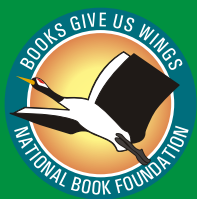


Textbook of

Chemistry

Grade

12



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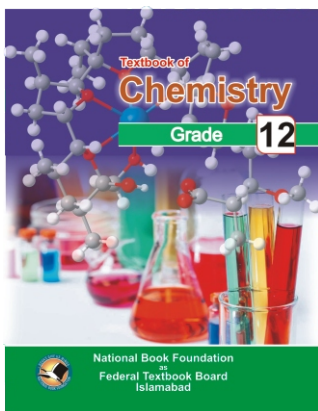
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Textbook of Chemistry Grade - 12



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

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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 of 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

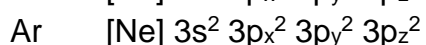
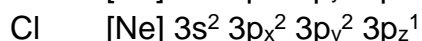
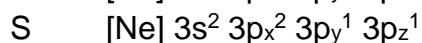
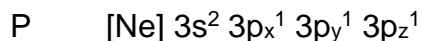
In Period 3 of the Periodic Table, the 3s and 3p orbitals are filling with electrons. Just as a reminder, the shortened versions of the electronic structures for the eight elements are:

Na [Ne] 3s¹

Mg [Ne] 3s²

Al [Ne] 3s² 3p_x¹

Si [Ne] 3s² 3p_x¹ 3p_y¹



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



Quick Quiz

1. The electron structure of Mg is 1s², 2s², 2p⁶, 3s². 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 Å⁰) 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				
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
1							
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)	Tl 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)	Ra 1.40 (+2)					



Trends in Electronegativity

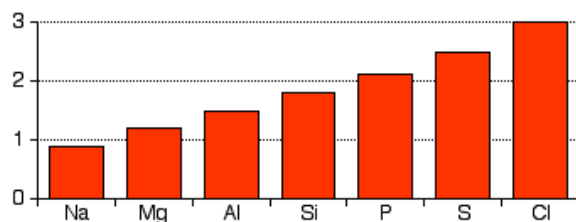
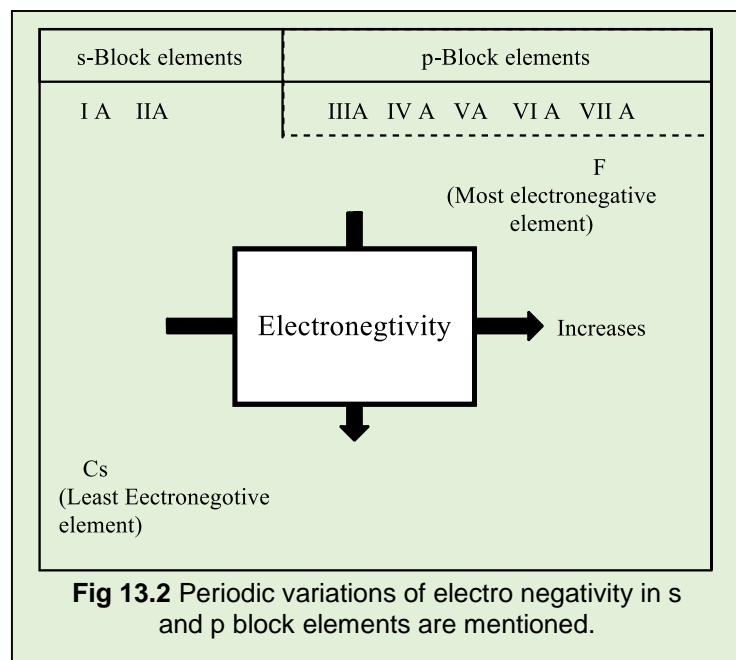


Fig. 13.1 Electronegativities

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.



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.

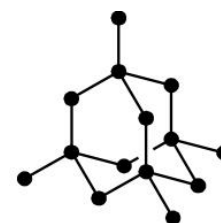


Fig 13.3

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 argon 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.

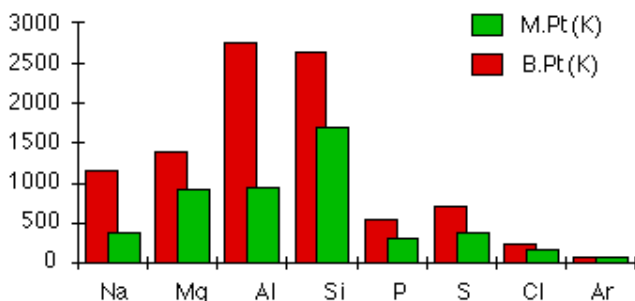


Fig 13.4 Melting and Boiling Point

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.

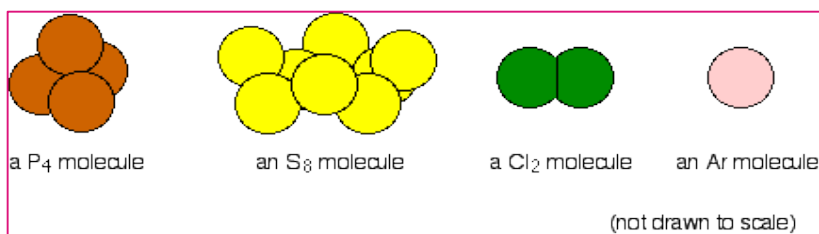


Fig. 13.5

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

Phosphorus

Phosphorus contains P₄ 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 S₈ rings of atoms. The S₈ molecules 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, Cl₂, 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

- List the symbols of elements present in the third period of the periodic table, in order of increasing atomic number.
- Which of the above elements are:
 - s-block elements
 - d-block elements
- Write the empirical formula of the chloride formed by the element with atomic number 13.
 - 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

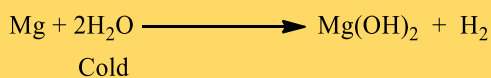
Sodium has a very exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide.



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.



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



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.





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).



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:



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.



For the simple oxide:

For the peroxide:



Magnesium

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



Silicon

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



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:



For the phosphorus (V) oxide:





Sulphur

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



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 ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
					(P ₄ O ₆)	(SO ₂)	(Cl ₂ O)
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 ₄ O ₁₀ reacts to form H ₃ PO ₄ acid solution	SO ₃ reacts to form H ₂ SO ₄ acid solution	Cl ₂ O 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.



Magnesium

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





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.



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).



Phosphorus(III) chloride is a colourless fuming liquid.



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

Sulphur



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 .



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 simple; 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))

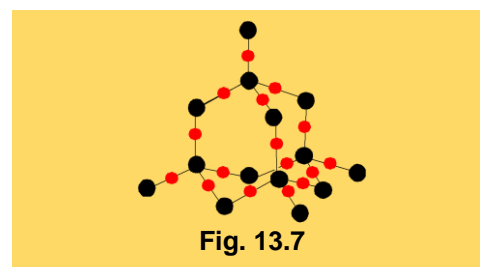
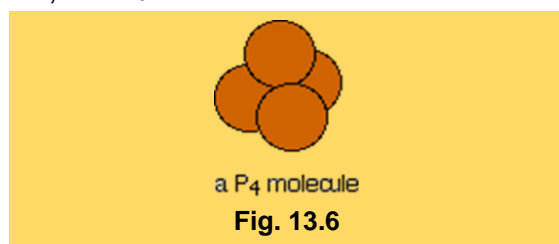
Structure

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)

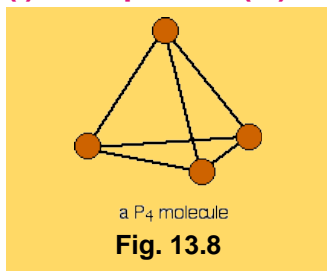
(a) The Phosphorus oxides

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



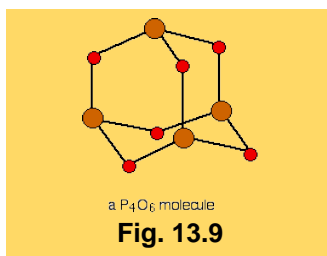


(i) Phosphorus (III) oxide



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 P₄ 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.

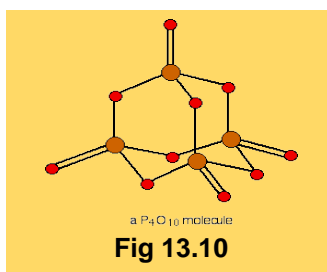


(ii) Phosphorus(V) oxide

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 P₄O₆. The other four oxygens are attached to the four phosphorus atoms via double bonds.

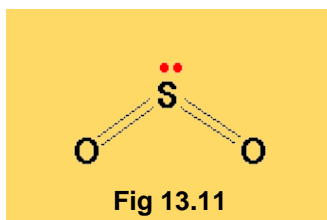


(b) The Sulphur Oxides

Sulphur has two common oxides, sulphur dioxide (sulphur(IV) oxide), SO₂, and sulphur trioxide (sulphur(VI) oxide), SO₃.

(i) Sulphur dioxide

Sulphur dioxide is a colourless gas at room temperature with an easily recognised choking smell. It consists of simple SO₂ 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 SO₂ is due to this lone pair.



(ii) Sulphur trioxide

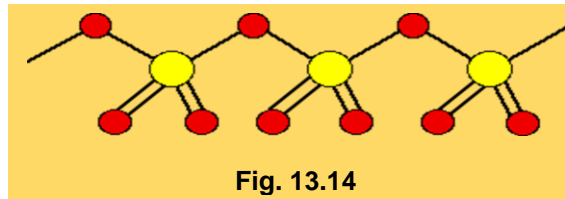
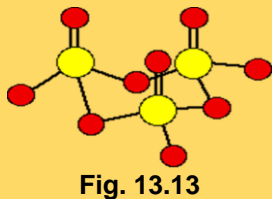
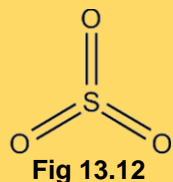
Pure sulphur trioxide is a white solid with a low melting and boiling point.

Gaseous sulphur trioxide consists of simple SO₃ 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, S₃O₉, where three SO₃ molecules are joined up and arranged in a ring.

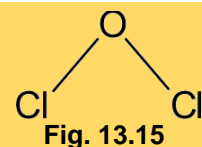
There are also other polymeric forms in which the SO₃ molecules join together in long chains. For example:

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.



(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 .



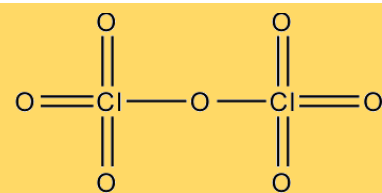
Chlorine (I) oxide

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.



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.

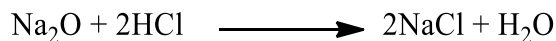
Reaction with Water

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



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.

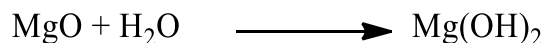


Magnesium oxide (MgO)

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.

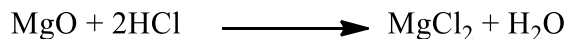
Reaction with Water

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.



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.



Aluminium oxide (Al_2O_3)

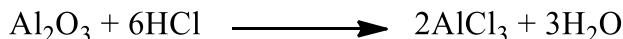
As it is amphoteric oxide, it has reactions as both a base and an acid.

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.



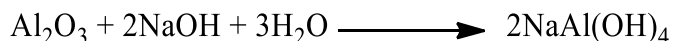
Reaction with Bases

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.



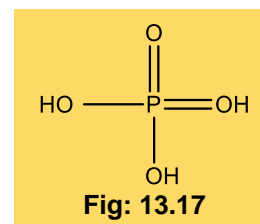
With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroaluminate.



Phosphorus (V) oxide (P₄O₁₀)

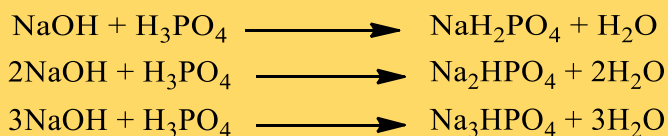
Reaction with Water

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, H₃PO₄ (also known just as phosphoric acid or as orthophosphoric acid).



Reaction with Base:

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



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.



The Sulphur oxides (SO_x)

We are going to be looking at sulphur dioxide, SO₂, and sulphur trioxide, SO₃.

Sulphur dioxide

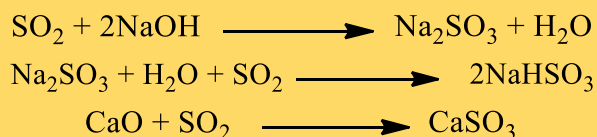
Reaction with Water:

Sulphur dioxide is fairly soluble in water, reacting with it to give a solution of sulphurous acid, H₂SO₃.



Reaction with Base:

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



Sulphur trioxide

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





Reaction with Base:



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.



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.



Reaction with Base:

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



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



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.



Reaction with Base:

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





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



Quick Quiz

- What is the nature of bonds in the oxides formed when Na, Mg, Al and S react with excess oxygen?
- How do these oxides react with (i) Water (ii) dilute acids, (iii) alkali
- Magnesium chloride is a high melting point solid, aluminium chloride is a solid which sublimes readily at about 180°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

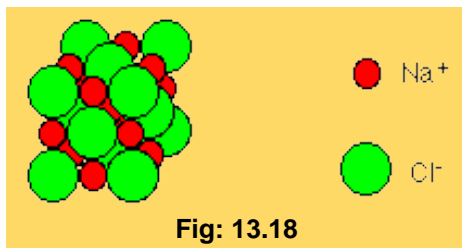
Sodium and magnesium chlorides are solids with high melting and boiling points because of the large amount of heat which is needed to break the strong ionic attractions.

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.



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.

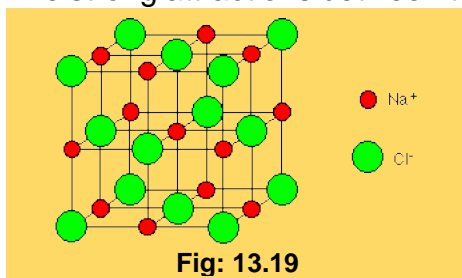
The Individual Chlorides

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.



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.

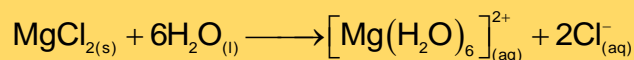
Magnesium Chloride, MgCl₂

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 Mg²⁺ 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(H₂O)₆]²⁺.



Ions of this sort are acidic.

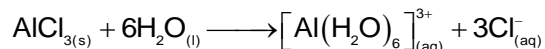
Aluminium Chloride, AlCl₃

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.



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.



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.



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 .



Do you know?

Phosphorus (V) chloride is a white solid which sublimates 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.

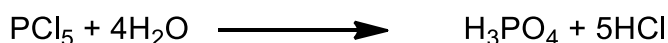


Solid phosphorus (V) chloride contains ions - which is why it is a solid at room temperature. The formation of the ions involves two molecules of PCl_5 .

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.



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



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:

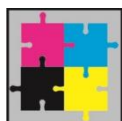
The reason for drawing the shape is to give a

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 hydrochloric acid, colourless solutions of sodium chloride or magnesium chloride are formed.



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.

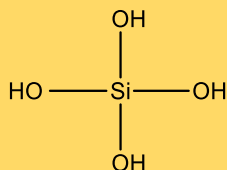


But aluminium hydroxide also has an acidic side to its nature. It will react with sodium hydroxide solution to give a colourless solution of sodium tetrahydroxoaluminate.

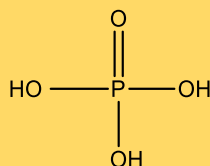


Hydroxides of Si, P and S have hydroxides -OH groups covalently bonded to the atoms. These compounds are all acidic - ranging from the very weakly acidic silicic acids (one of which is shown below) to the very strong sulphuric or chloric acids.

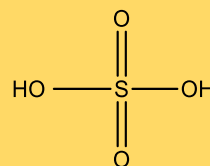
There are other acids (also containing -OH groups) formed by these elements, but these are the ones where the Period 3 element is in its highest oxidation state.



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)

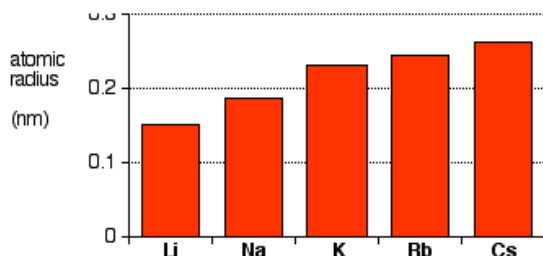


Fig. 13.22 Atomic Radii of the Group 1 Elements

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	85.47	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)	520.3	495.8	418.9	403.0	375.7
	I_2	7298.1	4562.4	3051.4	2633.0
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 25°C (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:





Notice that first ionization energy falls as you go down the group. We know that alkali metals 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.

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 Li and goes 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.

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 spectrum. 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 interatomic bonds in the solid state of the alkali metals. These bonds are due to their atomic radii and mainly due to their electronic configuration having a single valence electron as

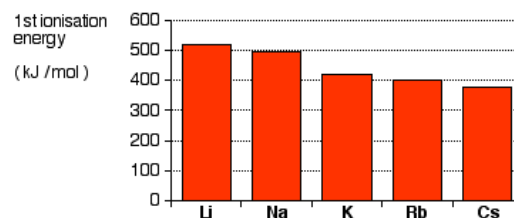


Fig. 13.23 First Ionization Energy of the Group 1 elements

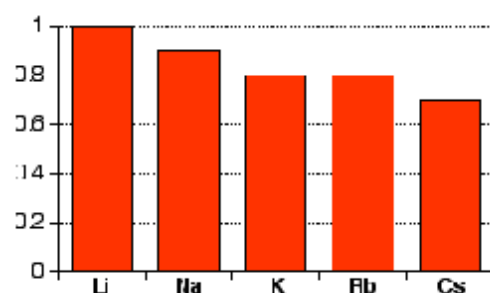


Fig 13.24 Electronegativities of the Group 1 elements

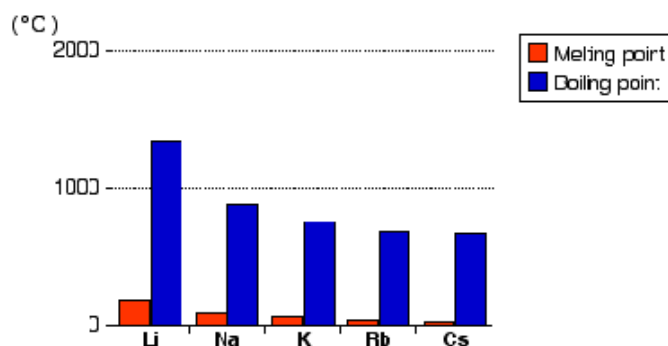


Fig 13.25: Melting and Boiling Points of the Group 1 elements

As you go down the group, the atomic radii increase and the electronic configuration remains the same, having a single valence electron.



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).

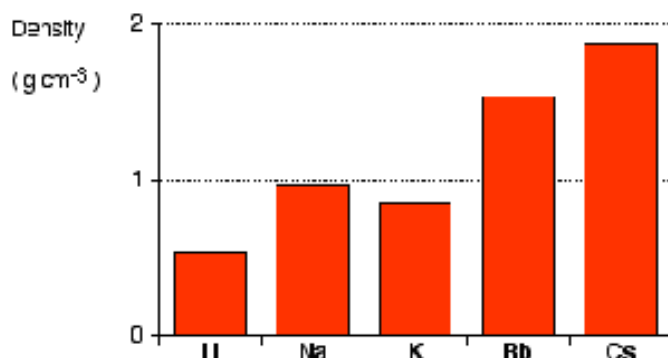


Fig. 13.26: Densities of the Group 1 elements

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°C (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 2nd ionization energy is greater than 1st 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

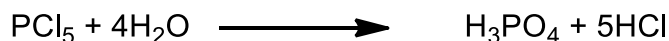
Looking at the enthalpy changes for the reactions

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:

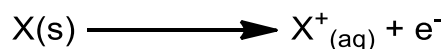


	enthalpy change (kJ / mol)
Li	-222
Na	-184
K	-196
Rb	-195
Cs	-203

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:



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.

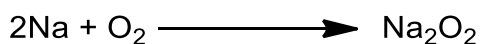
The Reactions with Air or Oxygen

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 .



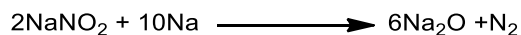
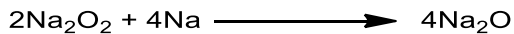
Na when burnt in O_2 forms sodium peroxide, Na_2O_2



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

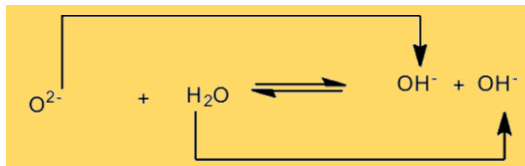


Since the normal oxides of alkali metals other than that of Li (Li_2O) are not formed by the direct reaction between the metals and O_2 they are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metals itself.



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

Gains proton
Loses proton

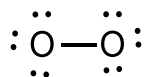


The peroxides (O_2^{2-}) and superoxides (O_2^-) are strong oxidising agents and react with H_2O to give H_2O_2 and O_2 .



Normal oxides have anti-fluorite structure and are ionic in nature since they contain monoxide ion, 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:



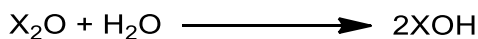
The presence of one unpaired electron in it makes this in paramagnetic and coloured.

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.



Reaction with dilute Acids

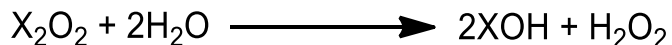
These simple oxides all react with an acid to give a salt and water. For example, sodium oxide will react with dilute hydrochloric acid to give colourless sodium chloride solution and water.



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.





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!



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!



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!



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!



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).



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 carbonates 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



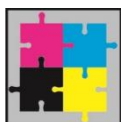
Rb	red (reddish-violet)	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	greyish-white

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. Since 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

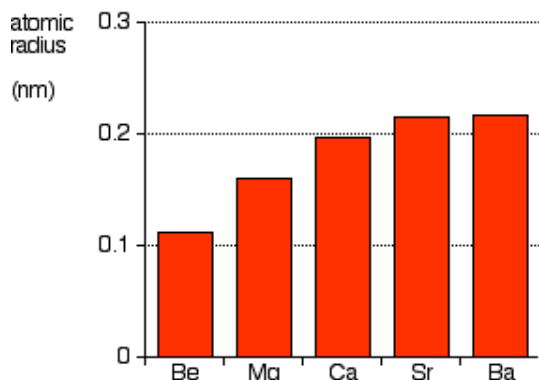


Fig. 13.27 Atomic Radii of the Group 2 elements

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 radium (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	<u>1757.1</u>	<u>1450.7</u>	<u>1145.4</u>	<u>1064.3</u>	<u>965.2</u>	<u>979.06</u>
$I_1 + I_2$	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 $M(s)$	1.70	1.37	2.87	2.89	2.90	2.92
$M_{(s)} \longrightarrow M_{(aq)}^{2+} + 2e$	1.70			163.21	175.77	--
Heat of atomization at 25 °C and 1 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			
Ionic potential of M^{2+} ion (i.e., charge/radius ratio).	6.66	3.08	2.12	1.82	1.55	1.33

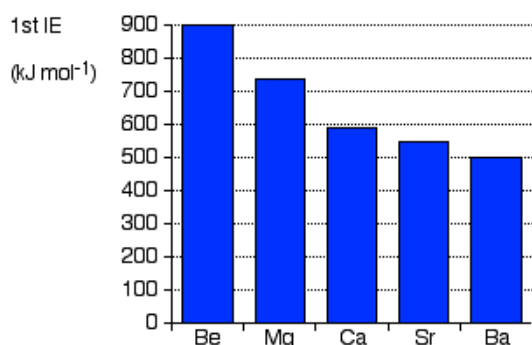
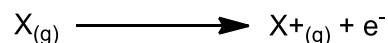


Fig. 13.28 First Ionisation energy of the Group 2 elements

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 +1 charged gaseous ions - in other words, for 1 mole of this process:



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)

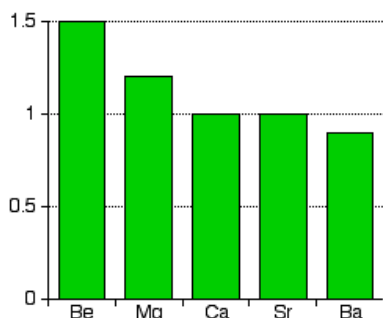


Fig. 13.29 Electronegativity of the Group 2 elements

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.

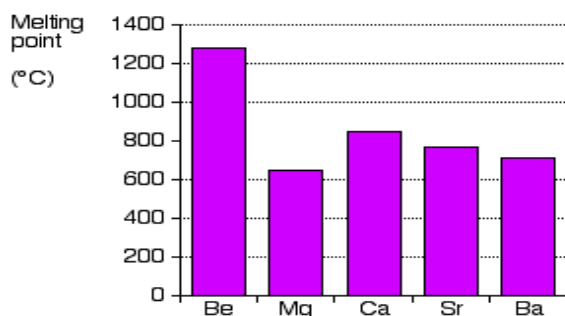


Fig. 13.30: You will see that there is no obvious pattern in boiling points. It would be quite wrong to suggest that there is any trend here whatsoever.

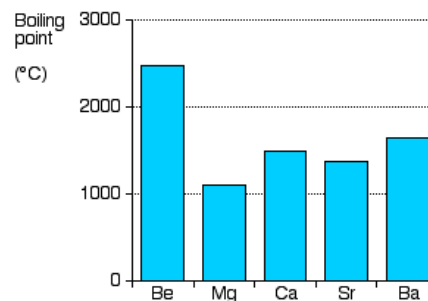


Fig. 13.31: you will see that (apart from where the smooth trend is broken by magnesium) the melting point falls as you go down the Group.

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.

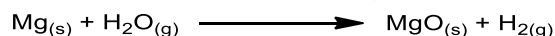
The Facts

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.

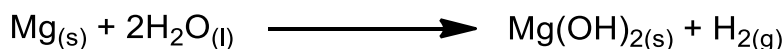


Summarising the trend down the Group

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).

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.





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:



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.



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)₃ 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 M²⁺ 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 Be²⁺ in, Be(OH)₂ is covalent while other hydroxides are ionic.

Be(OH)₂ and Mg(OH)₂ are almost insoluble in H₂O 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 × 10⁻²⁶; Mg(OH)₂ = 8.9 × 10⁻¹²; Ca(OH)₂ = 1.3 × 10⁻⁴;

Sr(OH)₂ = 3.2 × 10⁻⁴; Ba(OH)₂ = 5.4 × 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 O₂ or by heating their carbonates at high temperature e.g.



Properties:

- (i) These oxides are extremely stable white crystal line solids due to their high crystal lattice energy obtained by packing doubly charged ions in a sodium chloride type of lattice.
- (ii) BeO and MgO are quite insoluble in H₂O while CaO, SrO and BaO react with H₂O 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.



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

(iv) Due to small size Be²⁺ ion, BeO is covalent while other oxides 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 O₂ at high temperature.



