		2	2	6	2	6	10	2	6	10	14	2	6	0		2			
	Yb$_{70}$		2	2	6	2	6	10	2	6	10	14	2	6	0		2			
	Lu$_{71}$		2	2	6	2	6	10	2	6	10	14	2	6	1		2			
	Hf$_{72}$		2	2	6	2	6	10	2	6	10	14	2	6	2		2			
	Ta$_{73}$		2	2	6	2	6	10	2	6	10	14	2	6	3		2			
	W$_{74}$		2	2	6	2	6	10	2	6	10	14	2	6	4		2			
	Re$_{75}$		2	2	6	2	6	10	2	6	10	14	2	6	5		2			
	Os$_{76}$		2	2	6	2	6	10	2	6	10	14	2	6	6		2			
	Ir$_{77}$		2	2	6	2	6	10	2	6	10	14	2	6	7		2			
	Pt$_{78}$		2	2	6	2	6	10	2	6	10	14	2	6	9		1			
	Au$_{79}$		2	2	6	2	6	10	2	6	10	14	2	6	10		1			
	Hg$_{80}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2			
	Ti$_{81}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
	Pb$_{82}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
	Bi$_{83}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
	Po$_{84}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
	At$_{85}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
	Rn$_{86}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
7	Fr$_{87}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
	Ra$_{88}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
	Ac$_{89}$		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
	Th$_{90}$		2	2	6	2	6	10	2	6	10	14	2	6	10	0	2	6	2	2
	Pa$_{91}$		2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
	U$_{92}$		2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
	Np$_{93}$		2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
	Pu$_{94}$		2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	0	2
	Am$_{95}$		2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	0	2
	Cm$_{96}$		2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	5	1	2
	Bk$_{97}$		2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	0	2
	Cf$_{98}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0	2
	Es$_{99}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0	2
	Fm$_{100}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0	2
	Md$_{101}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0	2
	No$_{102}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	0	2
	Lw$_{103}$		2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
	Ku$_{104}$															14				

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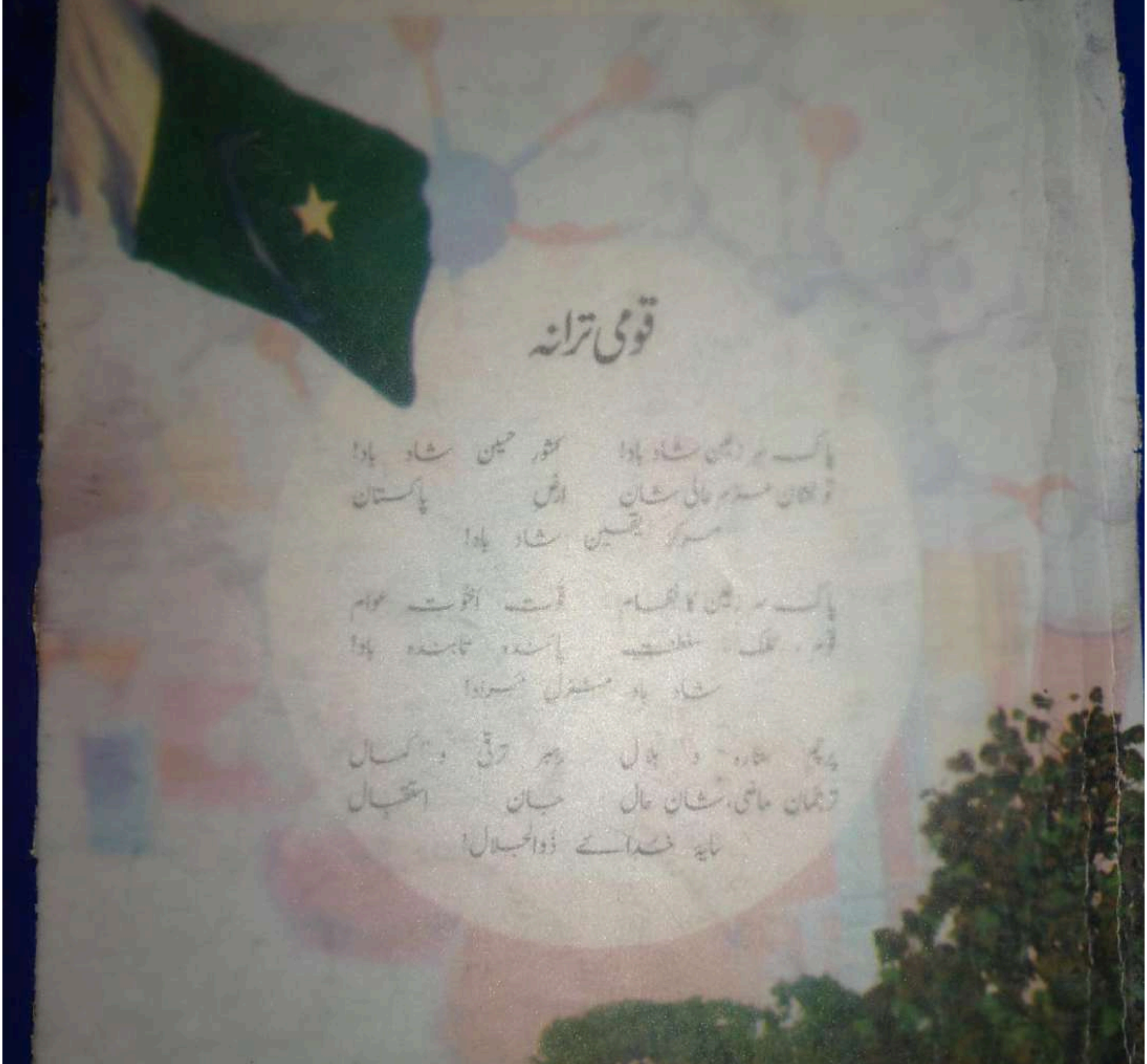

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