Properties: The peroxides are white, ionic solids having peroxide anion, [O-O]²⁻. They react with acids to produce H₂O₂.

Formation of Nitrides on Heating in Air

All the elements burn in nitrogen to form nitrides, M₃N₂ e.g.



These react with H₂O to liberate NH₃ e.g.

Be₃N₂ 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.



13.3.5. Trends in Thermal Stability of the Carbonates and Nitrates

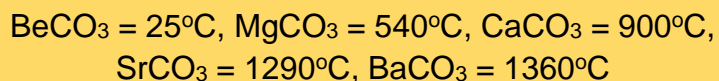
This topic looks at the effect of heat on the carbonates and nitrates of the Group 2 elements - beryllium, magnesium, calcium, strontium and barium. It describes and explains how the thermal stability of the compounds changes as you go down the Group.

The effect of heat on the Group 2 Carbonates

All carbonates decompose on heating at appropriate temperature evolving CO_2



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:



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:



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.

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.

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 H₂ gas.



- 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.



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.



- 8. Behaviour of Carbides:** Beryllium carbide is decomposed by water to form methane (CH₄).



The carbide of other alkaline earth metals are decomposed by water to form acetylene (C₂H₂). For example:



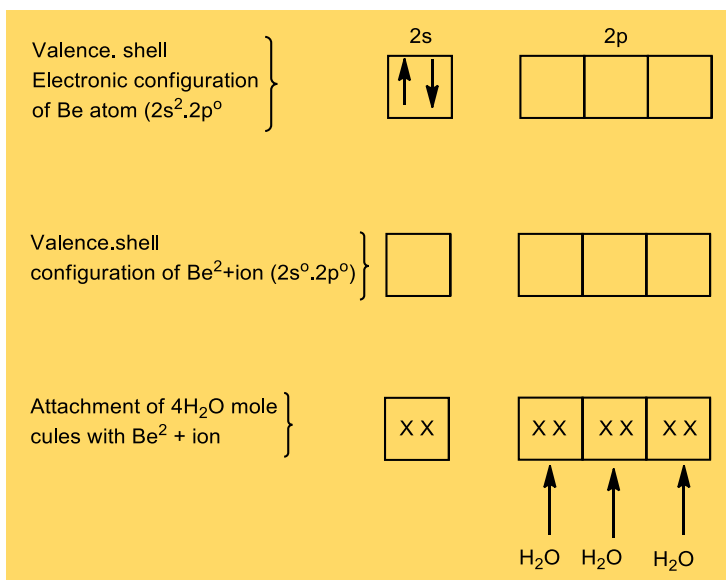


9. Behaviour of Nitrides: Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

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.

On 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 $[\text{BeF}_3]^-$, $[\text{BeF}]^{2-}$ while M^{2+} ions derived from other alkaline earth metals form very few complex compounds.



Quick Quiz

- Among the alkaline earth metals atoms which has the highest ionisation potential?
- Explain why Ca, Cr, Ba, and Ra are placed in one group of the periodic table.
- Explain the following
 - Alkaline earth metals form M^{2+} ions but no M^+ ions.
 - 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.
 - Beryllium salts have never more than four molecules of water of crystallisation.
 - The solubility of the sulphates of alkaline earth metals decreases whereas the solubility of their hydroxides increases on moving down the group.
 - The thermal stability of carbonates of alkaline earth metals increases in atomic numbers.
 - Alkaline earth metals salts impart colour to the Bunsen flame.
 - MgSO_4 is more soluble in water than BaSO_4 .
 - Alkaline earth metals form M^{2+} ions but not M^{3+} ions.
- How do the elements of group IIA differ from alkali metals?
- Explain the following.
 - The hydroxides of group IIA metals are weaker than those of group IA metals.
 - The carbonates of group IIA metals are less stable to heat than those of group IA metals.
 - KOH is stronger base than $\text{Ba}(\text{OH})_2$.



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

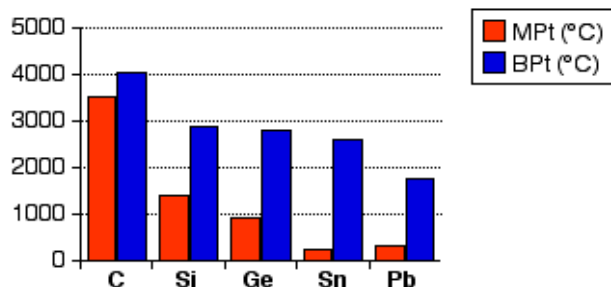


Fig. 13.32 Melting and Boiling Points of Group 4 elements

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.

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 from C to Pb, although the decrease does 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.

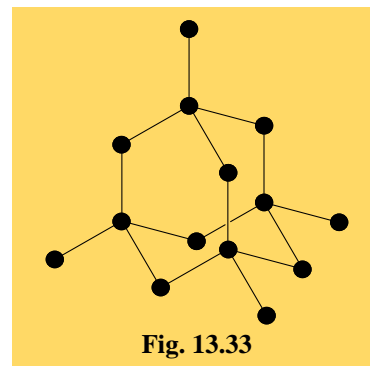


Fig. 13.33

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

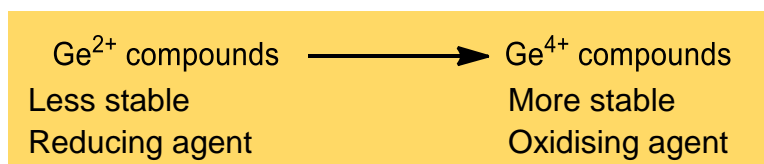
This topic explores the oxidation states (oxidation numbers) shown by the Group IV elements - carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). It looks at the increasing tendency of the elements to form compounds in which their oxidation states are +2, particularly with reference to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

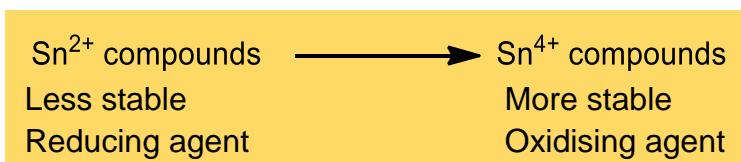
When all the four ns^2p^2 electrons are lost we get the elements in +4 oxidation state, i.e. M^{4+} cations are formed. On descending the group stability of +4 oxidation state decrease i.e. the stability of M^{4+} cations decreases from Ge^{4+} to Pb^{4+} i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$



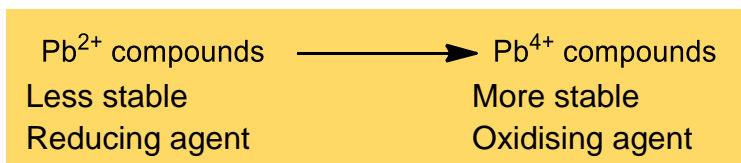
Compounds of Ge^{2+} are less stable than those of Ge^{4+} and hence the compounds of Ge^{2+} are readily oxidised into those of Ge^{4+} . In other words compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidising agents.



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.



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.



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 $\text{Ge}^{2+} < \text{Ge}^{4+}$; $\text{Sn}^{2+} < \text{Sn}^{4+}$; $\text{Pb}^{2+} > \text{Pb}^{4+}$

(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. $\text{Be}_4^{2+}\text{C}_2^{4-}$ or Be_2C (Be^{2+} and C^{4-} ions), $\text{Al}_4^{3+}\text{C}_3^{4-}$ (Al^{3+} and C^{4-} ions) $\text{Na}^+\text{CH}_3^{-1}$ (Na^+ , C^{4-} and H^+ ions), $\text{Na}_2^{2+}\text{C}_2^{2-}$ (Na^+ and C_2^{2-} ions), $\text{Ca}^{2+}\text{C}_2^{2-}$ (Ca^{2+} and C_2^{2-} ions).

The inert pair effect in the formation of Ionic Bonds

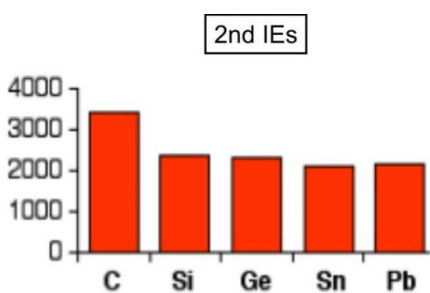


Fig. 13.34

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.

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.

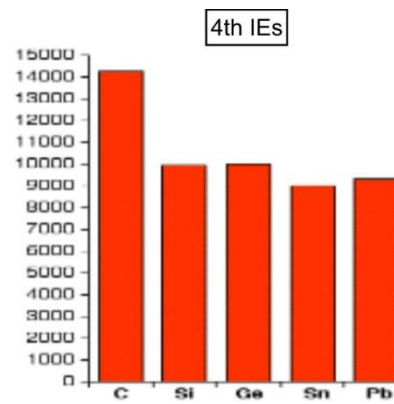
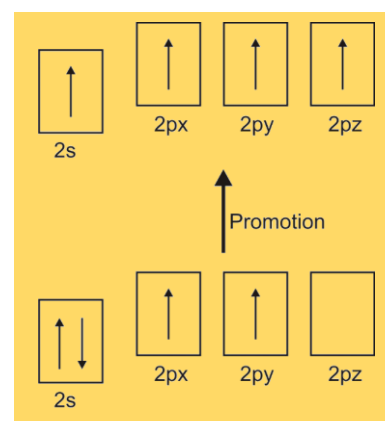
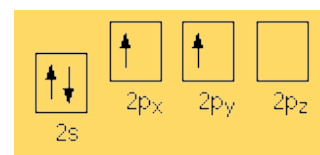


Fig. 13.35

The inert pair effect in the formation of covalent bonds

- You need to think about why carbon normally forms four covalent bonds rather than two.
- Using the electrons-in-boxes notation, the outer electronic structure of carbon looks like this:
- There are only two unpaired electrons. Before carbon forms bonds, though, it normally promotes one of the s electrons to the empty p orbital.
- That leaves 4 unpaired electrons which (after hybridisation) can go on to form 4 covalent bonds.
- 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.
- 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 .

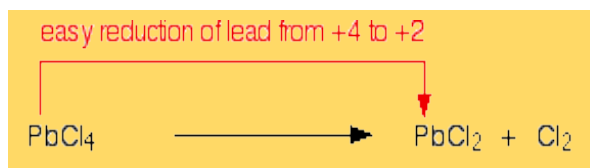
They are all simple covalent molecules with a typical tetrahedral shape. All of them are liquids at room temperature. (Although at room temperature, lead(IV) chloride will tend to decompose to give lead(II) chloride and chlorine gas - see below.)

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 $\text{MX}_4\cdot\text{H}_2\text{O}$

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 valence shell and hence is unable to accommodate the lone pair donated by the donor oxygen atom of H₂O 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 H₂O decreases from Si to Sn as the metallic character of the central atom increase in this order. Thus GeX₄ and SnX₄ tetrahalides are less readily hydrolysed than SiX₄ 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., CCl₄ undergoes hydrolysis when superheated steam is used.



Hydrolysis of tetrahalides of Pb follows essentially the same pattern but due to the instability of tetravalent compounds of Pb, some decomposition of PbCl₄ to PbCl₂ also takes place.



PbCl₄ is hydrolysed by H₂O as follows:



Excepting the tetrahalides of C, those of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ions like [SiF₆]²⁻, [GeX₆]²⁻. For example



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.

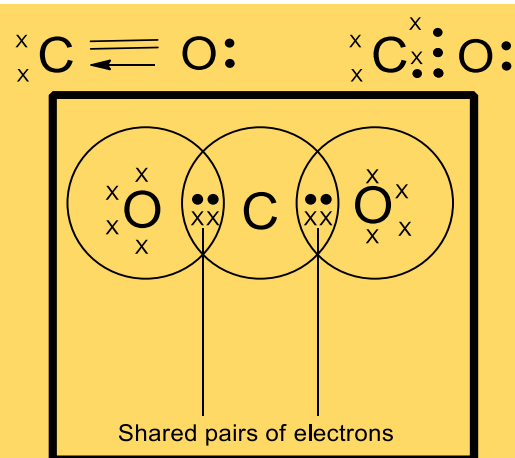


Fig 13.36: Structure of carbon dioxide



The Structure of Carbon Dioxide

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

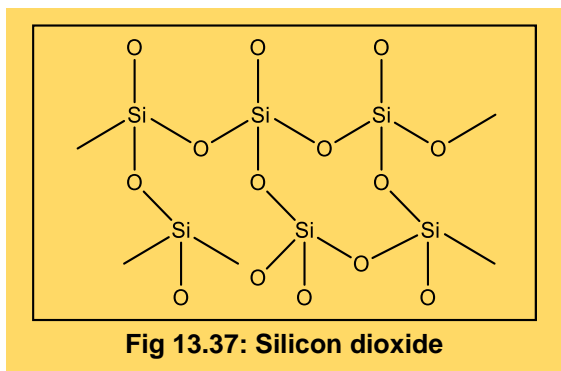
The Structure of Silicon Dioxide

It is a macromolecular compound, in which silicon and oxygen atoms are linked together covalently in tetrahedral basic unit. In cristobalite, 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 forms only single bonds with oxygen atoms while carbon forms double bonds.
- (iii) Carbon forms a linear molecule of CO₂ with two oxygen atoms while silicon atom is bound to four oxygen atoms in a tetrahedral structure which results in the formation of silicon dioxide crystal. The simplest formula for silica is SiO₂. However, the whole crystal of silicon can be considered as one molecule.

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.



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:



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.



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



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.



Germanium, 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:



. . . 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.



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.



The Acidic Nature of the Oxides

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



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 :



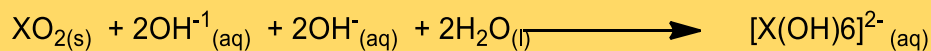
These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-} .



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 $[\text{X}(\text{OH})_6]^{2-}$.



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





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 charge.

Trends in Electronegativity

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

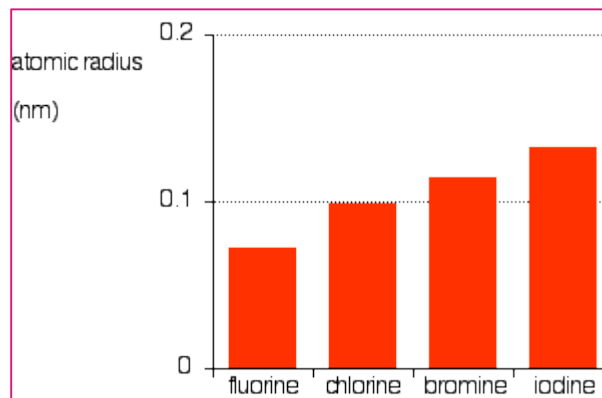


Fig. 13.38

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

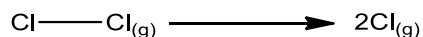
The melting and boiling points of the halogens regularly increase from F to I. This indicates that the attractive forces between molecules become progressively more prominent as the number of molecules increase in halogens. F and Cl are gases at ordinary temperature Br is a heavy liquid while I is a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

Bond enthalpies (bond energies or bond strengths)

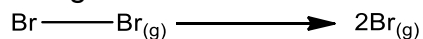
Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms.



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



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



Note: GAS not liquid!

Bond enthalpy in the halogens, $\text{X}_{2(g)}$ s

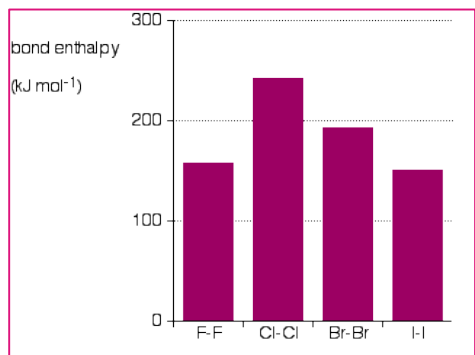


Fig. 13.35

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.

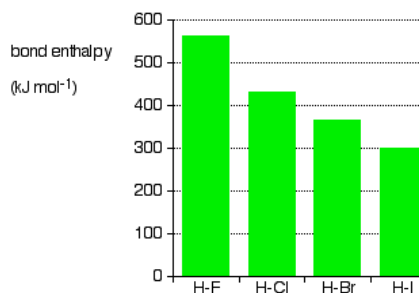


Fig. 13.28

Bond Enthalpies in the Hydrogen Halides, $\text{HX}_{(g)}$

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

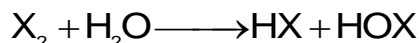
data. There is nothing complicated happening in this case.



13.5.2 Strength of Halogens as Oxidising Agents: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

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;





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 order $F_2 > Cl_2 > Br_2 > I_2$ (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.



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



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.



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 split 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.





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.



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



With Iodide Ions

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



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:



Combining these last two half-equations gives:



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**

- HI is stronger acid than HF.
 - Although H-bonding in HF is stronger than that in H₂O, H₂O has much higher boiling point.
 - The acidic character of hydrides of VIIA elements increases on descending the group.
- Illustrate the oxidising properties of halogens by giving example of two typical reactions.
 - Arrange the halogens in the decreasing order of their oxidising power.
 - Give reasons for the following;
 - Chlorine is a stronger oxidising agent than iodine.
 - Halogens are the best oxidising agents.
 - Fluorine is a better oxidising than chlorine.
 - 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, Juggling 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 point, 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

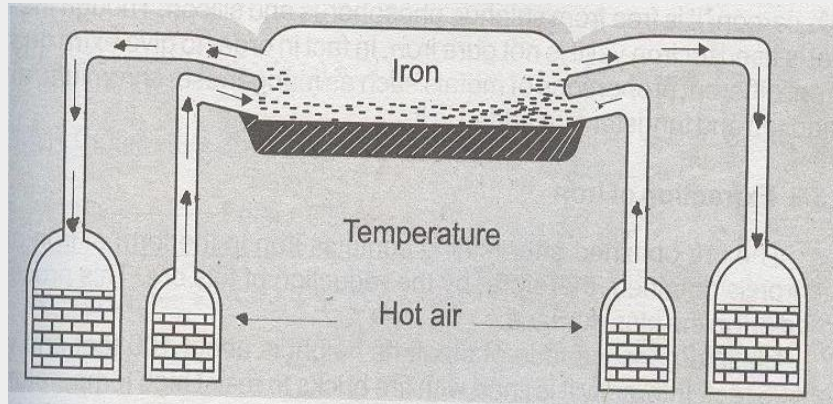
It is lined inside with fire bricks. Its height and capacity are kept according to the requirement. Hot gases enter from lower side and ores are charged from the top of the furnace. Temperature is maintained at 1500°-3000°C. This furnace is usually used for iron and copper metallurgy.

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 from 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 ($\text{Ca}(\text{OCl})_2$) and the basic chloride CaCl_2 , H_2O with some slaked lime, $\text{Ca}(\text{OH})_2$.

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 dishwasher 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**.

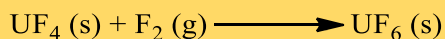
Bleaching powder is used for bleaching cotton and linen. It is also used in bathroom cleaners, household disinfectant sprays, moss and algae removers, and weedkillers.

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 dairy equipment.
3. Small quantities of fluorine are used in rocket propulsion. Much larger quantities are used to make uranium (VI) fluoride for the separation of ^{238}U and ^{235}U :



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

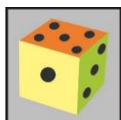


Key Points

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

(a) bright crimson	(b) violet	(c) golden yellow	(d) bright blue
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- iii. When sodium burn in air, it forms sodium:

(a) monoxide	(b) peroxide	(c) oxide	(d) superoxide
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- 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
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- v. Green is characteristic flame color of

(a) calcium	(b) barium	(c) strontium	(d) sodium
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- vi. All the carbonates, sulphates and phosphates of alkaline earth metals are In water.

(a) sparingly soluble	(b) soluble	(c) insoluble	(d) less soluble
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- 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) CO₂ (d) SnO₂
- 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) F₂ (b) I₂ (c) Br₂ (d) Cl₂
- 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 Na₂O is basic while P₂O₅ 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 from 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 than 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 points 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 is 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.

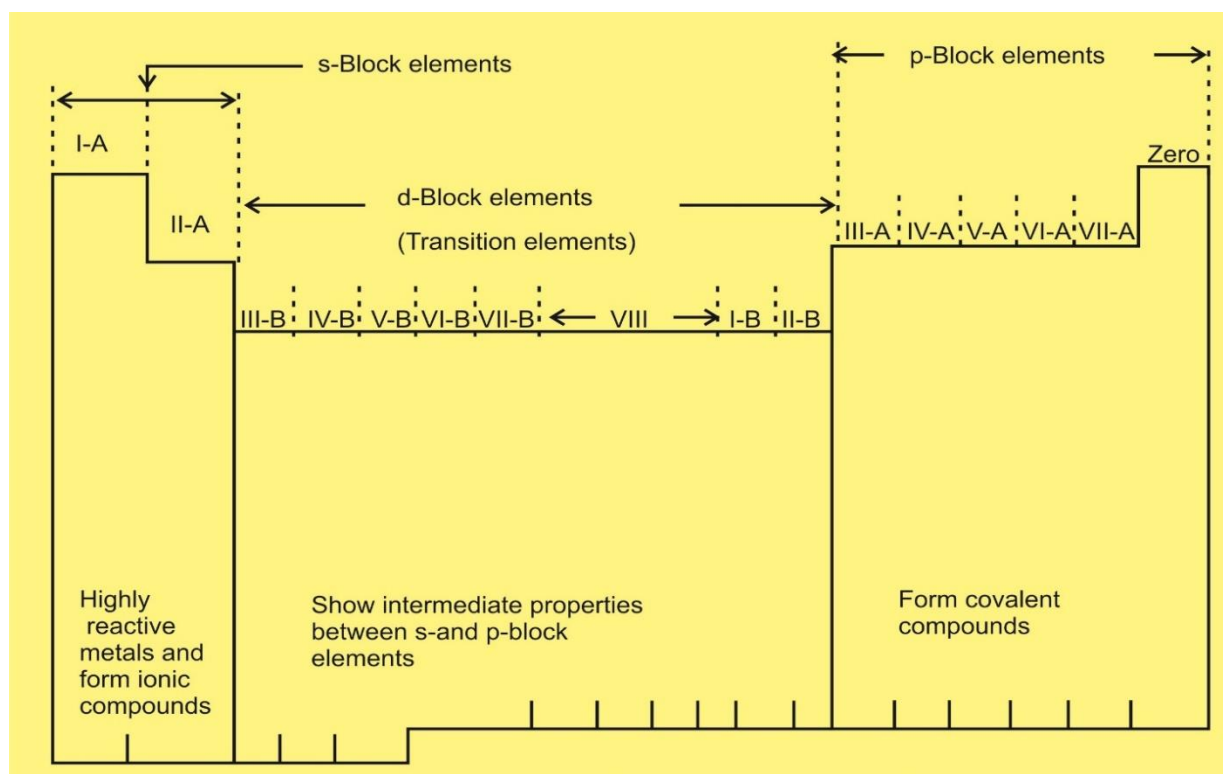


Fig. 14.1: Position of d-block elements in the periodic table

- **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





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 Sc₂₁, Y₃₁ and La₅₇. 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:



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 ¹ 4s ²	Y (39)	[Kr]4d ¹ 5s ²	La (57)	[Xe]5d ¹ 6s ²
Ti (22)	[Ar]3d ² 4s ²	Zr (40)	[Kr]4d ² 5s ²	Hf (72)	[Xe]4f ¹⁴ 5d ² 6s ²
V (23)	[Ar]3d ³ 4s ²	Nb (41)	[Kr]4d ⁴ 5s ¹	Ta (73)	[Xe]4f ¹⁴ 5d ³ 6s ²
Cr (24)	[Ar]3d ⁵ 4s ¹	Mo (42)	[Kr]4d ⁵ 5s ¹	W (74)	[Xe]4f ¹⁴ 5d ⁴ 6s ²
Mn (25)	[Ar]3d ⁵ 4s ²	Tc (43)	[Kr]4d ⁶ 5s ²	Re (75)	[Xe]4f ¹⁴ 5d ⁵ 6s ²
Fe (26)	[Ar]3d ⁶ 4s ²	Ru (44)	[Kr]4d ⁷ 5s ¹	Os (76)	[Xe]4f ¹⁴ 5d ⁶ 6s ²
Co (27)	[Ar]3d ⁷ 4s ²	Rh (45)	[Kr]4d ⁸ 5s ¹	Ir (77)	[Xe]4f ¹⁴ 5d ⁷ 6s ²
Ni (28)	[Ar]3d ⁸ 4s ²	Pd (46)	[Kr]4d ¹⁰	Pt (78)	[Xe]4f ¹⁴ 5d ⁹ 6s 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.

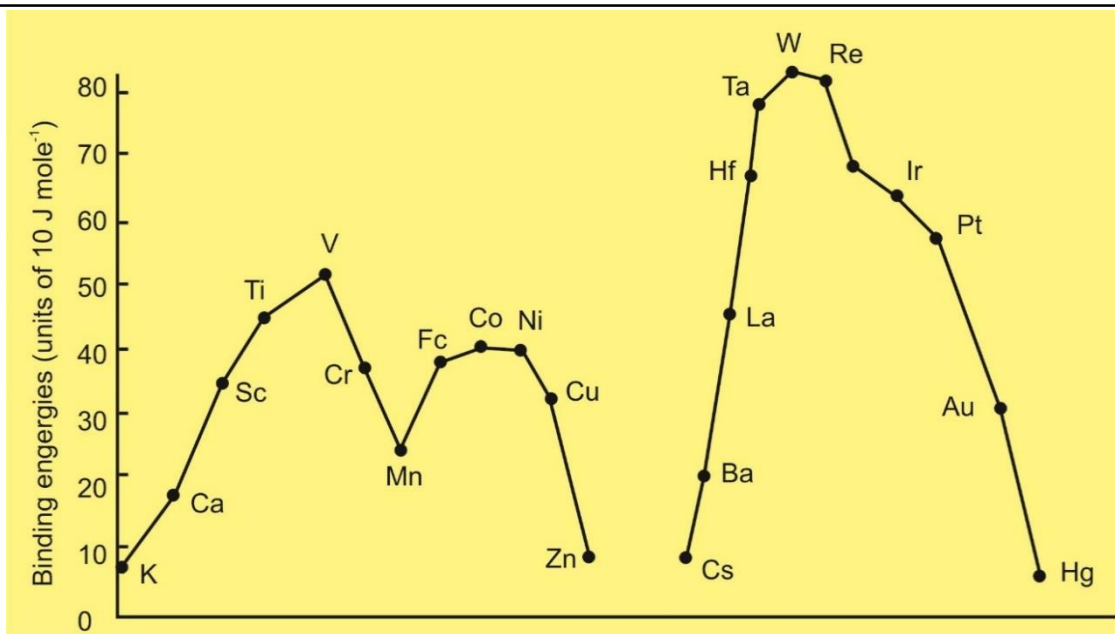


Fig. 14.2: Atomic number of elements Graphical picture of binding energy of 3 d and 5 d series of transition elements (qualitative view)

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	1					1↓		2	3						
Ti	[Ar]	3d ² 4s ²	1	1				1↓		2	3	4					
V	[Ar]	3d ³ 4s ²	1	1	1			1↓		2	3	4	5				
Cr	[Ar]	3d ⁵ 4s ¹	1	1	1	1	1	1		2	3	4	5	6			
Mn	[Ar]	3d ⁵ 4s ²	1	1	1	1	1	1↓	1	1	2	3	4	5	6	7	
Fe	[Ar]	3d ⁶ 4s ²	1↓	1	1	1	1	1↓		1	2	3	4	5	6		
Co	[Ar]	3d ⁷ 4s ²	1↓	1↓	1	1	1	1↓		2	3	4	5				
Ni	[Ar]	3d ⁸ 4s ²	1↓	1↓	1↓	1	1	1↓		2	3	4					
Cu	[Ar]	3d ¹⁰ 4s ¹	1↓	1↓	1↓	1↓	1↓	1	1	1	2	3					
Zn	[Ar]	3d ¹⁰ 4s ²	1↓	1↓	1↓	1↓	1↓	1↓		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 Cr₂O₃ 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. MnO₂ can be used as a catalyst for the decomposition of H₂O₂.
4. TiCl₄ is used as catalyst for the manufacture of plastics.
5. V₂O₅ is used to oxidize SO₂ to SO₃ in the manufacture of H₂SO₄.
6. Fe is used as a catalyst for synthesis of NH₃ in Haber's process about 1% of Na₂O or K₂O and about 1% SiO₂ or Al₂O₃ are added as promoters. Mo is also sometimes used as a promoter.

14.2.6 Magnetic Behaviour

Many transition elements and their compounds are paramagnetic. The compounds attracted into the magnetic field are called paramagnetic. Paramagnetism 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) decomposition 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

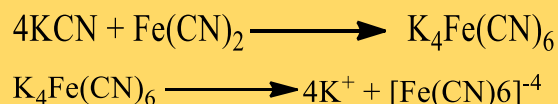
Definition:

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 $\text{Fe}(\text{CN})_2$. When this mixture is evaporated, a new compound is obtained. This compound when dissolved in water ionizes into K^+ and $[\text{Fe}(\text{CN})_6]^{-4}$. On this basis the new compounds has been given the formula $\text{K}_4[\text{Fe}(\text{CN})_6]$ (potassium ferrocyanide).



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

Parts of Complex Compound after Dissociation in a Solvent:

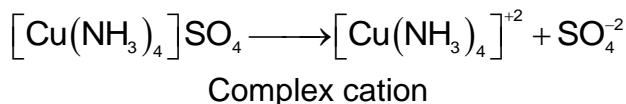
A complex compound is mostly made up of two parts:

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

For example in $\text{K}_4\text{Fe}(\text{CN})_6$, K^+ is a cation and $[\text{Fe}(\text{CN})_6]^{-4}$ is the anion.

Complex ion as cation:

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



Complex ion as anion:

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



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 $\text{K}_4[\text{Fe}(\text{CN})_6]$, Fe^{+2} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
2. In $\text{K}_3[\text{Fe}(\text{CN})_6]$, Fe^{+3} is the central metal ion. Six ligands (CN^- ions) are surrounding it.



- In $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, Cu^{+2} is the central metal ion. Four ligands (NH_3 ions) are surrounding it.
- In $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, 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:

- In $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$, CN^- is the ligand.
- In $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ and $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, NH_3 is the ligand.

Types of Ligands:

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

1) Monodentate Ligands:

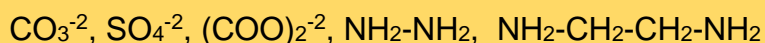
Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral.

Examples:

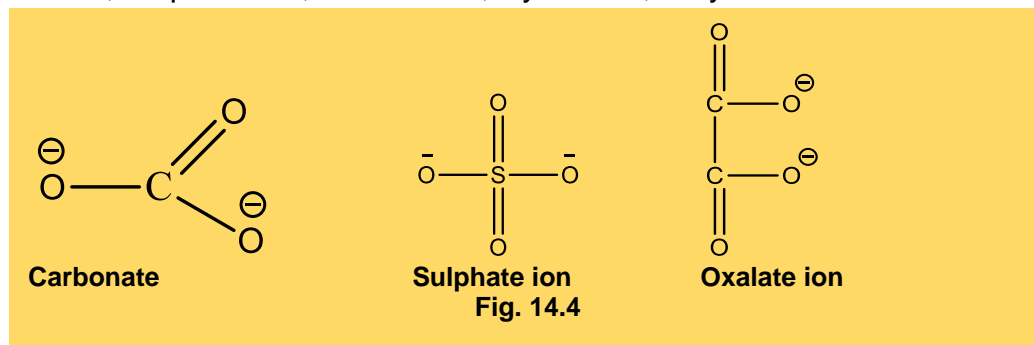
- Negatively charged ligands F^- , Cl^- , Br^- , I^- , OH^- , CN^-
- Neutral ligands H_2O , NH_3 , CO

2) Bidentate Ligands:

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

**Examples:**

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

**3) Tridentate Ligands:**

Those ligands which have three donatable electron pairs

Examples

Diethylene triammine



Fig. 14.5

4) Hexadentate Ligands:

Those ligands which have six donatable electron pairs.

**Example:**

Ethylenediaminetetracetate (EDTA)

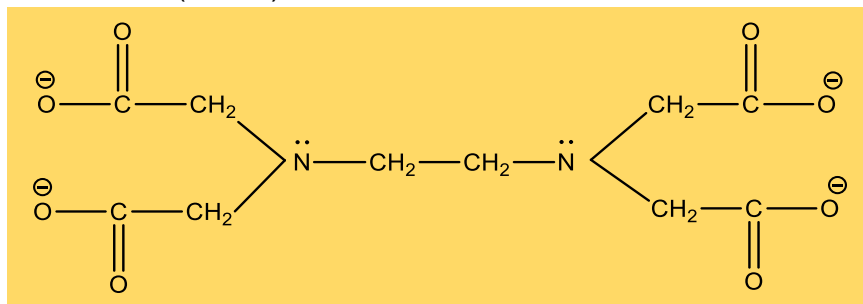


Fig. 14.6

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-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) $[Co(en)_2Cl_2]Cl$ Dichlorobisethylenediamminecobalt (III) chloride
- (10) $Ni(CO)_4$ Tetracarbonylnickel (0)
- (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⁻)
 $[Zn(CN)_4]^{2-}$,
 $[Zn(NH_3)_4]^{2-}$

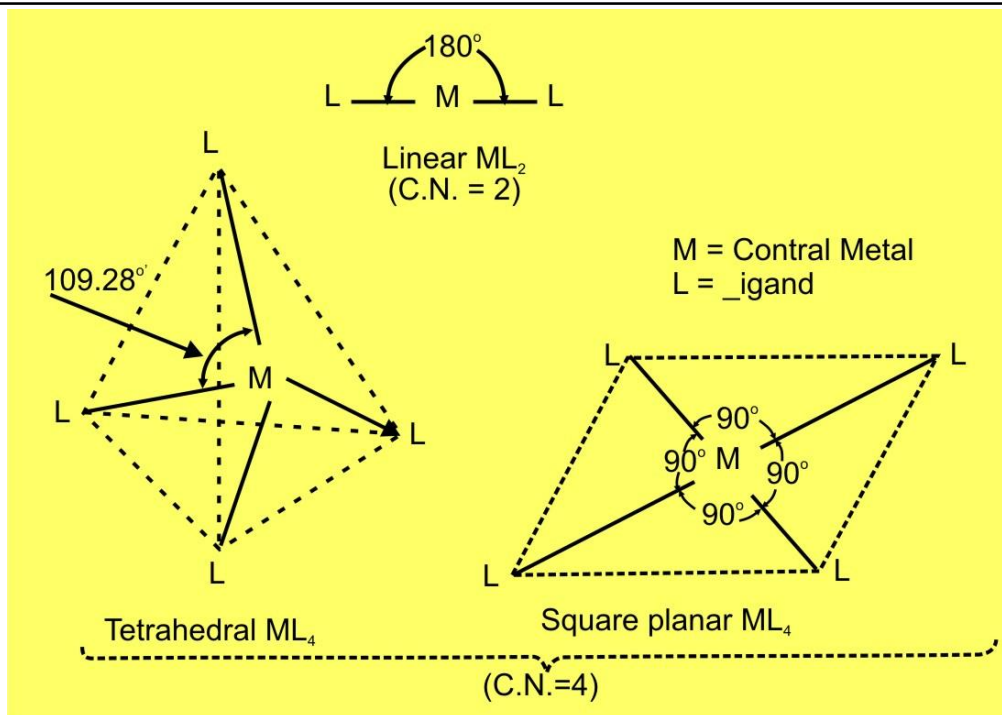


Fig. 14.7

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.

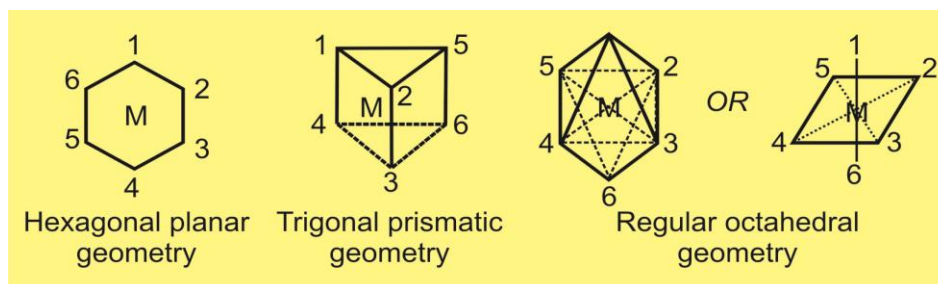


Fig.14.8



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

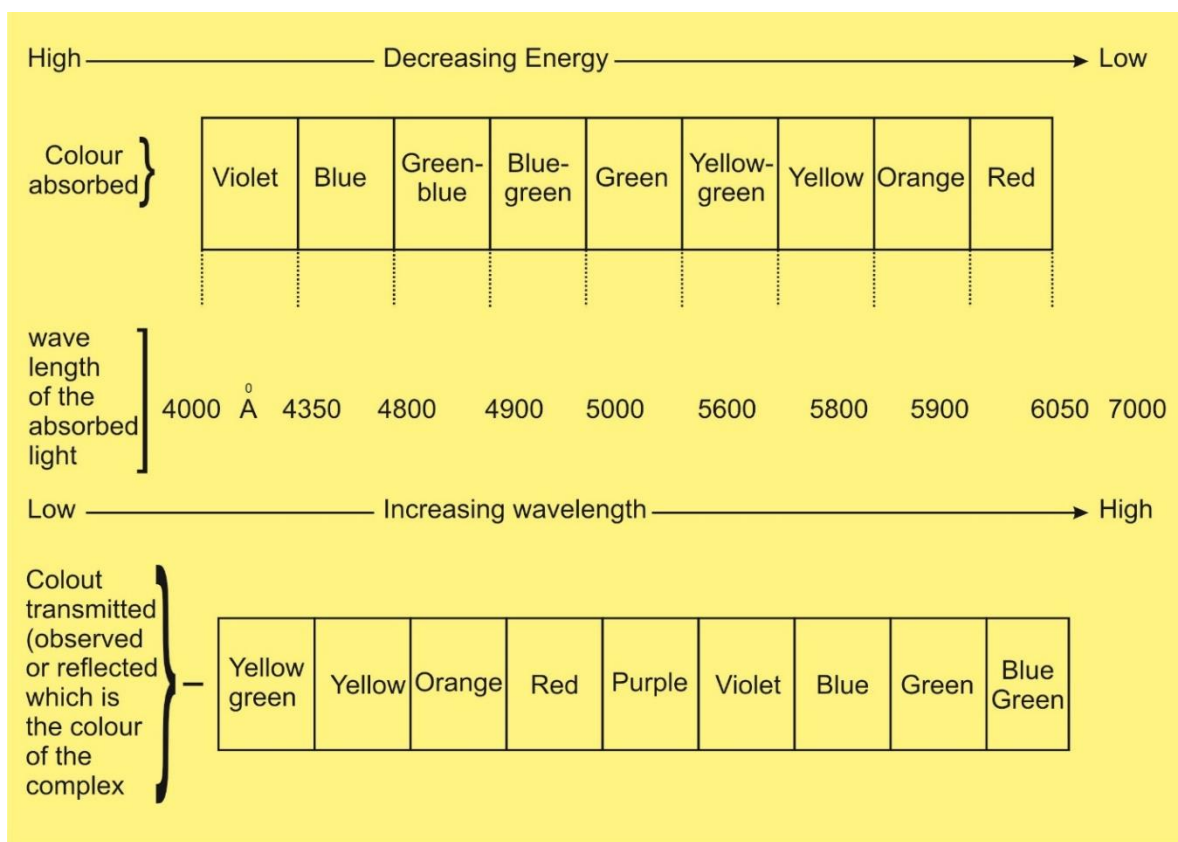


Fig.14.9

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.

Thus:

- (i) Hydrated cupric sulphate containing $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions is blue color of the transmitted light because it absorb yellow light.
- (ii) Cuprammonium sulphate containing $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions is violet because it absorbs yellow green light.
- (iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ 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) $[\text{Cu}(\text{CN})_4]^{4-}$ 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, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000\AA which corresponds to the wave number $\nu = 20000\text{ cm}^{-1}$ as shown below:

Since $1\text{\AA} = 10^{-8}\text{cm}$. wavelength, $\lambda = 5000\text{\AA} = 5000 \times 10^{-8}\text{cm}$

Consequently wave number,

$$\begin{aligned} \nu &= 1/\lambda = 1/5000 \times 10^{-8} \\ &= 1/5 \times 10^{-5} \text{ cm}^{-1} = \\ 0.2 \times 10^5 \text{ cm}^{-1} &= 20000 \text{ cm}^{-1} \end{aligned}$$

Light of this wavelength (5000\AA) 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.

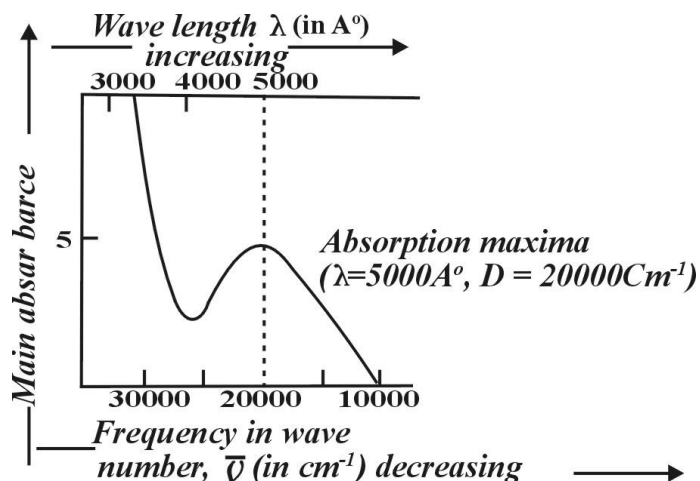
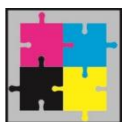


Fig.14.10



Quick Quiz

1. Why do most of the transition metal ions possess a definite color?
2. What is wavelength of green color?
3. When complex compound appears 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 $[\text{VO}_2(\text{H}_2\text{O})_4]^+$.

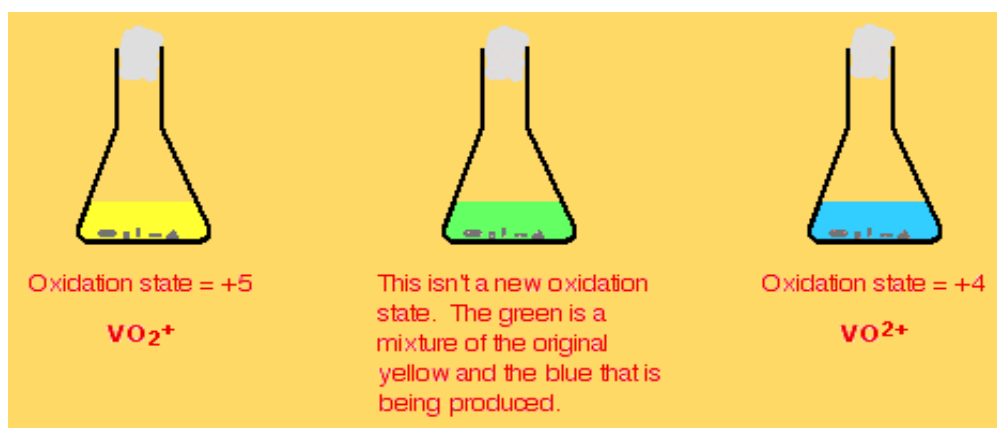


Fig.14.11

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 - $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$. We usually use the simpler form.

The reduction from +4 to +2

The colour changes just continue.

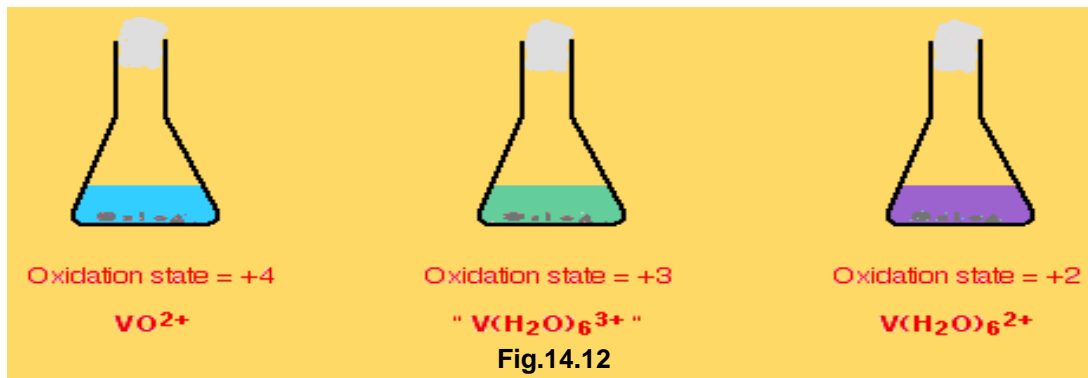


Fig.14.12

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)

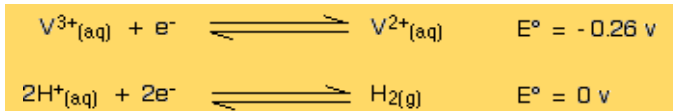
The vanadium (II) oxidation state is easily oxidized back to vanadium(III) - or even higher.

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:

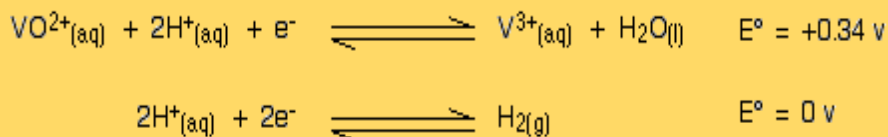


The reaction with the more negative E° value goes to the left; the reaction with the more positive (or less negative) one to the right.

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?

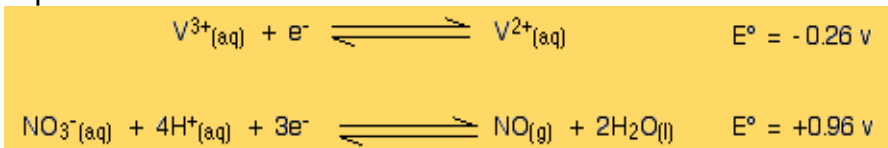
Have a look at the E° values and decide:



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:





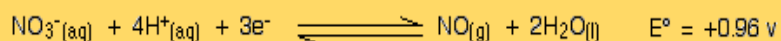
The vanadium reaction has the more negative E° value and so will move to the left; the nitric acid reaction moves to the right.

Nitric acid will oxidize vanadium (II) to vanadium (III).

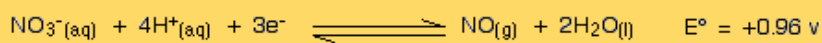
The second stage involves these E° values:

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).



Will it go all the way to vanadium (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.



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.



The vanadium (IV) oxide is then re-oxidized by the oxygen.



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 $\text{SO}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$

14.4. 2 Chromium

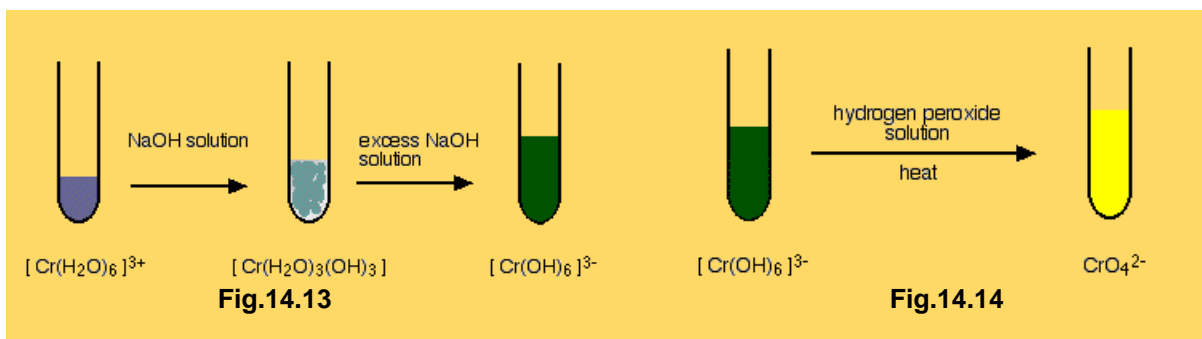
In this topic we will discuss;

- 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.



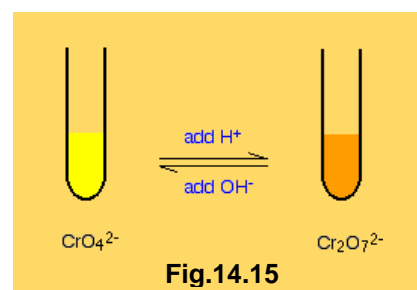
The equation for the oxidation stage is:

**Some Chromium(VI) Chemistry****The Chromate(VI)-Dichromate(VI) Equilibrium**

You are probably more familiar with the orange dichromate(VI) ion, $\text{Cr}_2\text{O}_7^{2-}$, 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.





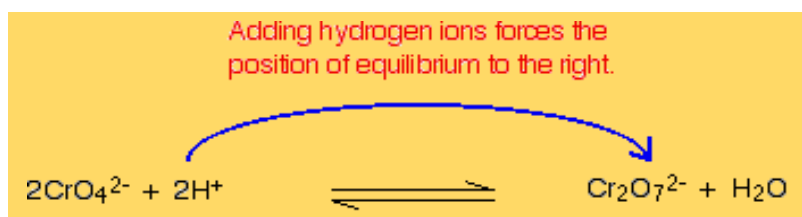
The most important: If you had just produced the yellow chromate (VI) ions by oxidising chromium (III) ions using hydrogen peroxide, you can't convert them into dichromate (VI) ions without taking a precaution first.

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.

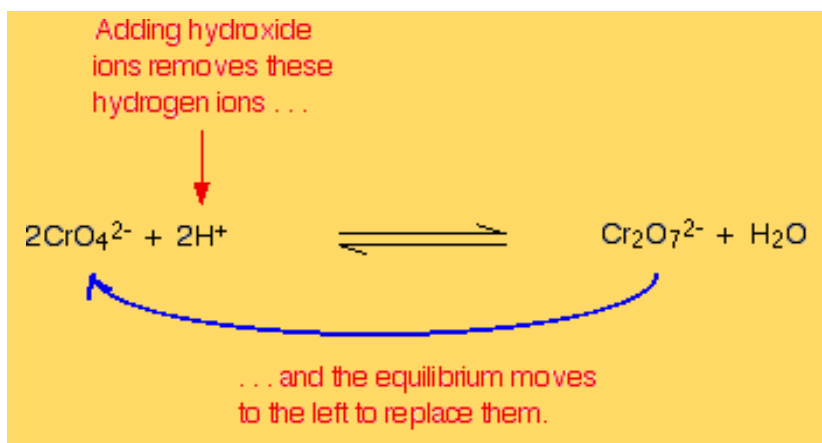
The equilibrium reaction at the heart of the interconversion is:



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.

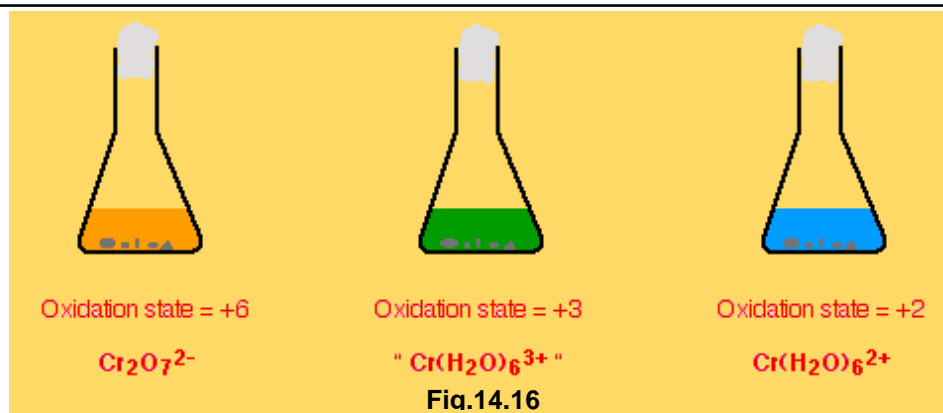


The Reduction of Di-chromate (VI) Ions with Zinc and an Acid

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.



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:



For the reduction from +3 to +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.



- 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.



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:



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.

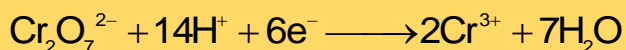
Unfortunately potassium dichromate(VI) solution turns green as you run it into the reaction, and there is no way you could possibly detect the colour change when you have one drop of excess orange solution in a strongly coloured green solution.

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:



... and for the iron(II) ions is:





Combining these gives:



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.

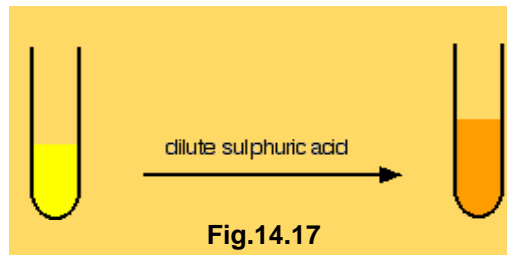
Testing for Chromate(VI) Ions in Solution

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

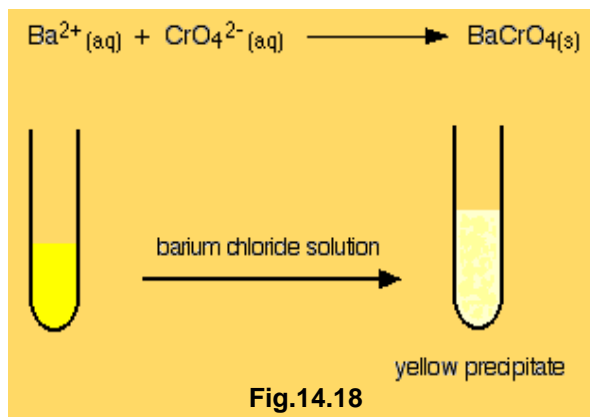
If you add some dilute sulphuric acid to a solution containing chromate(VI) ions, the colour changes to the familiar orange of dichromate(VI) ions.



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!

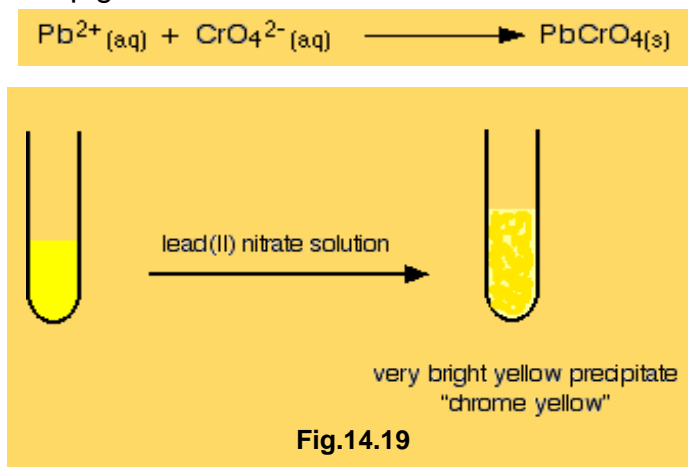
Testing by adding Barium Chloride (or Nitrate) Solution

Chromate(VI) ions will give a yellow precipitate of barium chromate(VI).



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.





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 dichromate is preferred over potassium manganate in titration.
4. In which titration end point is clear potassium dichromate or potassium manganate
5. What color changes obscure when (i) Acid (ii) Lead nitrate solution are added separately in potassium chromate solution

14.4.3 Manganese

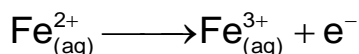
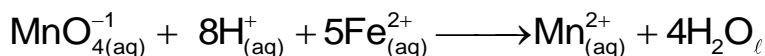
In this topic we will discuss:

- (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.

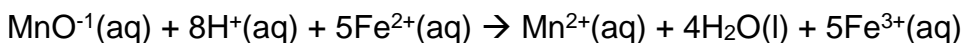
The Oxidation States

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^- . This can be reduced to the pale pink Mn^{2+} by Fe^{2+} in acidic solution:



Overall:



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.





In the test-tube, the colour changes are:

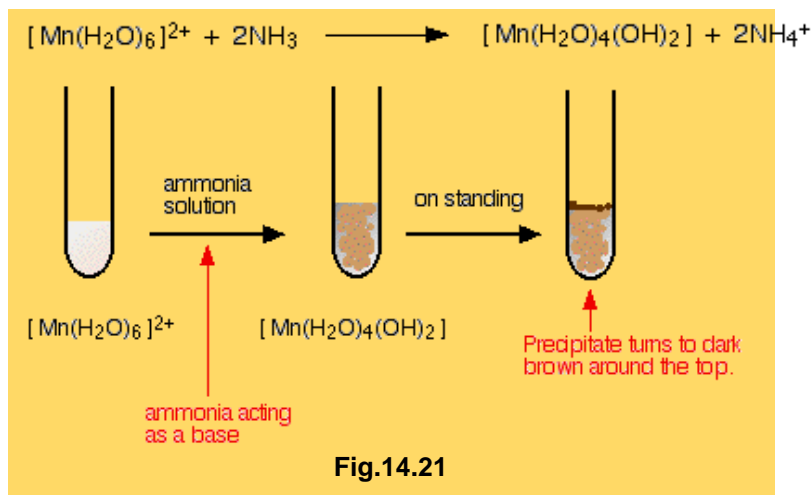
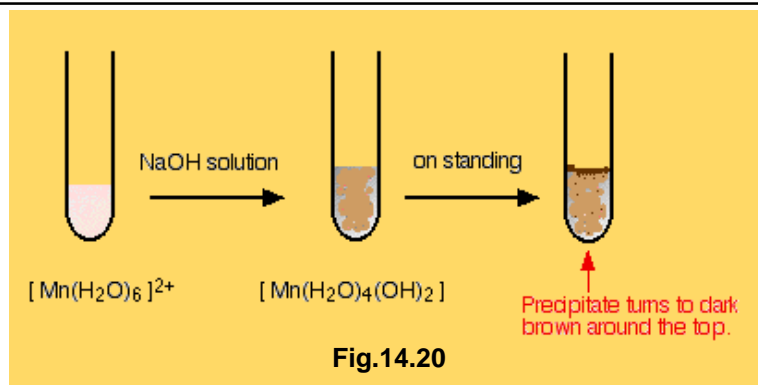
It has been shown the original solution is very pale pink, but in fact it is virtually colourless. The pale brown precipitate is oxidised to darker brown manganese(IV) oxide in contact with oxygen from the air.

II - The Reaction of Hexaaquamanganese(II) Ions with Ammonia Solution

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.

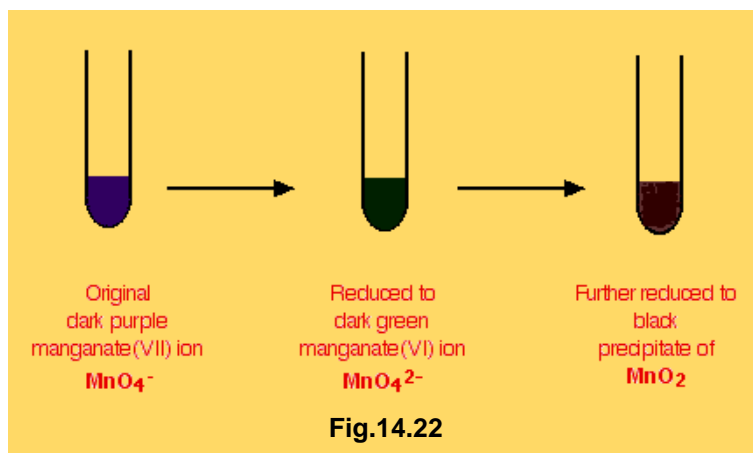
Using Potassium Manganate(VII) as an Oxidising Agent in Organic Chemistry

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:

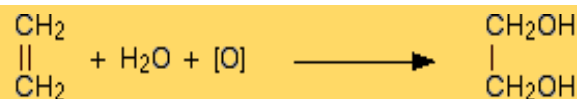
In Testing for a C=C Double Bond

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.



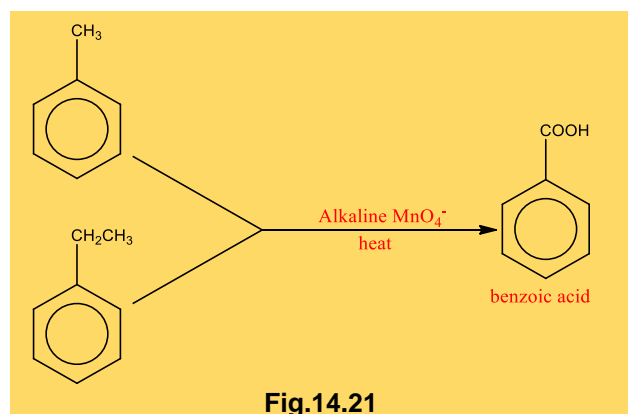
The oxygen in square brackets is taken to mean "oxygen from an oxidising agent". This abbreviated form of the equation is most commonly used in organic chemistry. You are very unlikely to have to write the complete ionic equation for this reaction at this level.

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.



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



- hydrogen peroxide solution to oxygen



- ethanedioic acid to carbon dioxide (This reaction has to be done hot.)



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



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





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 reaction of hexaaquamanganate(II) with $-\text{OH}$ ion. What color change is observed.

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 persulphate 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+} :



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.



Iron Ions as a Catalyst in the Reaction between Persulphate Ions and Iodide Ions

The reaction between persulphate ions (peroxodisulphate ions), $\text{S}_2\text{O}_8^{2-}$, and iodide ions in solution can be catalysed using either iron(II) or iron(III) ions.

The overall equation for the reaction is:



For the sake of argument, we'll take the catalyst to be iron(II) ions. The reaction happens in two stages.



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:

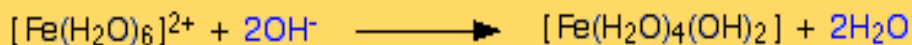
- the hexaaquairon(II) ion - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.
- the hexaaquairon(III) ion - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

(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:

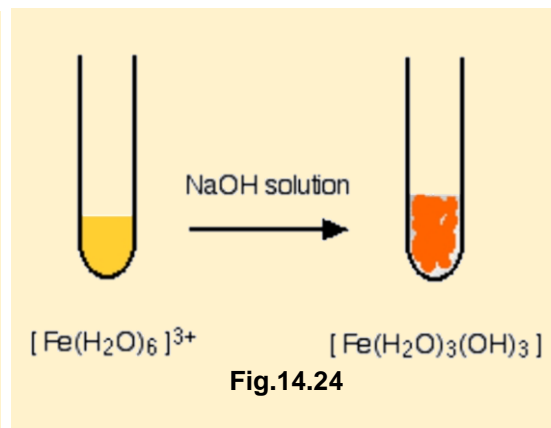
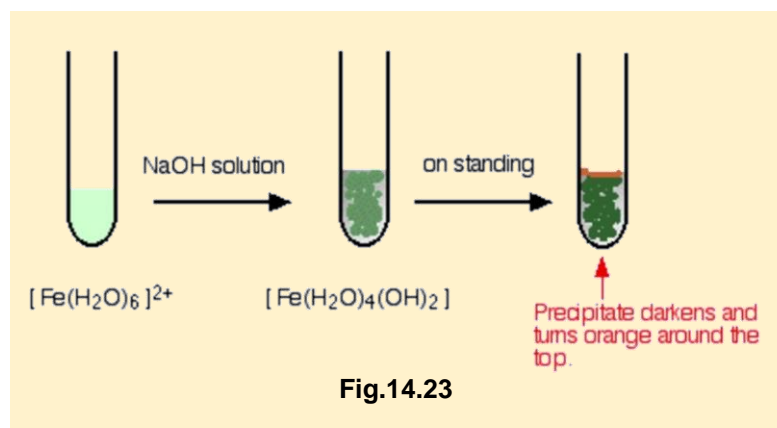


In the iron(III) case:



In the test-tube, the colour changes are:

In the iron(II) case:



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:

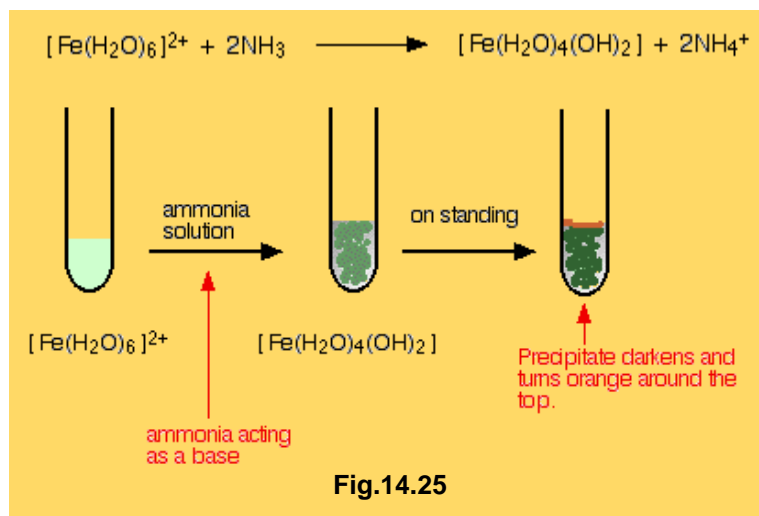
(b) Reactions of the Iron Ions with Ammonia Solution

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.

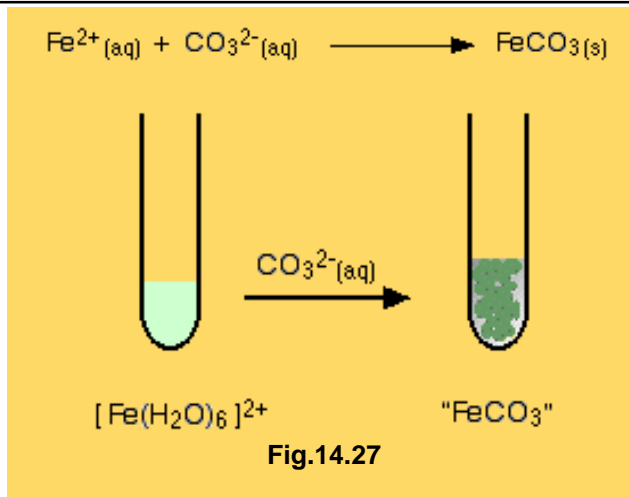
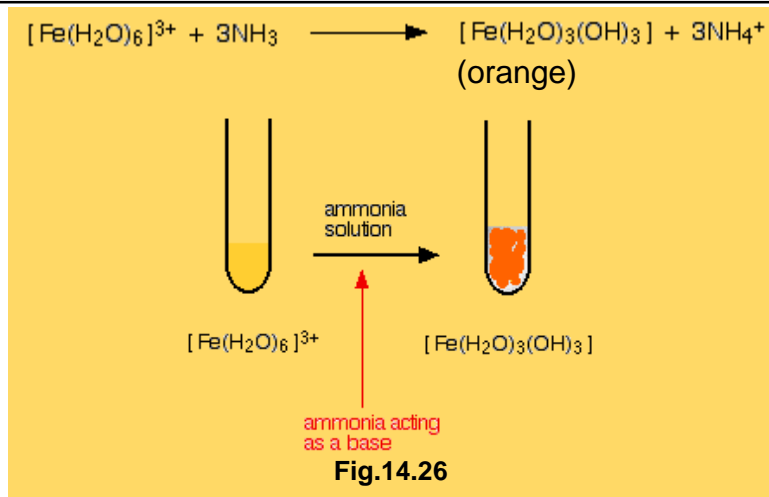
In the iron(II) case:

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.

In the iron(III) case:



The reaction looks just the same as when you add sodium hydroxide solution.

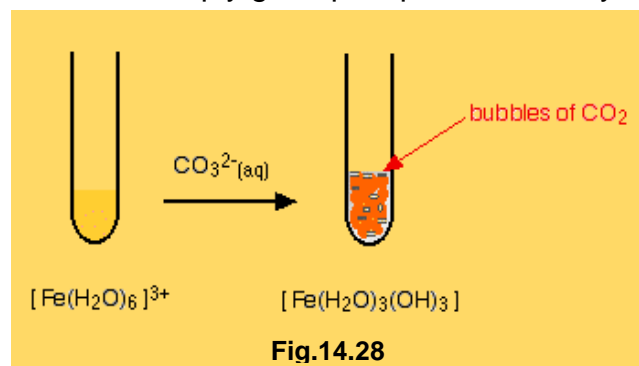


Reactions of the Iron (II) and (III) Ions with Carbonate Ions and Thiocyanate Ions

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.

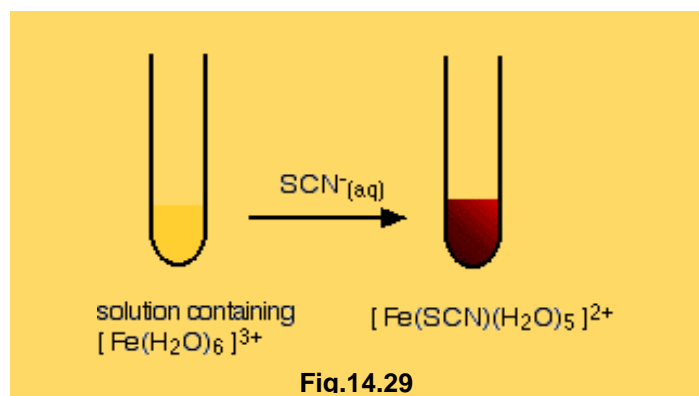
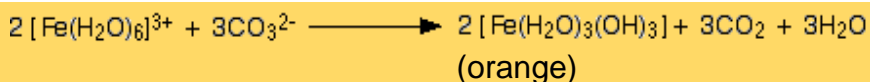


Iron(III) Ions and Carbonate Ions

The hexaaqua iron(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.

If you add sodium carbonate solution to a solution of hexaaqua iron(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.



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 $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$.

**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 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+} :



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.

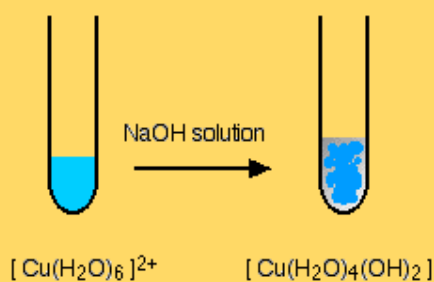


Fig.14.30

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.

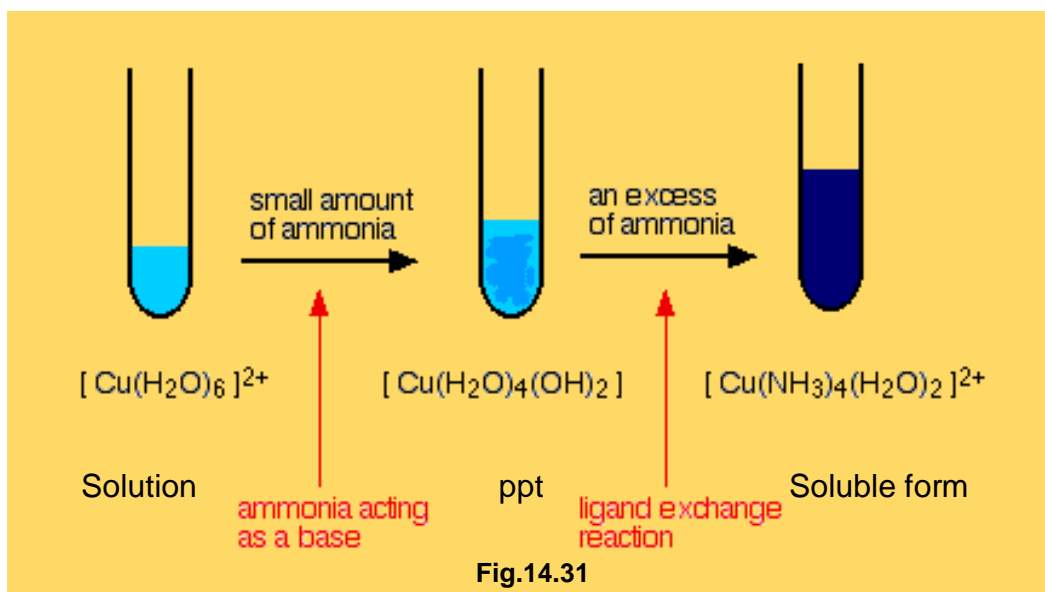


That precipitate dissolves if you add an excess of ammonia.

The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Notice that only 4 of the 6 water molecules are replaced.

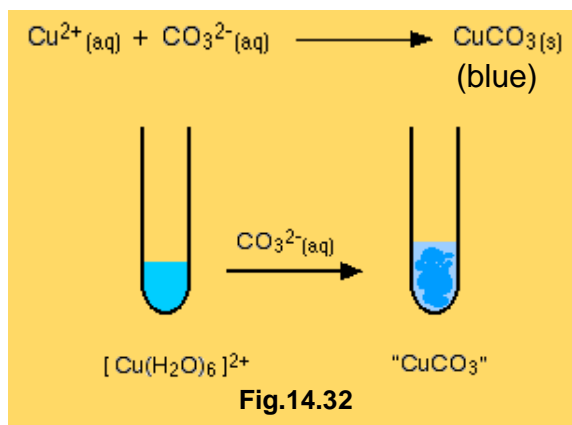


The colour changes are:



The Reaction of Hexaaquacopper(II) Ions with Carbonate Ions

You simply get a precipitate of what you can think of as copper(II) carbonate.



**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)	<ol style="list-style-type: none"> 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)	<ol style="list-style-type: none"> 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)	<ol style="list-style-type: none"> 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 [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$]	<ol style="list-style-type: none"> 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)	<ol style="list-style-type: none"> 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 chromate.



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 $\text{Fe}(\text{CO})_5$
- (a) Pentacarbonyl iron (III) (b) Pentacarbonyl iron (0)
(c) Pentacarbonyl iron (II) (d) Pentacarbonyl ferrate (III)
- x. Give the chemical formula of a complex compound sodium monochloropentacyanoferrate (III).
- (a) $[\text{Na}_3\text{FeCl}(\text{CN})_5]$ (b) $\text{Fe}_3[\text{NaCl}(\text{CN})_5]$
(c) $\text{Na}_3[\text{FeCl}(\text{CN})_5]$ (d) $\text{Na}_2[\text{FeCl}(\text{CN})_5]$
- 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 HNO_3 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.

- Why are d-block elements called transition elements?
- Why do the d-block elements show different oxidation states?
- Why does Mn show the maximum number of oxidation states in 3d-series?
- What is the difference between double salts and coordination or complex compounds?
- Explain the following terms: (a) Ligand (b) Coordination Sphere (c) Central Metal.
- How chromate ions are converted into dichromate ions?
- What is the difference between paramagnetism and diamagnetism?
- What are advantages of Potassium dichromate in titrations?
- How does dichromate ion converted in to chromate ions.

3. Give detailed answers for the following questions.

- (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.
- (a) Explain different types of ligand with examples
 (b) Describe the rules for naming the coordination complexes with examples.
- (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.
- (a) Write systematic names to following complexes:
 (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (iii) $\text{Na}_3[\text{CoF}_6]$
 (iv) $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3]$ (v) $\text{K}_2[\text{PtCl}_6]$ (vi) $[\text{Pt}(\text{OH})_2(\text{NH}_3)_4]\text{SO}_4$



(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 (CO₂), carbon disulphide (CS₂), carbonates (CO₃²⁻), bicarbonates (HCO₃⁻¹), 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 ($\text{CH}_2=\text{CH}_2$)

Acetylene ($\text{CH}\equiv\text{CH}$)

Propene ($\text{CH}_3\text{CH}=\text{CH}_2$)

Benzene C_6H_6

Toluene $\text{C}_6\text{H}_5\text{CH}_3$

Xylene $\text{C}_6\text{H}_4(\text{CH}_3)_2$

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 definition of organic chemistry.
2. List different sources of organic compounds.
3. Write important products from petroleum.
4. What are alkaloids?
5. Define fermentation?

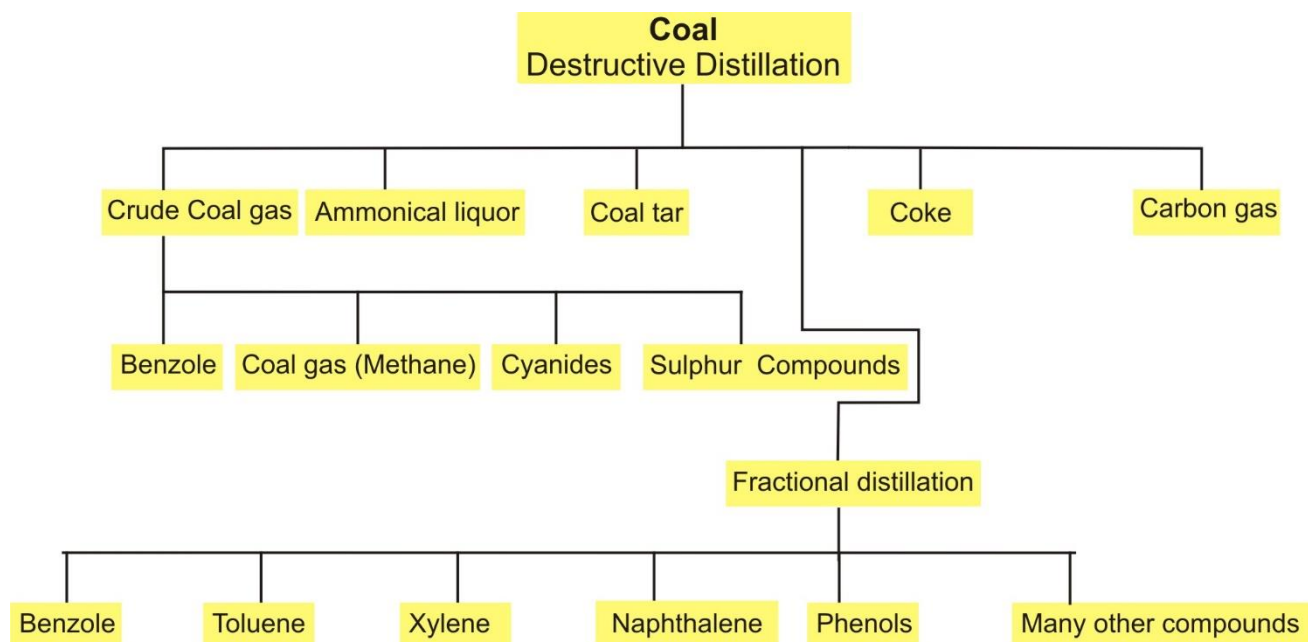
15.2 Coal (as a source of organic compound)

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°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 Chemistry:

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 Buckminster Fullerenes. Scientists named it after an architect Buckminster, 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**

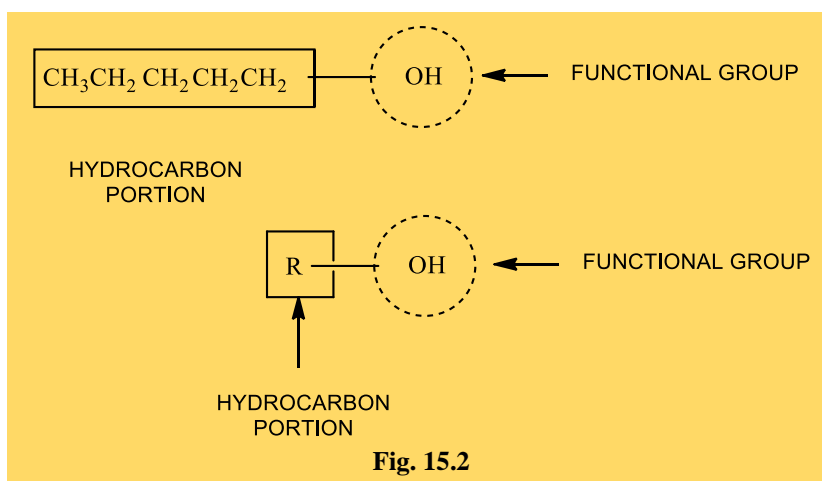
1. What are allotropes?
2. Why it was given the name Bucky balls?

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.



We often use the symbol R- to represent the hydrocarbon portion to which the functional group is attached. Thus R- can be CH₃-, CH₃CH₂-, (CH₃)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.

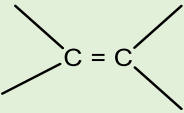
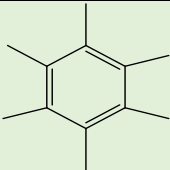
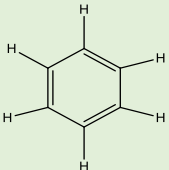
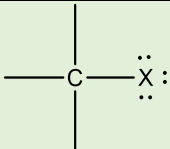
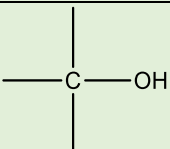
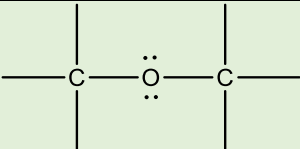
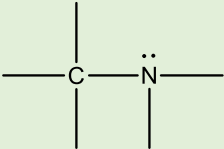
A molecule can contain more than one functional group. It is then said to be **Polyfunctional**, and the properties of each functional group may be modified by the presence of the others.



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	$\text{CH}_3 - \text{CH}_3$ Ethane
Alkene		$\text{H}_2\text{C} = \text{CH}_2$ Ethene
Alkyne	$-\text{C} \equiv \text{C}-$	$\text{H}-\text{C} \equiv \text{C}-\text{H}$ Ethyne (Acetylene)
Arene		 Benzene
Halide	 (X = F ₂ Cl ₂ Br ₂ I ₂)	$\text{H}_3\text{C}-\ddot{\text{Cl}}:$ Methyl chloride
Alcohol		$\text{H}_3\text{C}-\text{OH}$ Methanol (Methyl alcohol)
Ether		$\text{H}_3\text{C}-\ddot{\text{O}}-\text{CH}_3$ dimethyl ether
Amine		$\text{H}_3\text{C}-\text{NH}_2$ Methyl amine



Nitrile		$\text{H}_3\text{C}-\text{C}\equiv\text{N}$ Methyle Cyanide (Methyl nitrile)
Nitro		$\text{H}_3\text{C}-\text{N}^+\begin{matrix} \text{=O} \\ \text{O}^- \end{matrix}$ Nitromethane
Sulphide		$\text{H}_3\text{C}-\ddot{\text{S}}-\text{CH}_3$ Dimethyl sulphide
Sulphoxide		$\text{H}_3\text{C}-\overset{\uparrow}{\ddot{\text{S}}}-\text{CH}_3$ Dimethyl sulphoxide
Sulphone		$\text{CH}_3-\overset{\text{O}^-}{\underset{\text{O}^-}{\text{S}}}-\text{CH}_3$ Dimethyl sulphone
Thiol		$\text{H}_3\text{C}-\ddot{\text{S}}\text{H}$ Methane thiol (Methylthiol)
Carbonyl		Aldehydes, ketones, acids and derivatives of acids.
Aldehyde		$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ Acetaldehyde
Ketone		$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ Dimethyl Ketone (Acetone)



Carboxylic Acid	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{---C---C---}\ddot{\text{O}}\text{---H} \\ \\ \text{---} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3\text{---C---O---H} \\ \text{Acetic acid} \end{array}$
Ester	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{---C---C---}\ddot{\text{O}}\text{---C---} \\ \qquad \\ \text{---} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3\text{---C---O---CH}_3 \\ \text{Methyl acetate} \end{array}$
Amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{---C---C---}\ddot{\text{N}}\text{H}_2 \\ \\ \text{---} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}_3\text{C---C---NH}_2 \\ \text{Acetamide} \end{array}$
Carboxylic acid chloride	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{---C---C---}\ddot{\text{Cl}}\text{:} \\ \\ \text{---} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{H}_3\text{C---C---}\ddot{\text{Cl}}\text{:} \\ \text{Acetyl chloride} \end{array}$
Carboxylic acid anhydride	$\begin{array}{c} \text{:O:} \qquad \text{:O:} \\ \parallel \qquad \parallel \\ \text{---C---C---}\ddot{\text{O}}\text{---C---C---} \\ \qquad \\ \text{---} \end{array}$	$\begin{array}{c} \text{:O:} \qquad \text{:O:} \\ \parallel \qquad \parallel \\ \text{H}_3\text{C---C---}\ddot{\text{O}}\text{---C---CH}_3 \\ \text{Acetic anhydride} \end{array}$

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 $\text{C}_n\text{H}_{2n+1}\text{OH}$

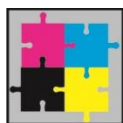
n	R	Formula
1	CH_3^-	CH_3OH
2	CH_3CH_2^-	$\text{CH}_3\text{CH}_2\text{OH}$
3	$\text{CH}_3\text{CH}_2\text{CH}_2^-$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^-$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

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 $\text{C}_n\text{H}_{2n+2}$, for alkene C_nH_{2n} and for alkyne $\text{C}_n\text{H}_{2n-2}$.
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

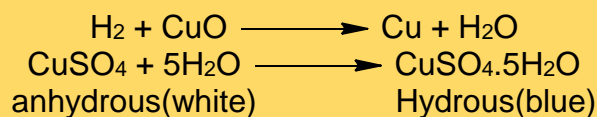
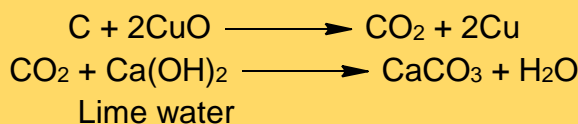
1. What are general formulas for alkanes, alkenes and alkyne
2. What are homologs?
3. Why we arrange compounds in homologous series?

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 CO₂ and H₂O respectively. CO₂ 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.



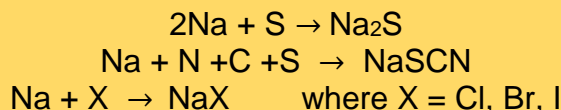
B) Detection of Nitrogen, Sulphur and Halogens

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 20cm³ of distilled water.
- 7) Mixed, boil and then filter the solution.
- 8) The filtrate obtained is called Lassaigne's solution or sodium extract.
- 9) Divide this filtrate into three portion and test, the presence of N, S ad (X) halogens respectively.

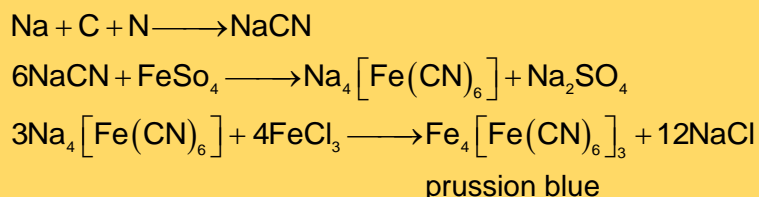


Reactions:

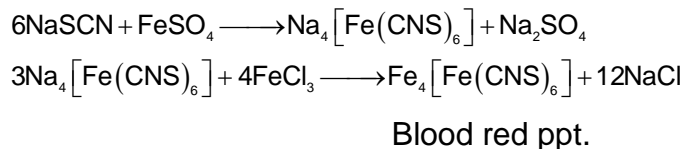
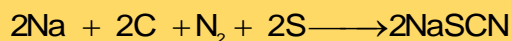


Nitrogen Test:

To one portion of Lassaigne's filtrate a few drops of NaOH is added to make it alkaline, then freshly prepared (FeSO₄) solution is added to it. The solution is boiled and a few drops of FeCl₃ 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.

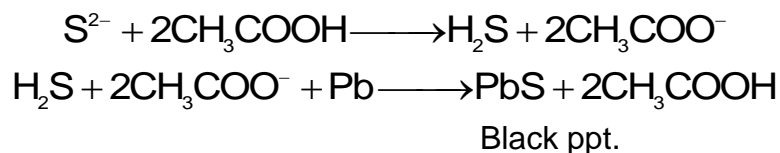


Note: if a blood red color is produced instead of prussian blue color then it proves that nitrogen and sulphur both are present in the organic compound.



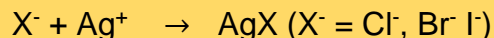
Sulphur Test:

The second portion of Lassaigne's filtrate is acidified with acetic acid and boiled to expel H₂S gas which turns lead acetate paper black that indicates the presence of Sulphur in the compound.



Halogen Test:

A third portion of Lassaigne's solution is boiled with nitric acid to expel cyanide ion and sulphide ions and AgNO₃ solution is added. The formation of precipitate shows the presence of a halogens, white ppt soluble in NH₄OH shows the presence of chlorine, a pale yellow ppt. partially soluble in NH₄OH shows the presence of bromine and a deep yellow ppt. insoluble in NH₄OH indicated iodine.





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 (NO₂) 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 molybdate 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 choloretic- is obtained from *Curcuma longa* (turmeric).

Cocaine- a local anaesthetic- is obtained from *Erythroxylum coca* (coca plant).

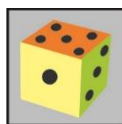
Caffeine- a CNS stimulant- is obtained from *Camellia sinensis* (tea, coffee and cocoa).

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) Thiphenes (d) All of the above
- vi. Select from the following the one, which is alcohol;
(a) $\text{CH}_3\text{-CH}_2\text{-OH}$ (b) $\text{CH}_3\text{-O-CH}_3$ (c) CH_3COOH (d) $\text{CH}_3\text{-CH}_2\text{-Br}$
- 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 cycloalkanes.
- Describe the mechanism of free radical substitution in alkanes exemplified methane and ethane.
- Describe the structure and reactivity of alkenes as exemplified by ethene.
- 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 alkynes.
- 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, halohydrate, 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

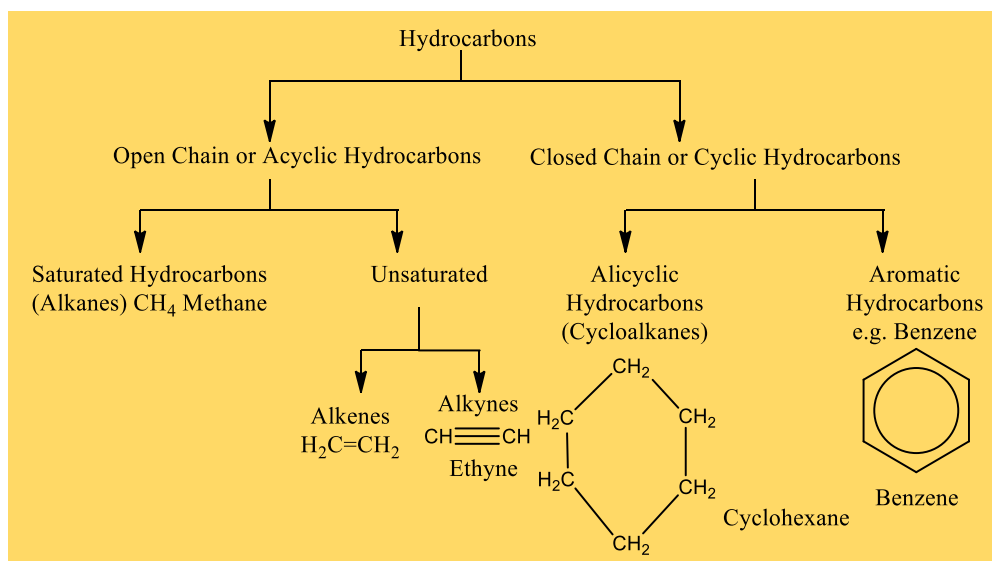
“Organic compounds which contain carbon and hydrogen only are called hydrocarbons.”

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:

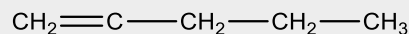
1. Saturated hydrocarbons: (Alkanes or Paraffins)
2. Unsaturated hydrocarbons: (Alkenes or Olefins) and (Alkynes or Acetylenes)

Explanation and Examples:

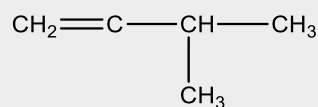
(1) Saturated Hydrocarbons	(2) Unsaturated Hydrocarbons
<p>These are the hydrocarbons in which carbon atoms are attached with each other through single bonds. Each carbon atom is sp^3 hybridized. For example, Alkanes. These may have straight chain or branched chain.</p> $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ <p style="text-align: center;">pentane (Straight Chain)</p> $\begin{array}{c} \text{CH}_3\text{—CH—CH}_2\text{—CH}_3 \\ \\ \text{CH}_3 \end{array}$ <p>2- Methyl butane (Branched Chain)</p> <p>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.</p>	<p>These are the hydrocarbons in which at least two carbon atoms are attached through double or triple bonds, and are sp^2 or sp hybridised. For example, alkenes and alkynes.</p> <p>(i) Alkenes or Olefins:</p> <p>These are the unsaturated hydrocarbons in which at least two carbon atoms are sp^2 hybridized, which cause to form a double bond between these carbon atoms. Alkenes may be straight chain or branched chain.</p> $\text{CH}_2\text{=CH—CH}_2\text{—CH}_3$ <p style="text-align: center;">1- pentene (Straight Chain)</p> $\begin{array}{c} \text{CH}_2\text{=CH—CH—CH}_3 \\ \\ \text{CH}_3 \end{array}$ <p style="text-align: center;">3-Methyl-1-butene (Branched Chain)</p> <p>(ii) Alkynes or acetylenes:</p> <p>These are the unsaturated hydrocarbons in which at least two carbon atoms are sp hybridised, which cause</p>



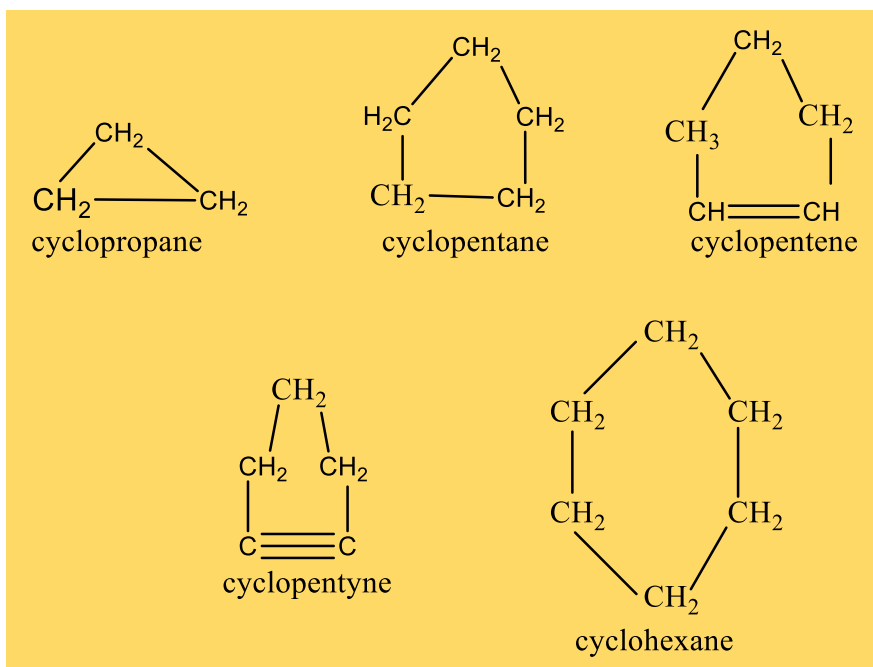
to form a triple bond between these carbon atoms. Alkynes may be straight chain or branched chain.



1 - pentene (Straight Chain)



3-Methyl-1-butene (Branched Chain)



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.

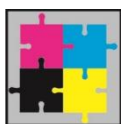
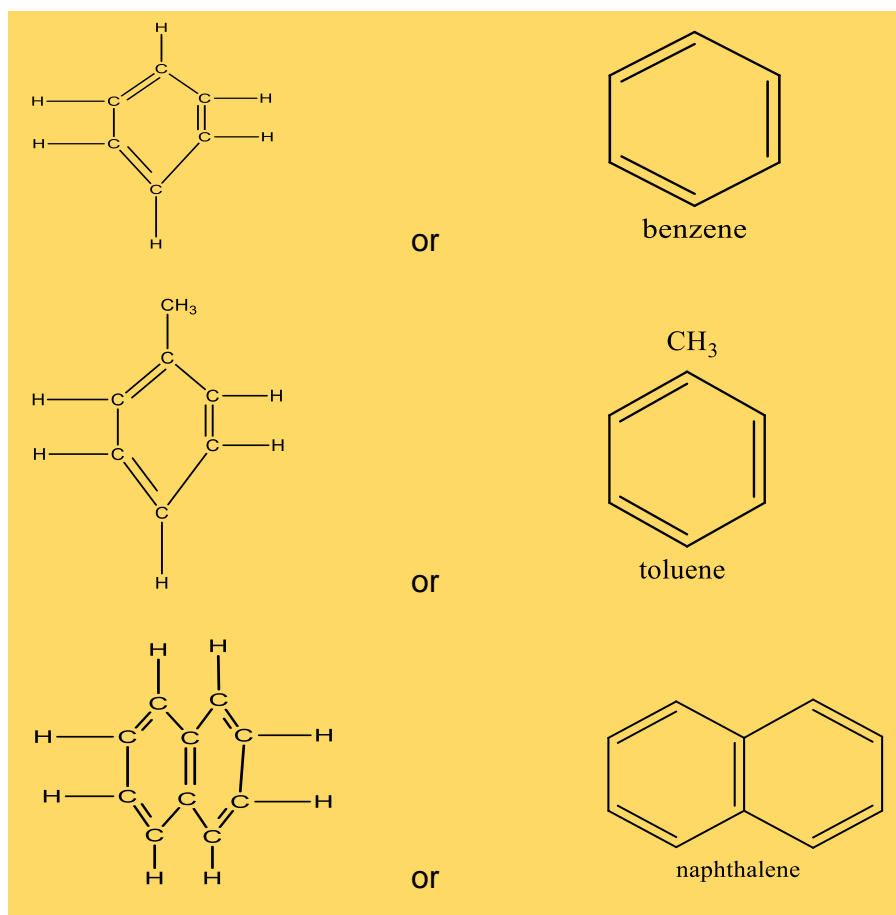
(1) Alicyclic Hydrocarbons:

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 sp² hybridized. Benzene, which is the simplest aromatic hydrocarbon, has a regular hexagonal structure with alternate single or double bonds between carbon atoms.



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?

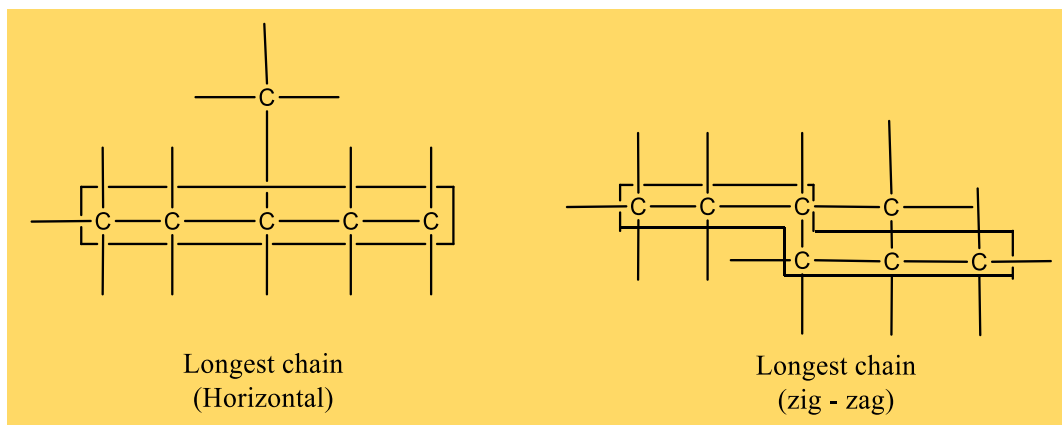
16.2 ALKANES AND CYCLOALKANES

Alkanes

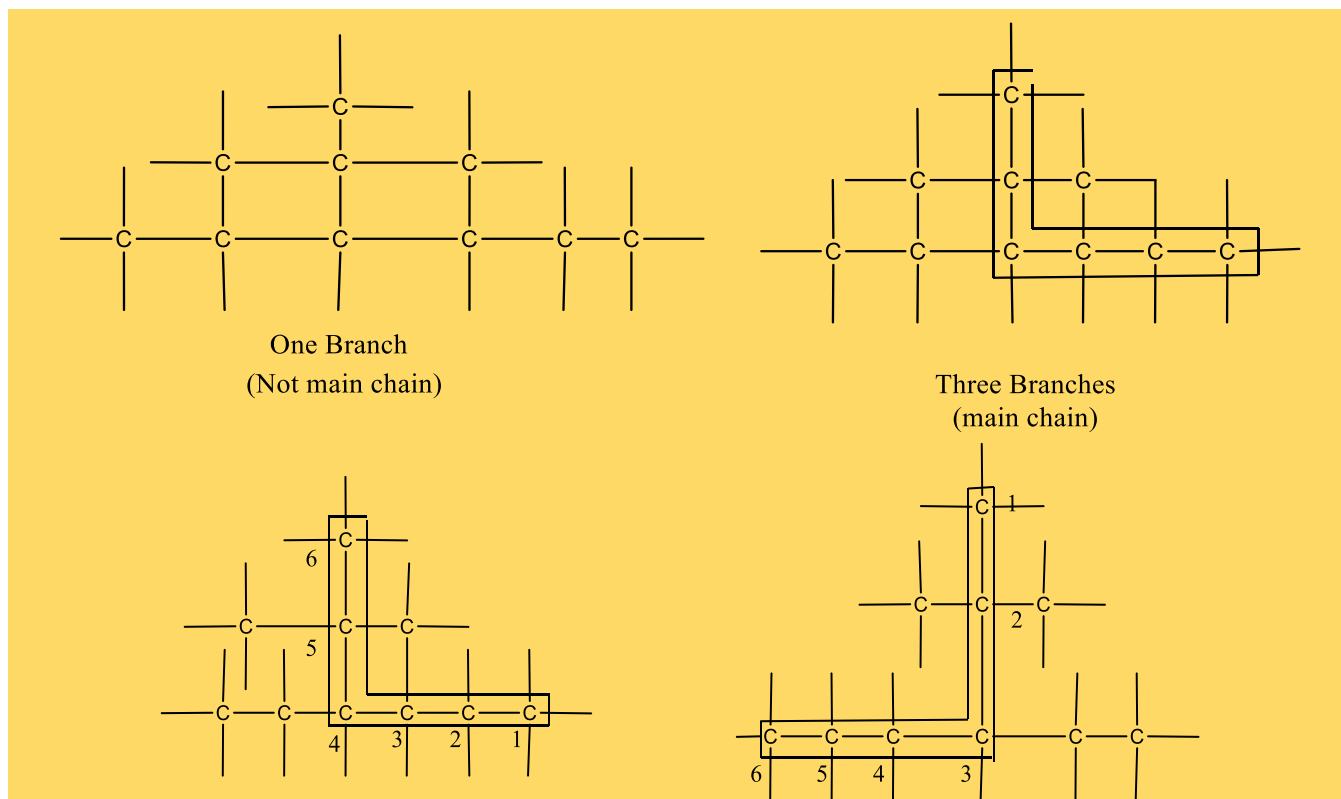
Simplest organic molecules with only C and H atoms. Commercially important as fuels and oils.

16.2.1. Nomenclature

The I.U.P.A.C rules of naming alkanes are as:-



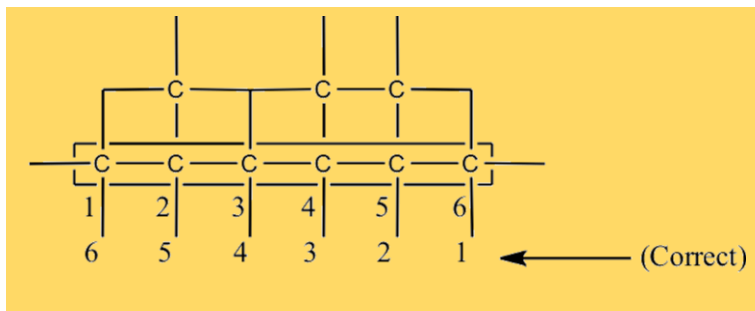
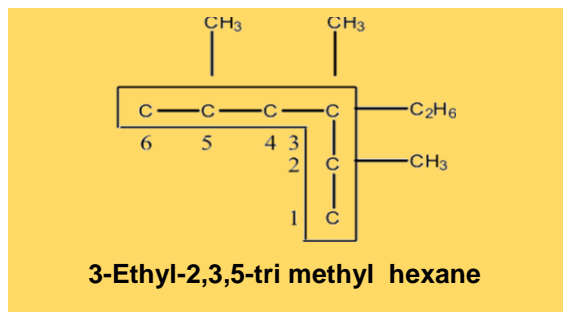
1. Locate the largest continuous chain of carbon atoms independent of direction of the chain. It is called main chain, stem, principal chain or parent chain.
2. If there are two or more chains of equal lengths, the chain with larger number of branches is selected as main chain.
3. Number the main chain starting from the end nearest to the substituent.



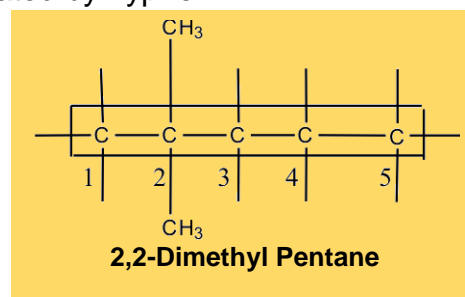
4. When two identical substituents are present at equal distance from either end, number the chain starting with end which gives their minimum sum.

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.



- Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical order or in order of increasing size, separated by hyphen.
- 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.
- If two identical groups appear at the same C-atom, the number is separated twice, separated by commas.
- 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.



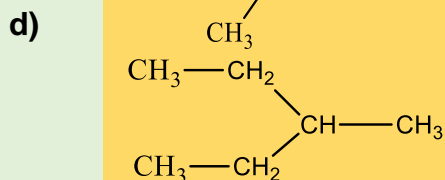
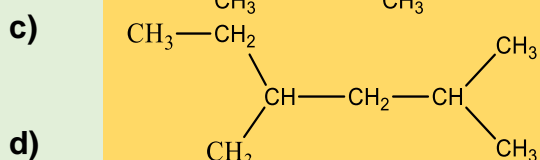
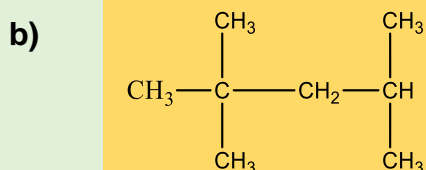
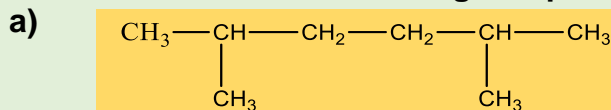
The structural formula and names for the simple alkanes are shown in the following table.

Number of C atoms	Formula	Line Drawing	Alkane Name
1	CH ₄	N/A	methane
2	C ₂ H ₆		ethane
3	C ₃ H ₈ or CH ₃ CH ₂ CH ₃		propane
4	C ₄ H ₁₀ or CH ₃ (CH ₂) ₂ CH ₃		butane
5	C ₅ H ₁₂ or CH ₃ (CH ₂) ₃ CH ₃		pentane
6	C ₆ H ₁₄ or CH ₃ (CH ₂) ₄ CH ₃		hexane
7	C ₇ H ₁₆ or CH ₃ (CH ₂) ₅ CH ₃		heptane
8	C ₈ H ₁₈ or CH ₃ (CH ₂) ₆ CH ₃		octane
9	C ₉ H ₂₀ or CH ₃ (CH ₂) ₇ CH ₃		Nonane
10	C ₁₀ H ₂₂ or CH ₃ (CH ₂) ₈ CH ₃		Decane



Activity

1:- Name each of the following compounds according IUPAC System.



2:- Indicate what is wrong with each of the following names. Give the correct IUPAC name if possible.

- 2-Dimethyl Propane
- 2,2,3-Methyl Butane
- 3,3-Dimethyle-5,5-Dimethyl Heptane
- 2,2-Diethyl-4,4-Dimethyl Pentane
- 2,4-Diethyl Pentane
- 3-Ethyl-4-,Methyl Pentane

3:- Write the structures of the following compounds.

- Neo heptane
- Iso Heptane
- Trimethyl Ethyl Methane
- Dimethyl Ethyl Isopropyl Methane
- Dimethyl Propyl Ethyl Methane
- 3-Ethyl Hexane

16.2.2 Physical Properties:

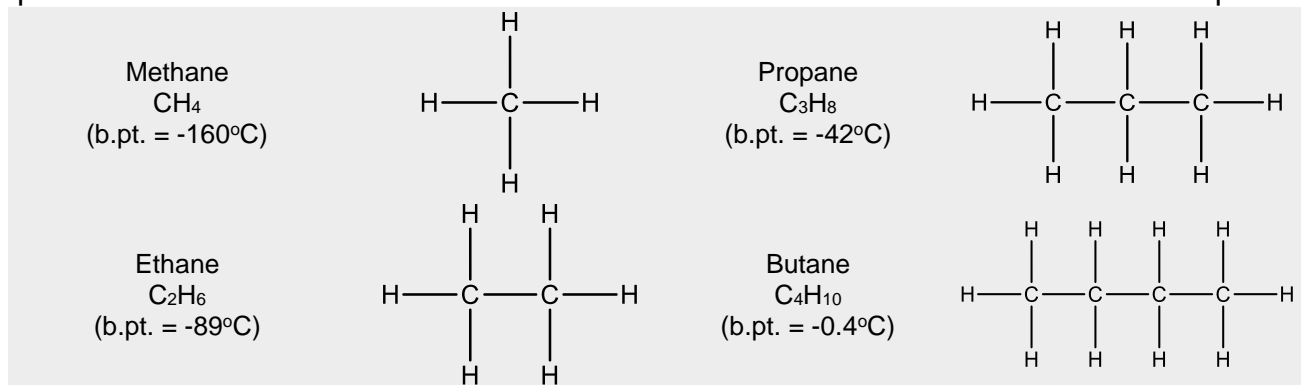
- Methane to Butane is colorless, odorless gases while pentane to heptadecane (C_5 to C_{17}) is colorless, odorless liquids. The higher members from C_{18} onwards are waxy solids, which are also colorless and odorless.



- (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 CH₂ 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).

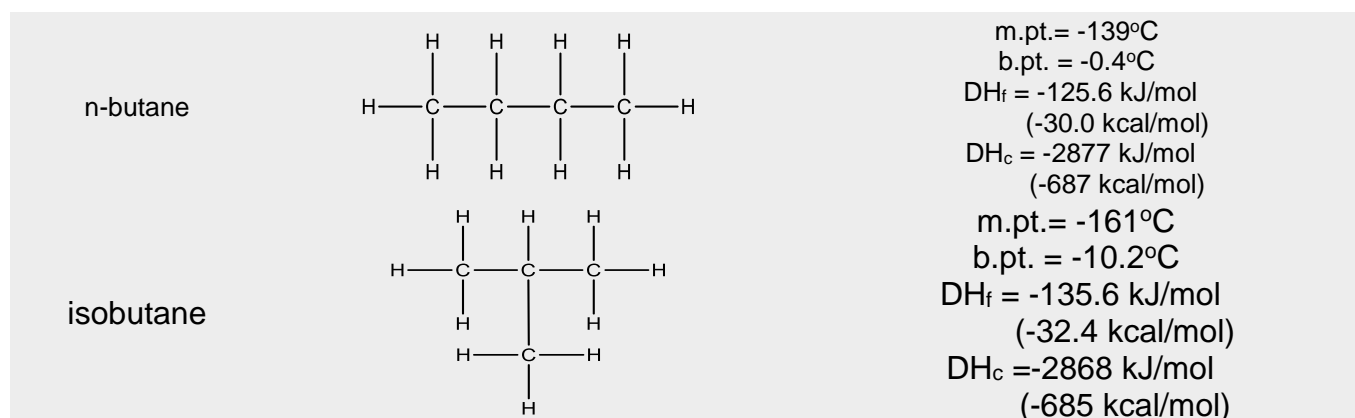
16.2.3. Structure

Alkanes are the simplest organic compounds, comprised of only sp³ 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 C₁ to C₄ alkanes are shown below in a variety of representations. As the number of C atoms increases then other isomeric structures are possible



Isomeric Alkanes

The molecular formula for the C₁ to C₃ alkanes lead to single, unique structures. However for C₄H₁₀, 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 C₄H₁₀ are shown below along with some properties:



C₅H₁₂ has three possible constitutional isomers:



n-pentane	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \end{array} $	b.pt. = 36.1 °C DH _f = -147 kJ/mol (-35.1 kcal/mol) DH _c = -3509 kJ/mol (-839 kcal/mol)
isopentane	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & & & & \\ & \text{H} & & & & \text{H} & & \text{H} & & \text{H} \\ & & & \text{H} & & & & & & \\ & & & & & & & & & \\ & & & \text{H} & & & & & & \end{array} $	b.pt. = 30 °C DH _f = -154.1 kJ/mol (-36.8 kcal/mol) DH _c = -3502 kJ/mol (-837 kcal/mol)
neopentane	$ \begin{array}{ccccccc} & & & \text{H} & & & \\ & & & & & & \\ & \text{H} & - & \text{C} & - & \text{H} & \\ & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - & \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & & & & \text{H} & \\ & & & \text{H} & & & \\ & & & & & & \\ & & & \text{H} & & & \end{array} $	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.

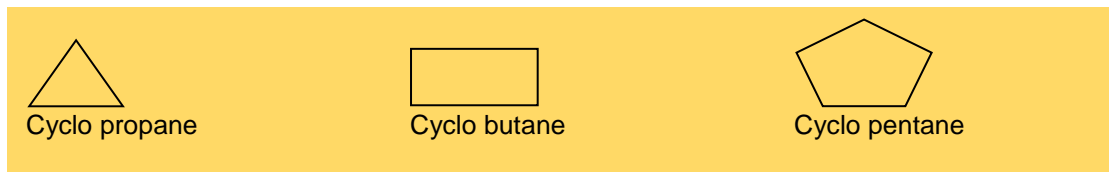


II. Cycloalkanes

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.

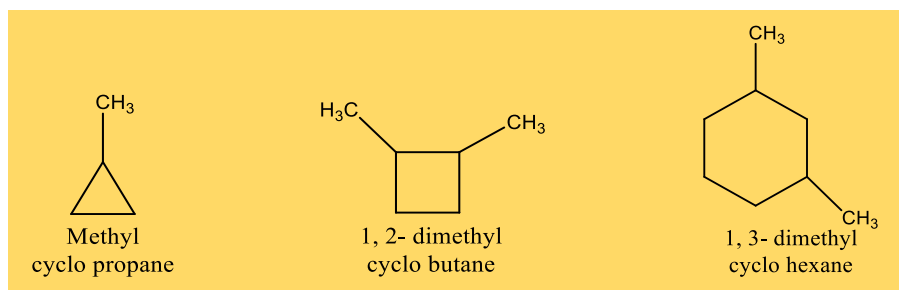
1. Nomenclature

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.

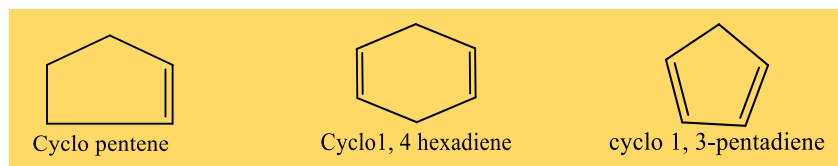


The substituents are numbered in such a way that the sum of numbers is kept minimum, e.g.

If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond) are used, e.g,



Multiple bonds are given the lowest possible number.



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 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 ₃ H ₆	
Cyclobutane	C ₄ H ₈	
Cyclopentane	C ₅ H ₁₀	
Cyclohexane	C ₆ H 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 intermolecular forces.

16.3 RADICAL SUBSTITUTION REACTIONS

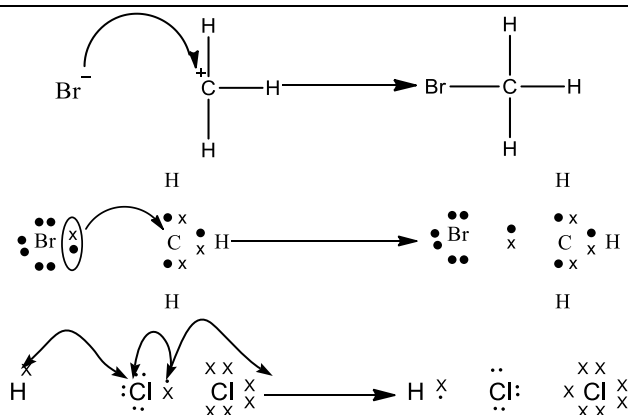
16.3.1 Overview

- 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 F₂ > Cl₂ > Br₂ > I₂.
- 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- 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.

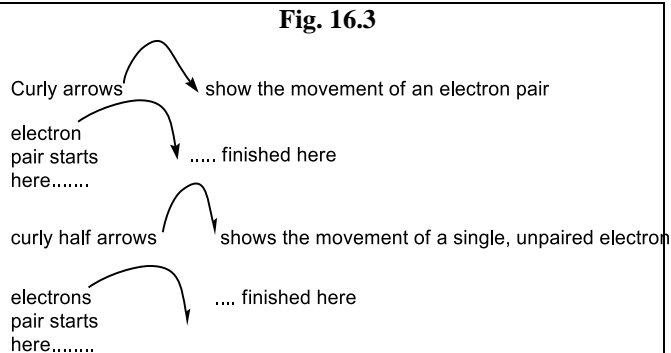


Fig. 16.4

RADICAL CHAIN MECHANISM FOR REACTION OF METHANE WITH Br₂

Step 1 (Initiation)

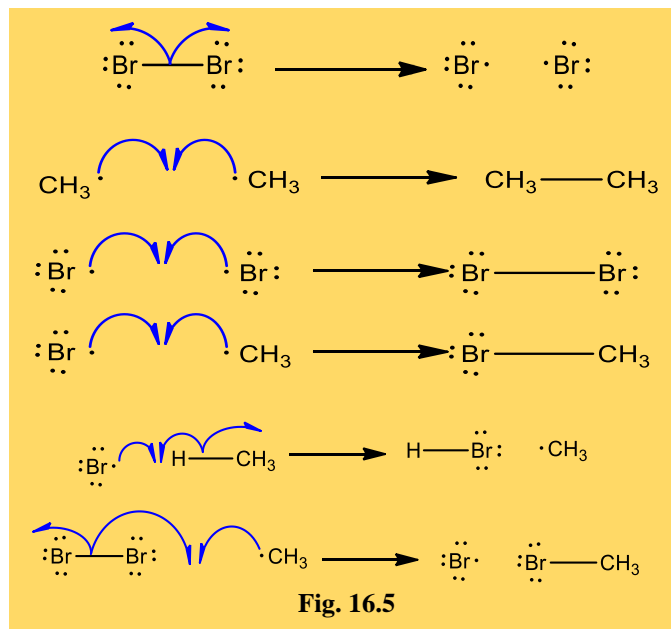
Heat or uv light cause the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.

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 Br₂ 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, Br₂ or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.



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:

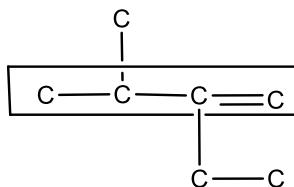
- more C-H bonds
- less C-O bonds (or other atoms more electronegative than C)
- gain of electrons
- decreased oxidation state, e.g. +1 to -1

16.5 ALKENES

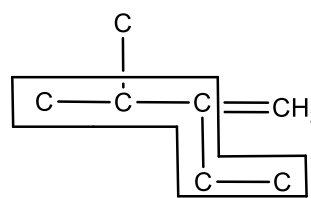
16.5.1. Nomenclature

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.

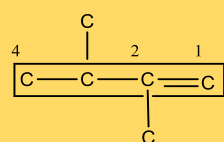


The parent chain containing double bond (correct)

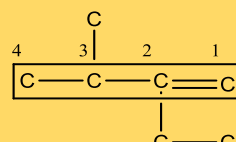


Longest chain with no double bond (incorrect)

- 4) The position of double bond is indicated by the lower number of C-atom.

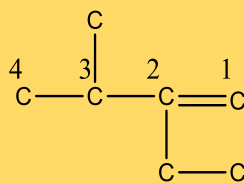


2 - ene (incorrect)



1 - ene (correct)

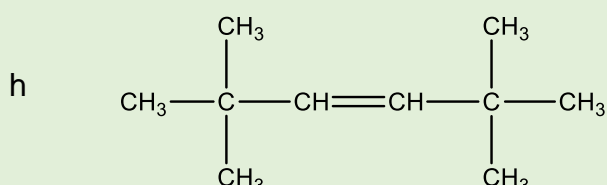
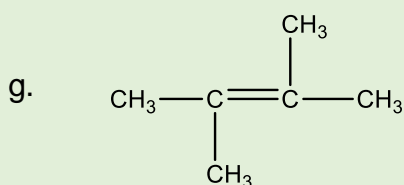
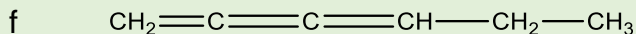
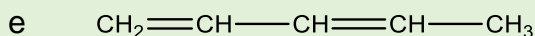
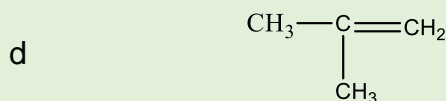
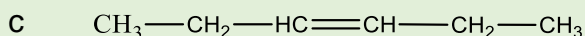
- 5) The lower number of C-atom is placed before the name of parent alkene.
- 6) The presence of more than one double bond is indicated by the suffix -diene for two double bonds, -triene for three double bonds and so on.
- 7) Alkyl groups are indicated by the methods mentioned in alkane.



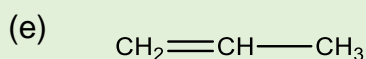
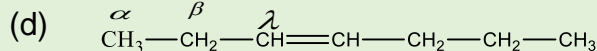
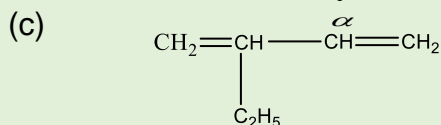
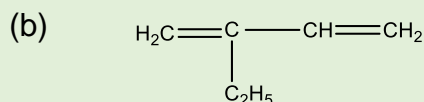
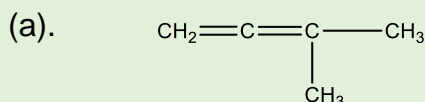
2-Ethyl-3-methyl-1-butene

**Activity**

1. Name the following Olefins by the IUPAC Systems



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.



3. Write structural formulas for the following compounds and discuss the geometric isomerism in each case.

(a) 1,3-Buta diene

(b) 1,2- Penta diene

(c) 2,4 -Hexa diene

(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 steric interactions when R groups are on opposite sides of the double bond.

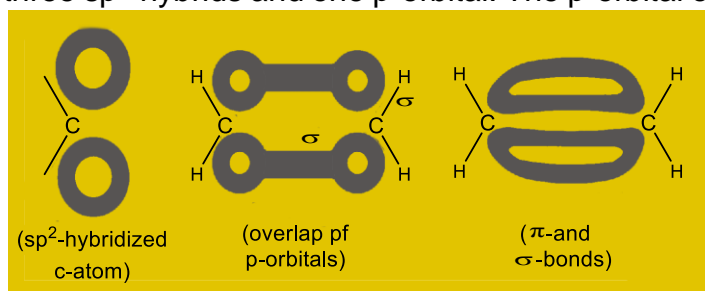
3. Conjugated alkenes are more stable than isolated alkenes.

1,3-Butadiene is more stable than 1,4-butadiene



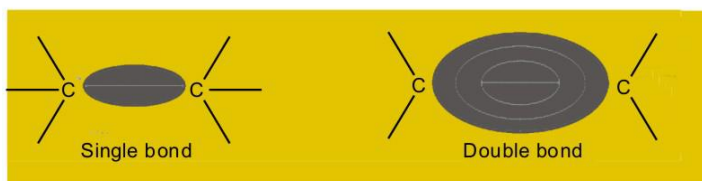
16.5.3 Structure

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 (1.34Å) than the C-C bond distance of ethane (1.54Å). 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.



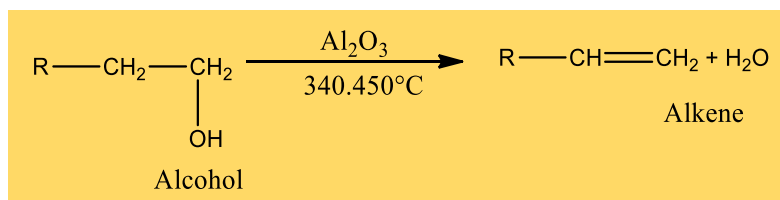
16.5.4. Preparation of Alkenes

1. Dehydration of Alcohols

Removal of water molecule is called dehydration.

Example

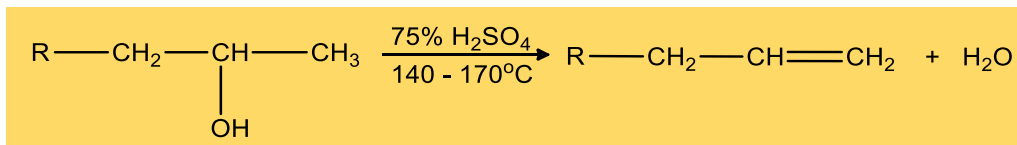
When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.



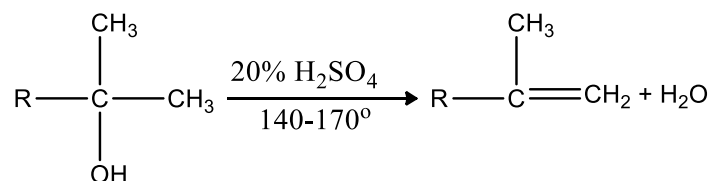
P_4O_{10} , H_2SO_4 , H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order.

Ter.alcohol > sec.alcohol > pri.alcohol

For secondary alcohol



For tertiary alcohol



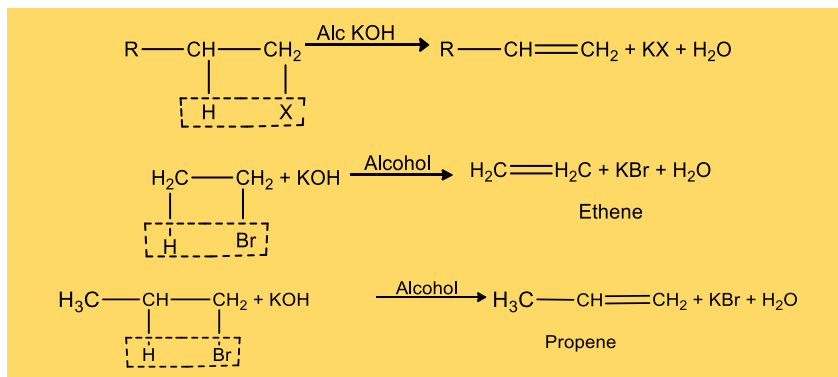


2. Dehydrohalogenation of Alkyl Halides

Removal of hydrogen halide (HX) from alkyl 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 -bond. Hence the reactions of alkenes involve weaker π -bond and electrophilic addition occurs. It involves the change of a π -bond to sigma bond through addition reactions.

16.5.6 Reactions

Hydrogenation

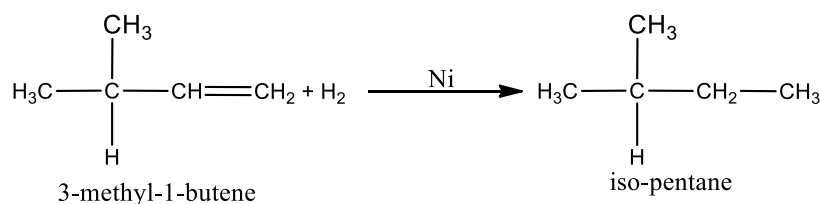
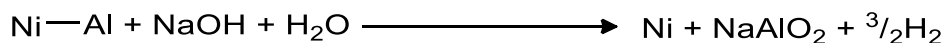
A process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5atm) to give a saturated compound is known as catalytic hydrogenation.

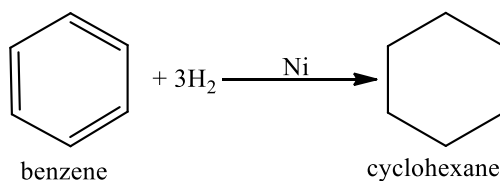
Explanation:

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.



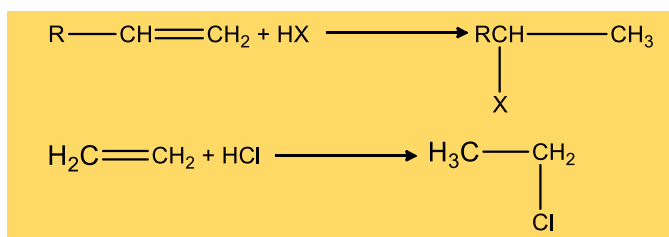


Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of vegetable ghee from vegetable oils. In the laboratory, it is used as a synthetic as well as an analytical tool.

Hydrohalogenation

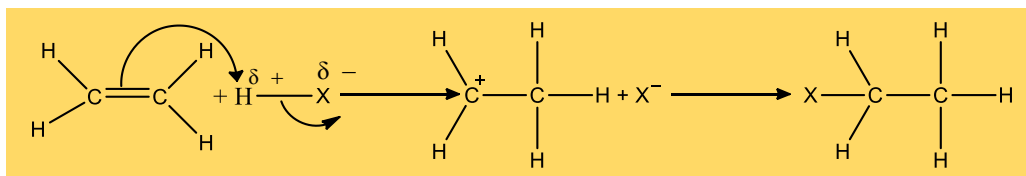
Alkenes react with aqueous solution of halogen acid to form alkyl halides.

The order of reactivity of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$



Mechanism of Reaction:

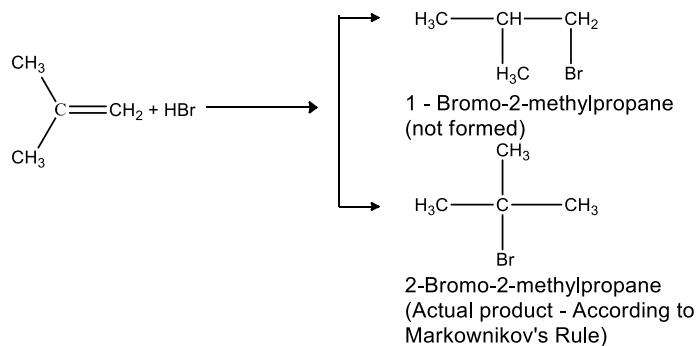
The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation. The carbocation then reacts with the halide ion.



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:

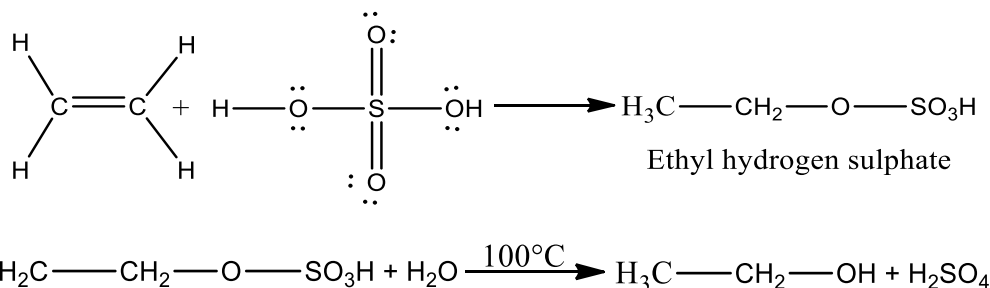




Hydration

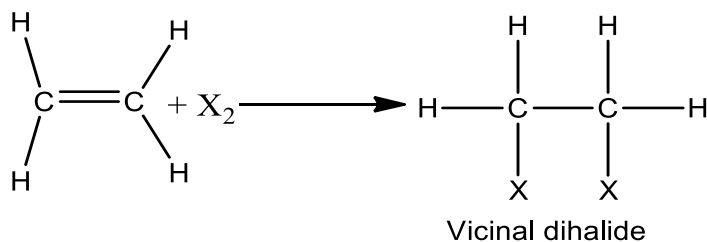
Addition of water is called hydration. Some reactive alkenes react with water in the presence of suitable substances as acid etc. to form alcohol. It is possible as alkenes are soluble in cold concentrated sulfuric acid. They react by addition to form alkyl hydrogen sulphate.

These alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.



Halogenation

The alkenes react with halogen in an inert solvent like carbon tetrachloride at room temperature to give vicinal dihalides or 1,2 dihalogenated products.

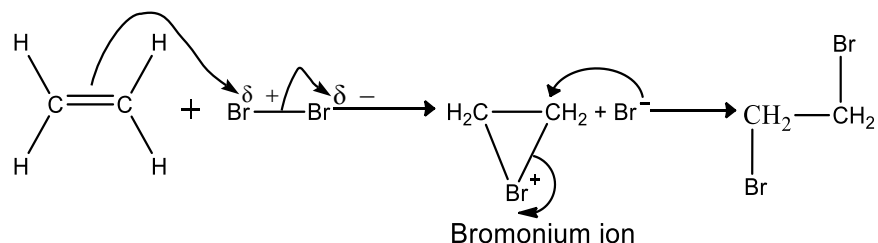


Br₂ and Cl₂ are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

Mechanism:

- 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.
- 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.

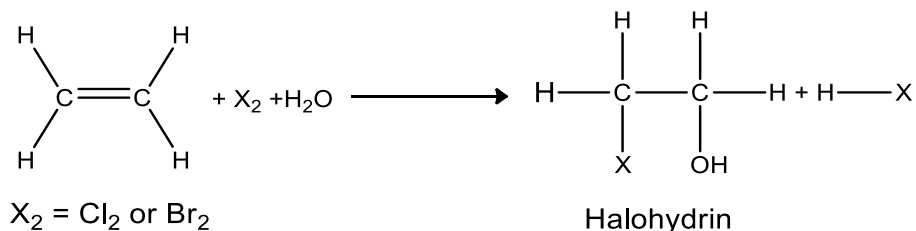




Halohydration

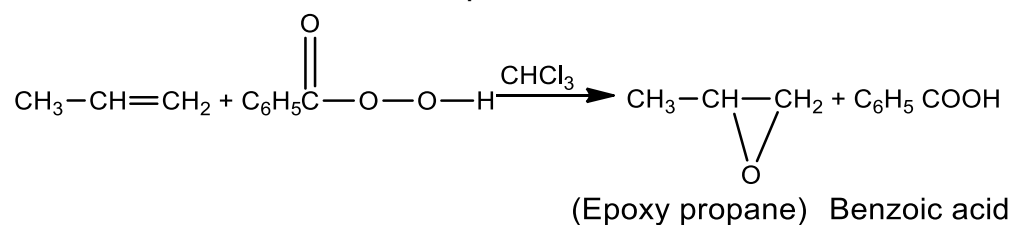
Addition of hypohalous acid (HOX) is called halohydration.

Alkenes react with hypohalous acid to give halohydrin. In this reaction, molecules of the solvent become reactants too.



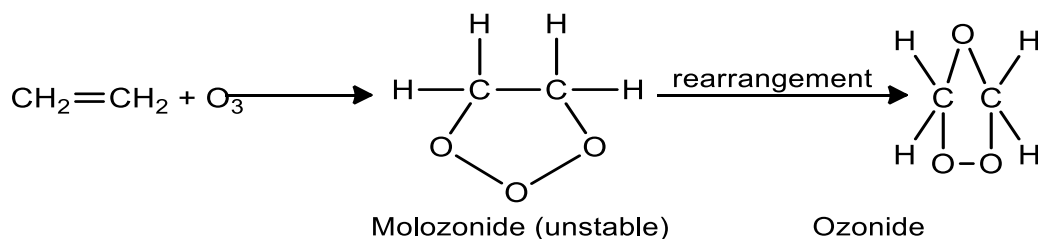
Epoxidation

It is the formation of epoxides. Peracids such as per oxyacetic acid or peroxy benzoic acid react with alkenes to form epoxides.



Ozonolysis

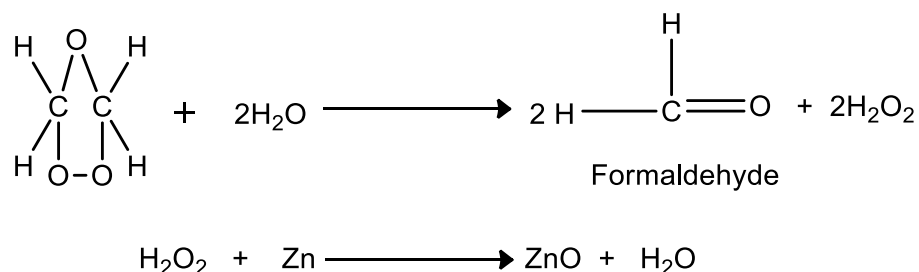
Ozone (O_3) reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.



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).

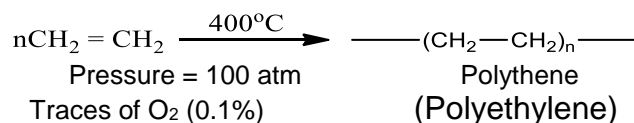
Ozonolysis is used to locate the position of double bond in an alkene. The C-atom of double bond is changed to carbonyl group.





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.



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 $\text{Al}(\text{C}_2\text{H}_5)_3$ and titanium tetrachloride (TiCl_4).

Interesting Information

Examples of natural and synthetic polymers

	Polymer	Monomer	Where you find it
Natural	Protein	Amino acids	Wool, silk, muscle, etc
	Starch	Glucose	Potato, wheat, etc
	Cellulose	Glucose	Paper, wood, dietary fibre
	DNA	Nucleotides	chromosomes, genes
Synthetic	Poly (ethane)	Ethane	Bags, washing-up bowls, etc
	Poly (chloroethene) (PVC)	Chloroethene	Fabric coatings, electrical insulation, toys, expanded polystyrene
	Poly (phenylethene) (polystyrene)	Phenylethene	Skirts, shirts, trousers
	polyester	Ethane-, 2-diol and benzene-	
		1, 2-dicarboxylic acid	

16.5.7 Conjugation

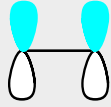
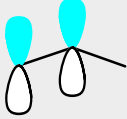
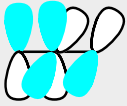
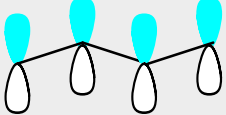
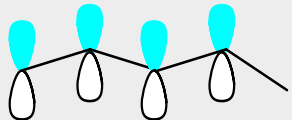
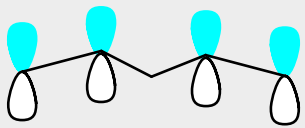

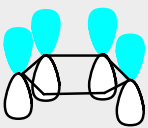
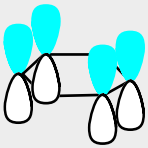
The word "**conjugation**" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when p systems are "linked together".

- An "**isolated**" p system exists only between a single pair of adjacent atoms (e.g. $\text{C}=\text{C}$)
- An "**extended**" p system exists over a longer series of atoms (e.g. $\text{C}=\text{C}-\text{C}=\text{C}$ or $\text{C}=\text{C}-\text{C}=\text{O}$ etc.).
- An extended p system results in an extension of the chemical reactivity.

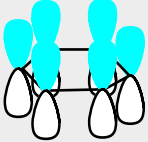
The fundamental requirement for the existence of a conjugated system is revealed if one considers the orbital involved in the bonding within the system.

- 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:

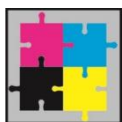


System	p system	Type
ethene		isolated
propene		isolated
1,2-propadiene (allene)		cumulated
1,3-butadiene		conjugated
1,3-pentadiene		conjugated
1,4-pentadiene		isolated
1,3-cyclopentadiene		conjugated
1,3-cyclohexadiene		conjugated
1,4-cyclohexadiene		isolated



benzene		conjugated
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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

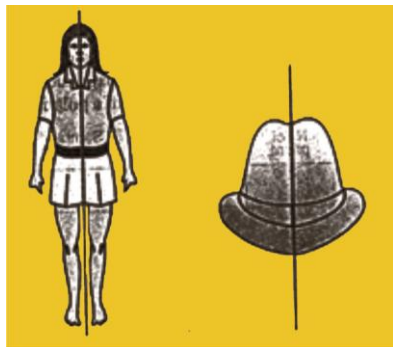


Fig.16.6 Planes of Symmetry

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.



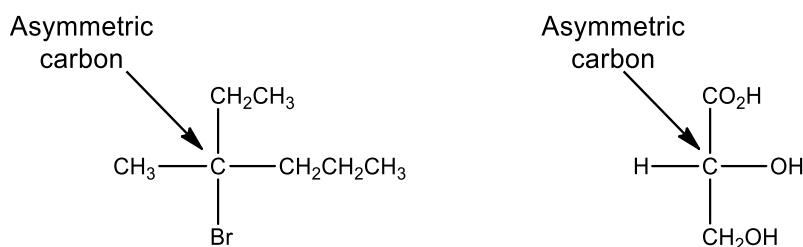
Fig 16.9 Achiral objects

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:



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.

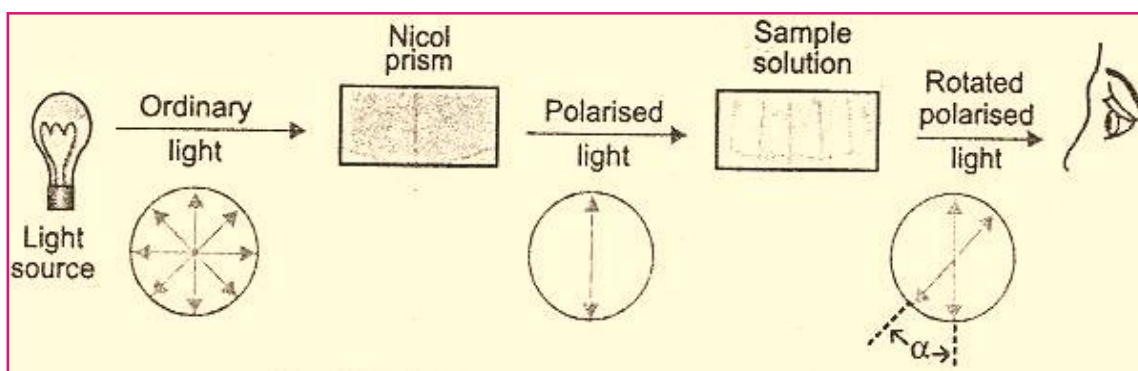


Fig.16.10 A simple polarimeter in operation

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 (anticlockwise). 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 be 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.



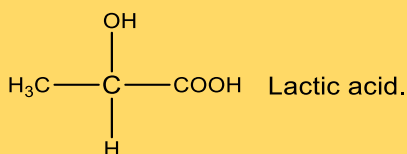
16.6.4. Optical isomerism

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.

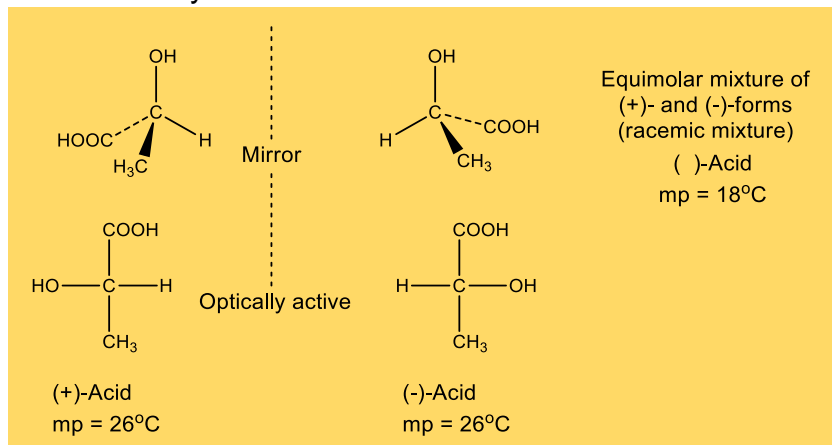
The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory Isomer** or (+) isomer. The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Laevorotatory Isomer** or (-) isomer.

Optical Isomerism of Lactic Acid

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.

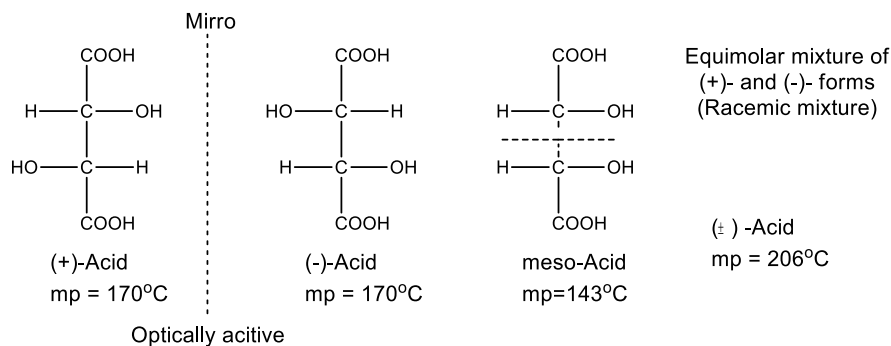
(±) Lactic Acid: it does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

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. Stereoisomerism - 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

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.

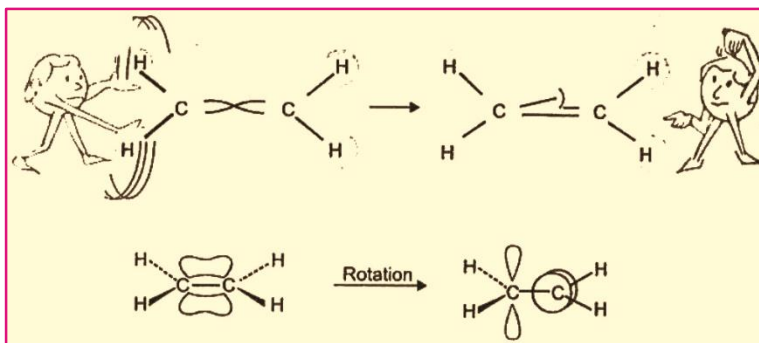


Fig. 16.11

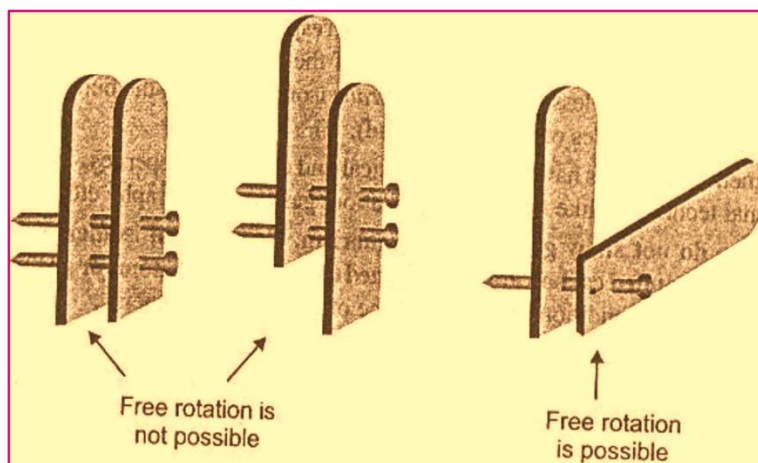


Fig. 16.12



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 boards and two nail. Driving one nail through two boards will not prevent free rotation of the two boards. But once a second nail used, the boards cannot be freely rotated.

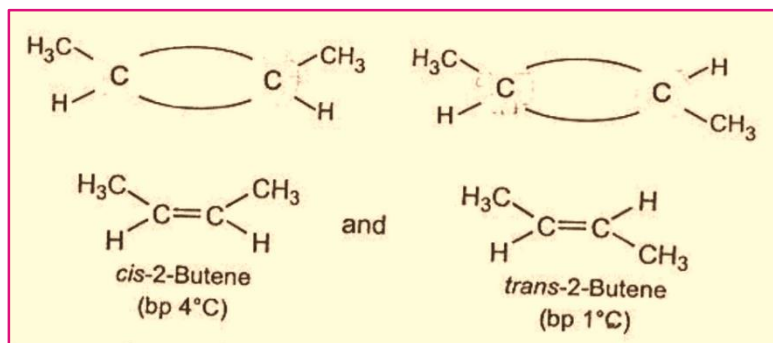


Fig. 16.13

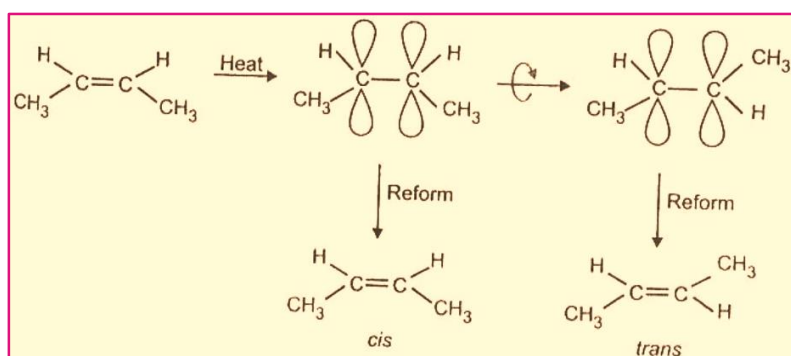


Fig. 16.14

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 steric 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).

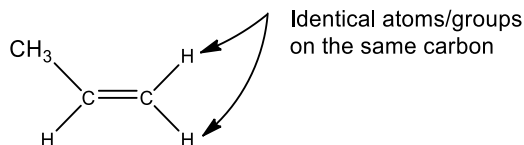
The geometrical isomers have different physical and chemical properties. They can be separated by conventional physical techniques like fractional distillation, gas chromatography etc.

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

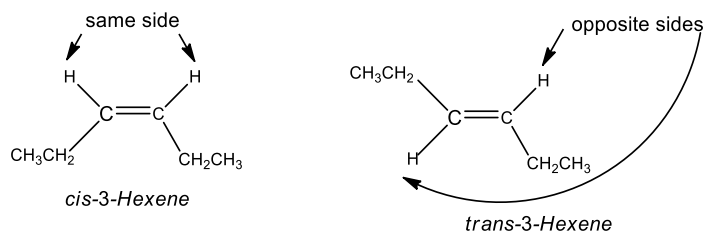


No geometrical isomers are possible for propene ($\text{CH}_3\text{CH}=\text{CH}_2$). This is because one of the double bonded carbons has two identical groups (H atoms) attached to it.



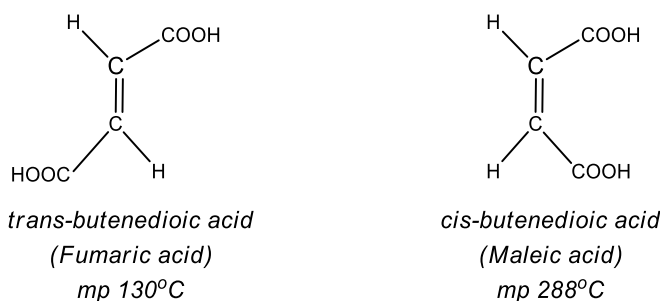
Example 2. Consider the case of 3-Hexene ($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$)

This is because each double bonded carbon atom is attached to two different groups (CH₂CH₃ and H). The cis and trans isomers of 3-hexene are shown below:



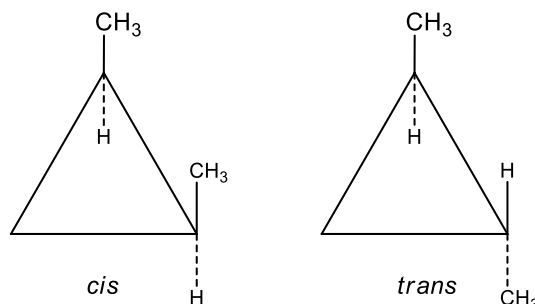
Example 3. Consider the case of Butenedioic acid. ($\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$)

Geometrical isomers are possible because each double bonded carbon atom has two different groups attached to it (H and COOH).



(2) Geometrical Isomerism in Cyclic Compounds

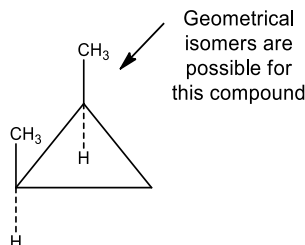
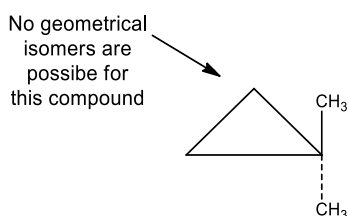
Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break the ring. For example, 1,2-dimethylcyclopropane exists in two isomeric forms.



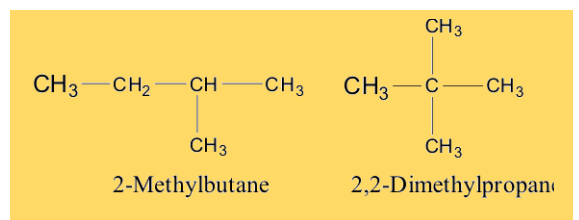
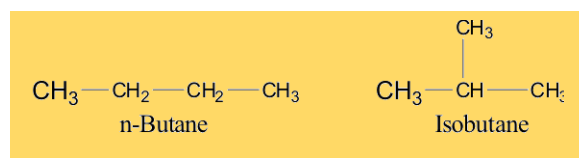
In cis-1,2-dimethylcyclopropane the two methyl groups are on the same side of the ring. In trans-1,2-dimethylcyclopropane, they are on opposite sides. A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups besides hydrogen.



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

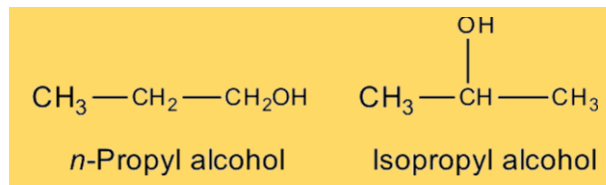
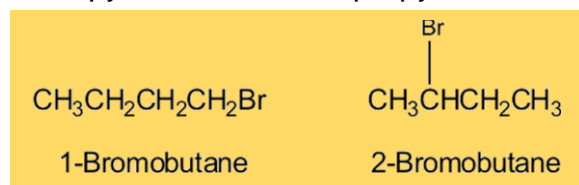
Example 2. 2-Methylbutane and 2,2-Dimethylpropane

2). Position Isomerism

Position isomers have the same molecular formula but differ in the position of a functional group on the carbon chain such as.

1-Bromobutane and 2-Bromobutane

n-Propyl alcohol and Isopropyl alcohol

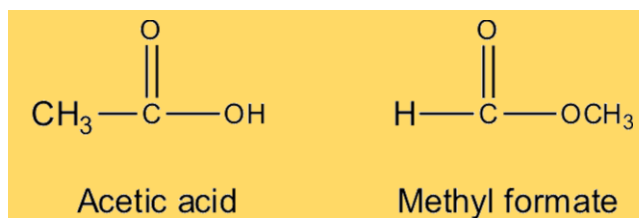
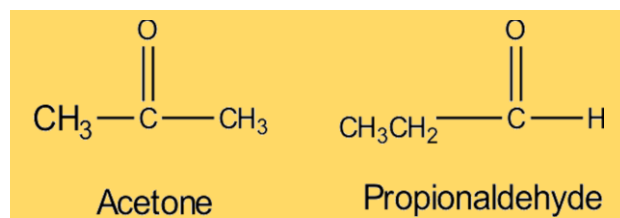


3) Functional group Isomerism

Functional isomers have the same molecular formula but different functional groups. For example

Acetone and Propionaldehyde

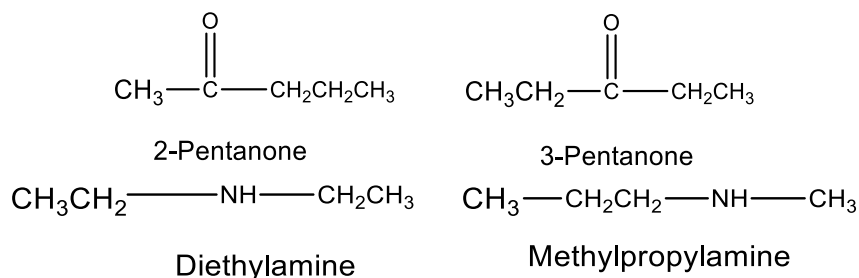
Acetic acid and Methyl formate



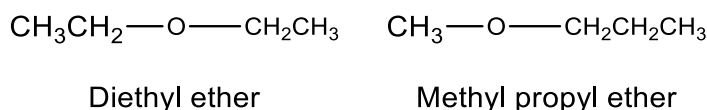


1) Metamerism

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:

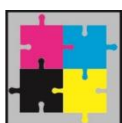
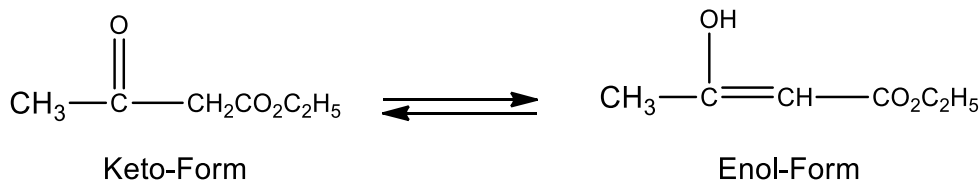


- 2-pentane and 3-pentane
- Diethyl ether and methyl propyl ether



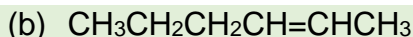
2) Tautomerism

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.



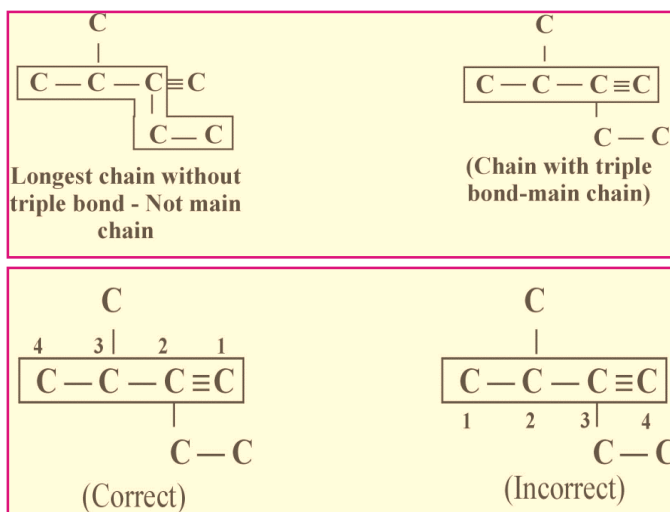
Quick Quiz

- Define or explain the following terms
 - Structural isomerism
 - Stereoisomerisms
 - Geometrical isomerism
 - Optical isomerism
 - Asymmetric carbon
 - Chiral molecule
- State the necessary condition for a compound to show geometrical isomerism. Illustrate your answer with examples.
- Which of the following compounds shows geometrical isomerism?
 - 2-Butene
 - 2-Methyl-Butene
 - 2-Pentene
 - 1,2-Dichloropropane
- Which of the following compounds show isomerism
 - $\text{CH}_3-\text{CH}=\text{CH}_2$



- What is optical activity: how is it measured?
- Write a note on Optical Isomerism of Lactic acid
- Write a note on Optical isomerism of tartaric acid
- An acid of formula $\text{C}_5\text{H}_{10}\text{O}_2$ is optically active. What is its structure?
- How does Cis-isomer convert into trans-isomer?
- The trans-isomer is more stable. Why?

16.7 ALKYNES



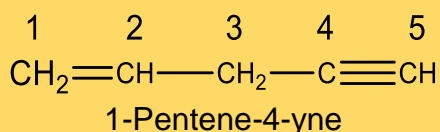
16.7.1 Nomenclature:

IUPAC System:

- The parent hydrocarbon is the continuous chain containing triple bond.
- The ending 'ane' of the alkane is changed by -yne.
- The main chain is numbered starting from the terminal carbon nearer to the triple bond.
- Triple bond is given the number of the lower carbon atom attached to triple bond separated by hyphen.
- If two or more triple bonds are there in the molecule, use the prefixes di-, tri-, etc.
- Alkyl groups are indicated by the methods described while naming alkanes.

Naming of Molecules Containing Both the Double and Triple Bonds

- The suffix 'ene' is used to denote the presence of Double bond the suffix -yne to denote the presence of triple bond.
- The suffix '-ene' always precedes '-yne' in the name of compound, even when the double bond is assigned the large number.
- The position number for the double bond is placed before the name of parent hydrocarbon.



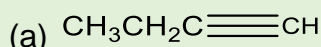
4) The position number of triple bond is placed between -'ene' and -'yne'.

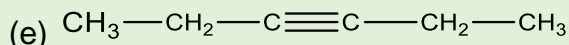
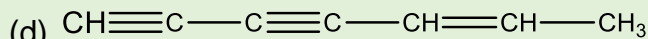
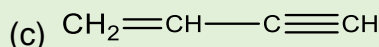
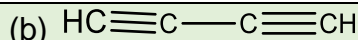
5) If same number would result from each terminal, the double bond is given the lower possible number. e.g,



Activity

Give the IUPAC name of the following:





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.

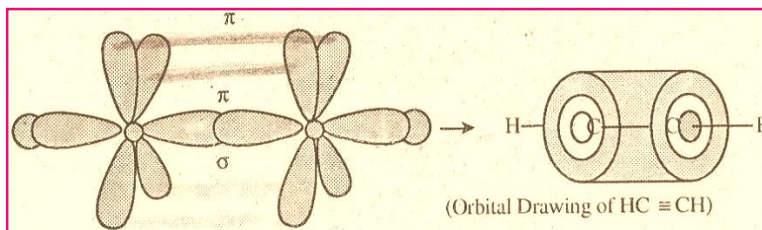


Fig. 16.15

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

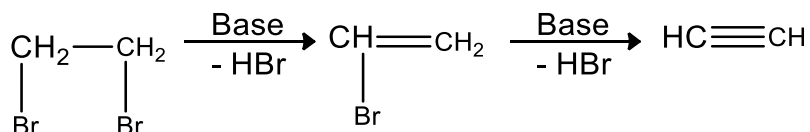
(i) Elimination of Hydrogen Halide:

Alkynes can be prepared by dehydrohalogenation of vicinal and geminal 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.

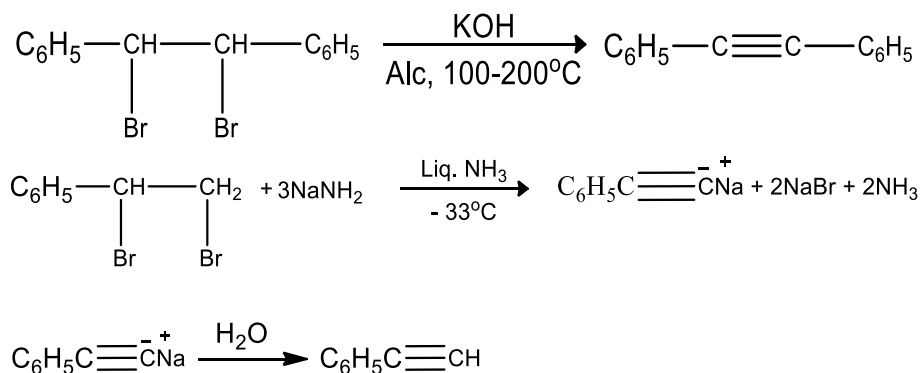
Higher alkynes are also formed in the presence of alcoholic KOH, e.g.



In the presence of strong base such as KOH and at high temperature triple bond at terminal C-atom migrates to give more disubstituted alkyne.

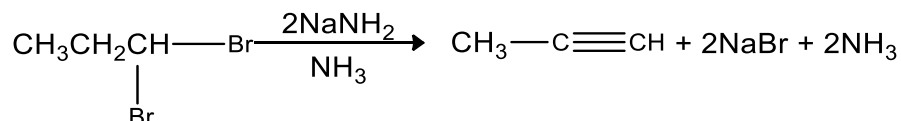
Therefore, alcoholic KOH is useful when rearrangement is not possible,

1-alkynes can be prepared from vic-dihalides with sodium amide in liquid ammonia



(b) Geminal Dihalide:

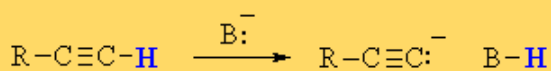
A dihalide containing two halogen atoms linked with the same carbon atom) on treatment with strong base gives alkyne, e.g.,



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 bonding. Therefore electrophile substitute reactions are possible in 1-alkynes.

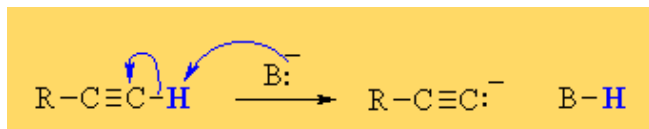
16.7.6. Acidity of Terminal Alkynes



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



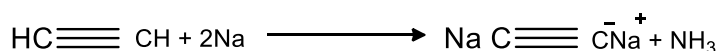
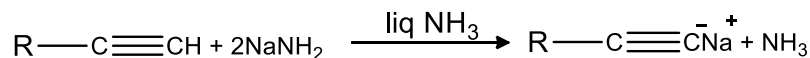
terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.



This $\text{H}^{\delta+}$ can be substituted with metal. Thus substitution reaction occurs due to $\text{H}^{\delta+}$

Examples:

(i) When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.



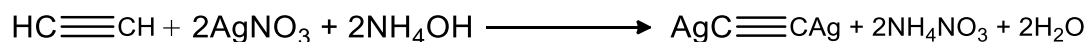
Disodium acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

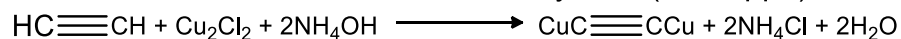
(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

Silver and copper acetylides react with acids to regenerate alkynes.

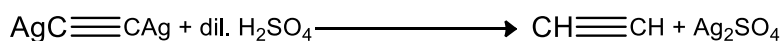
These alkynides are used for the preparation, purification separation, and identification of alkynes.



Disilver acetylide or silver ethynide, (white ppt.)



Dicopper acetylide or copper ethynide (Reddish brown)

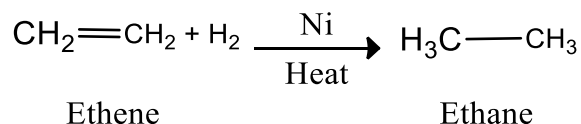
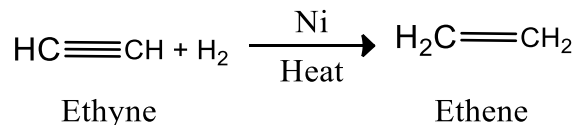


16.7.7 Addition Reactions of Alkynes

- 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:
 - increased nucleophilicity of the starting pi system, and
 - 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 then take up another molecule of hydrogen to form an alkane.



Dissolving Metal reduction

Reaction Type: Addition

Elaboration

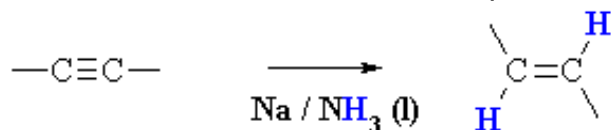
Alkynes can be reduced to **trans**-alkenes using Na in NH₃ (liq.)

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 NH₃

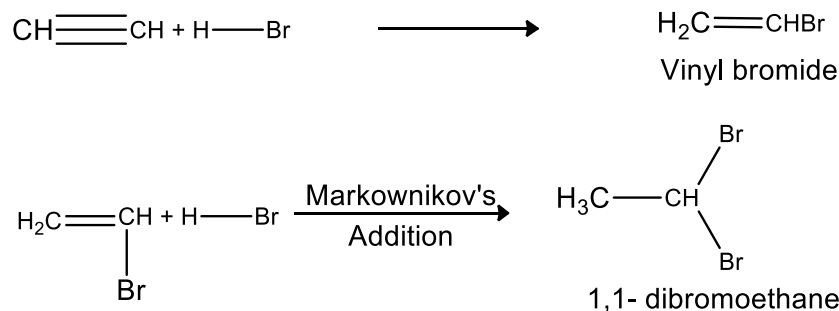
These reaction conditions do not reduce alkenes, hence the product is the alkene.



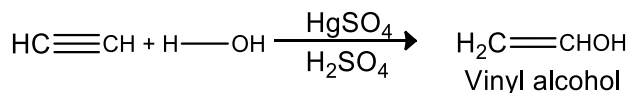
Hydrohalogenation

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.



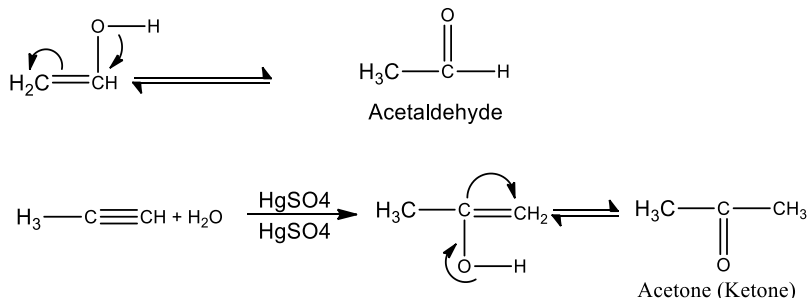
Hydration Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C.



Rearrangement of Alcohol

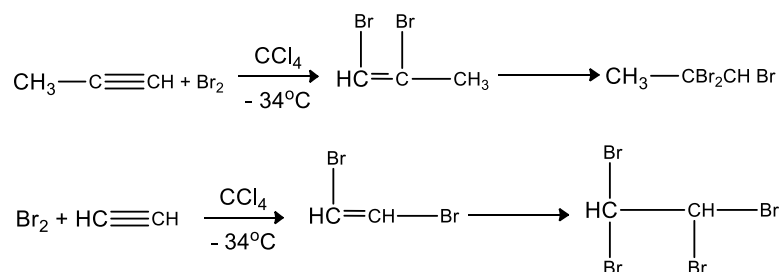
Vinyl alcohol is an unstable. It has the hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde. Except acetylene all other alkynes give ketones.

This reaction is industrially important because aldehydes can be prepared by this method.



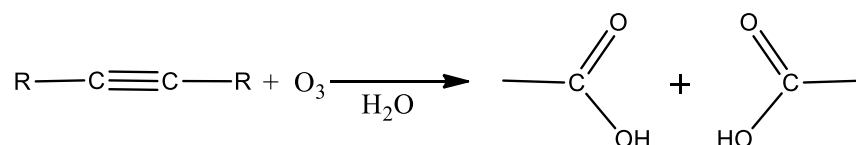
Bromination

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 $2\text{RCO}_2\text{H}$.



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 from coal tar.

As a functional group, benzene and substituted benzenes are called arenes.



16.8.1 Nomenclature

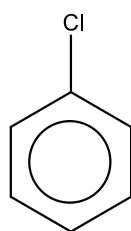
Mono Substituted Benzenes: Common system of naming:

The following procedures are adopted for naming mono substituted benzenes:

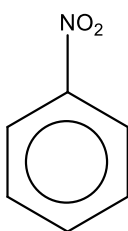
- (1) Parent name is benzene and the substituent is indicated by a prefix, e.g., methyl. Ethyl, chloro, Nitro etc.
- (2) The substituent and the benzene ring taken together may form a new parent name. The largest parent name is preferred e.g., $C_6H_5CH_3$ may be named as: (i) Methyl benzene (ii) Phenyl methane. According to "the largest rule" methyl benzene is preferred. The common name of some compounds are:

IUPAC System of Naming:

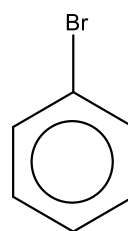
Mono substituted derivatives of benzene are named by prefixing the name of substituted to the word 'benzene'. e.g.,



Chlorobenzene



Nitrobenzene



Bromobenzene



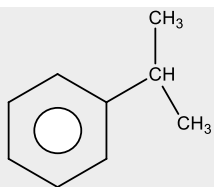
Methyl benzene



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

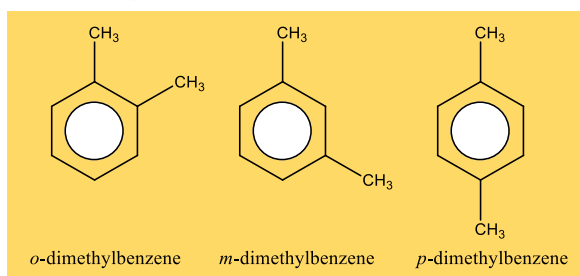


Cumene

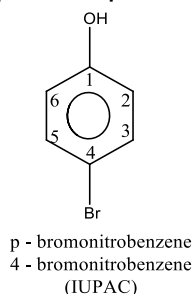
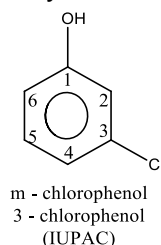
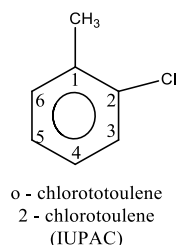
Disubstituted Benzene:

- 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.

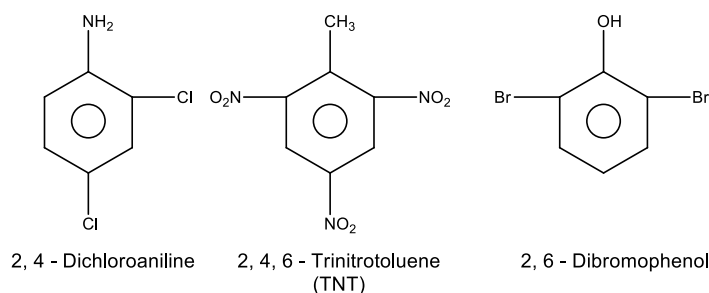
- 3) When a common name is used, the substituent which is responsible for name, e.g., CH_3 in toluene, and $-\text{OH}$ in phenol, is considered to be on carbon -1, i.e., numbering is started from the carbon of ring bearing that group such a disubstituted compound.



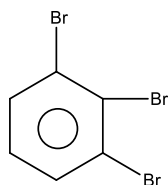
- 4) When two substituents are different, they are usually put in alphabetical order.



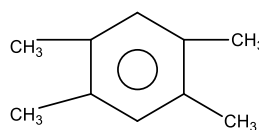
- 5) Poly substituted benzenes are named by numbering the substituent to ring so as to give the substituents lowest possible numbers. The last named substituent is assumed to be at position number 1. This number is not indicated in the name.



- 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.

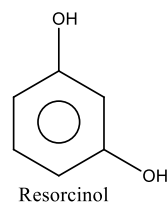
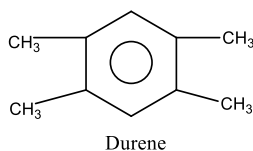
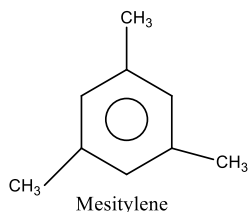


1, 2, 3 - Tribromoibenzene



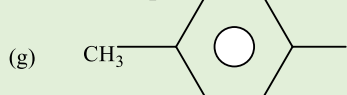
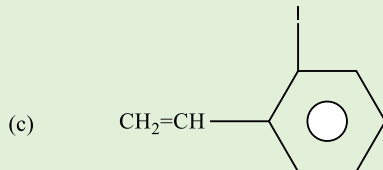
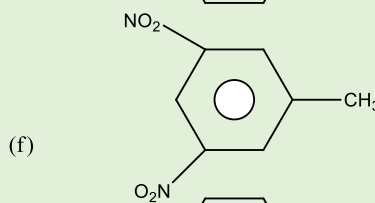
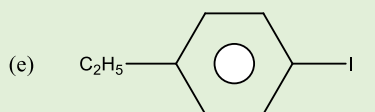
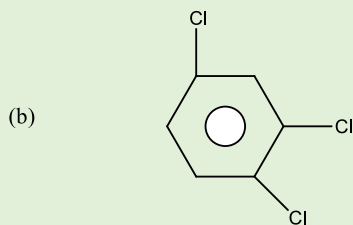
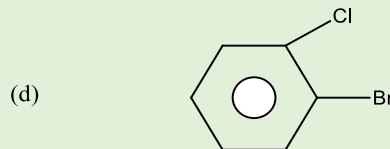
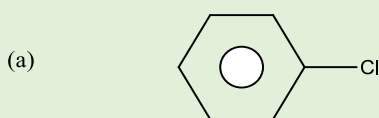
1, 2, 4, 5 - Tetramethylbenzene

7) Some poly substituted benzenes are still known by their common name.



Activity

1- Give the suitable name to each of following:



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.



These are two equally valid resonance contributors.

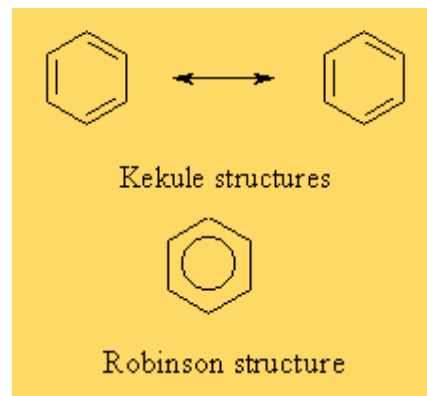
Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.

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 understand 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) $C-\hat{C}-C=120^\circ$, and (ii) $C-\hat{C}-H=120^\circ$

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 ($1s^1$) produces the following sigma framework of benzene.

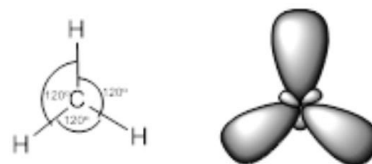


Fig. 16.16

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 sandwich like structure of benzene and decreases the energy of molecule. Consequently, the molecule becomes more stable and less reactive.

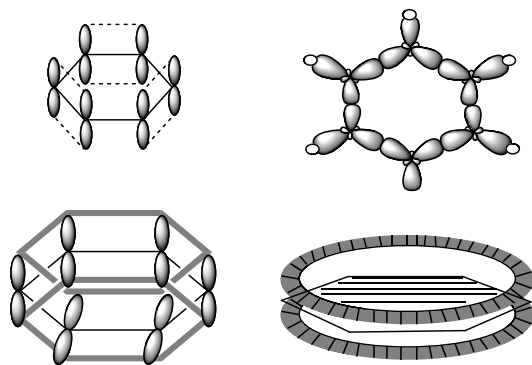
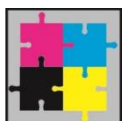


Fig. 16.17

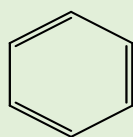
According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full sigma-bond and half a pi-bond. Because of this reason, the carbon-carbon bond length is equal and benzene shows substitution as well as addition reactions.



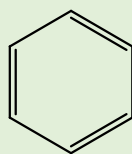
Quick Quiz

Criticize the following statement:

“Benzene is a mixture of molecules most of which have the structure.”



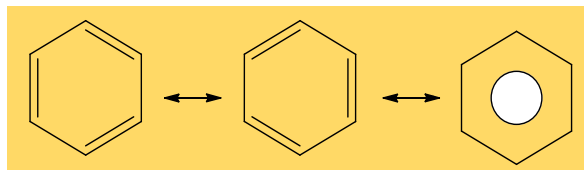
or



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.



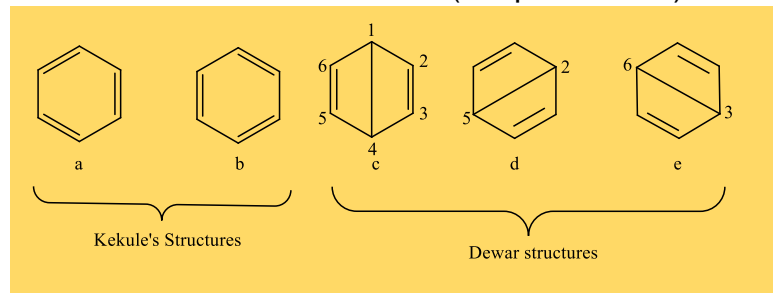
16.7.4. Resonance, Resonance Energy and Stabilization

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.



This 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 or resonating bonds.

Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal but different from those in alkanes, alkenes and alkynes. 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.

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

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

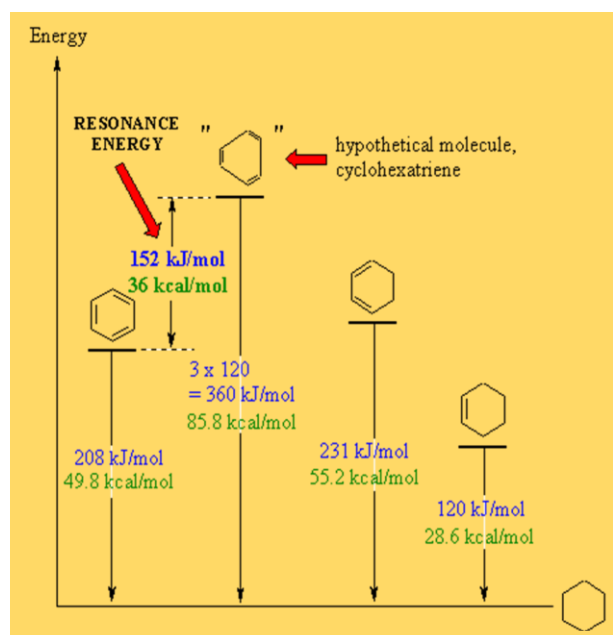


Fig. 16.18

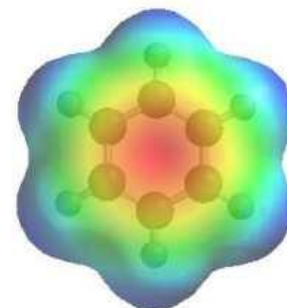


Fig. 16.19



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.

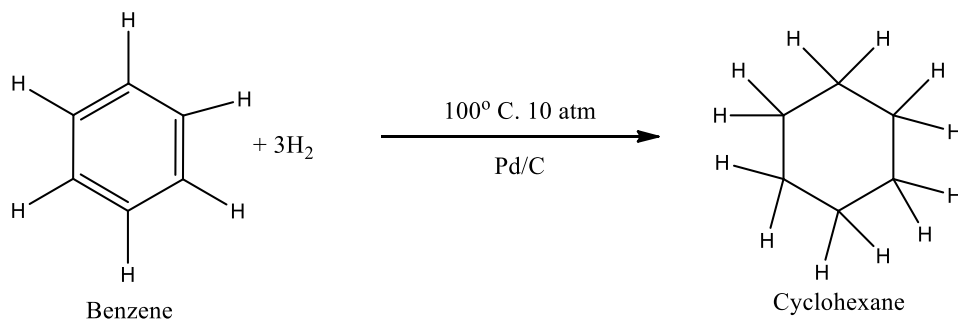
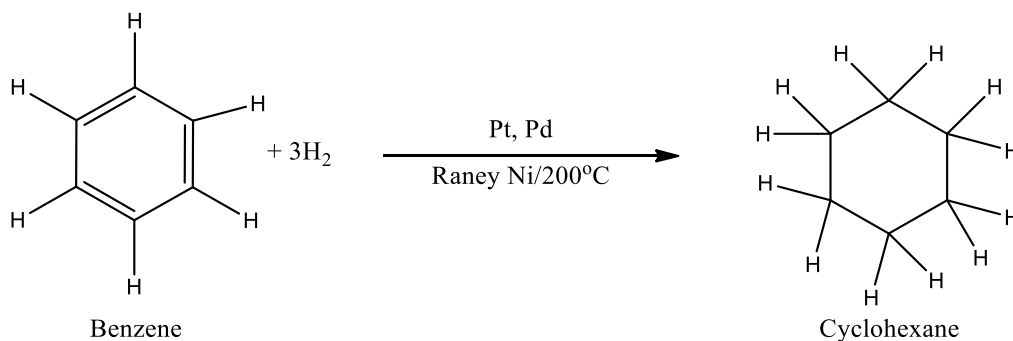
Addition Reactions

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.

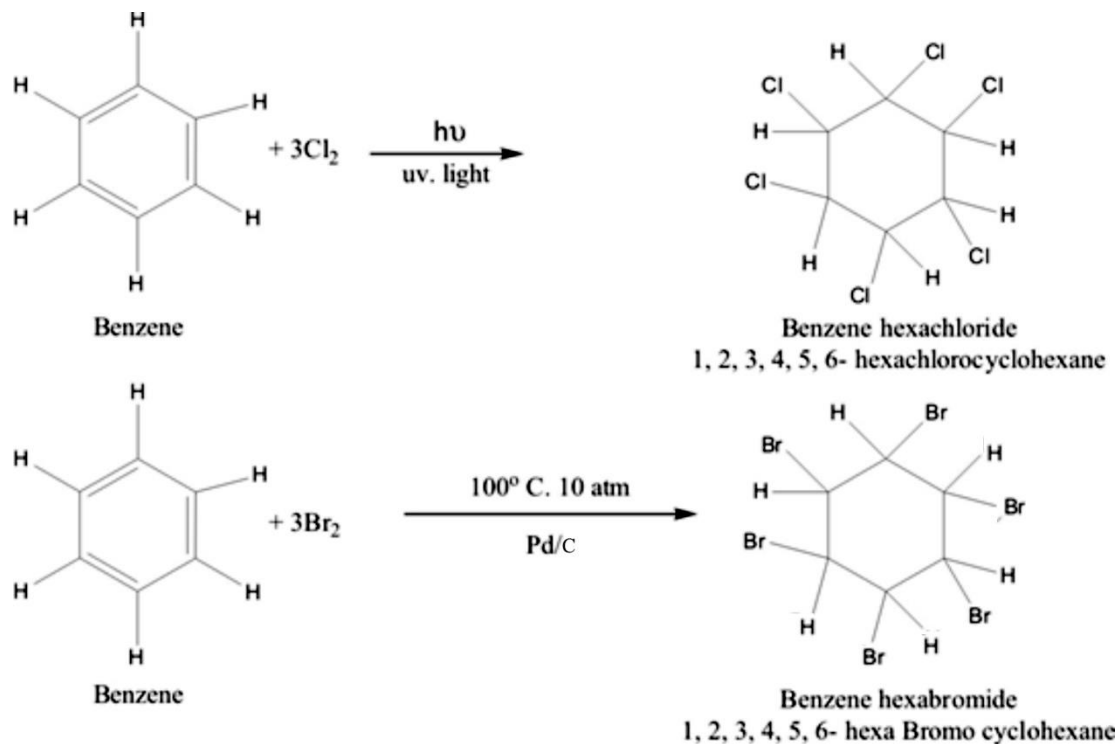


If we use the metals like Ru, Rh, supported at carbon then hydrogenation becomes easier



(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:

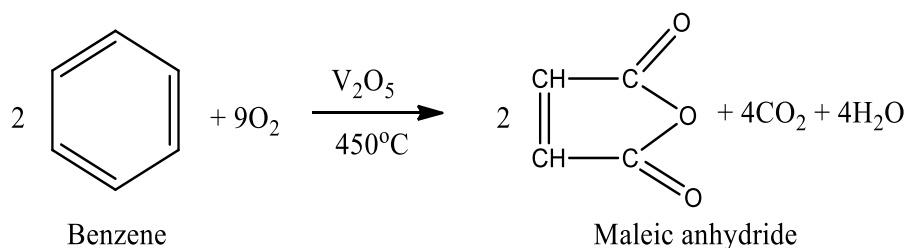
The addition reactions of hydrogen and chlorine with benzene show that benzene is unsaturated hydrocarbon and has three double bonds in it.

(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°C , then we get maleic anhydride

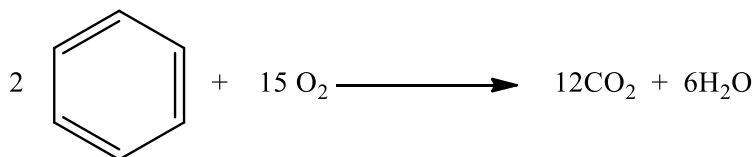




This is commercial method for the preparation of maleic anhydride. Benzene is not oxidized by KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$.

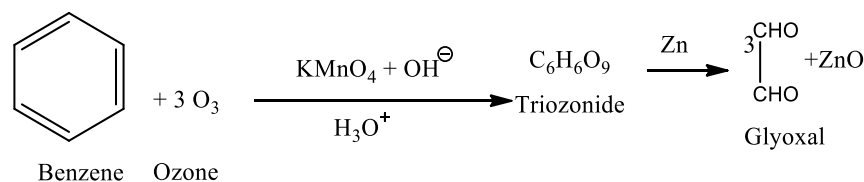
(ii) Combustion:

When benzene is burnt in the presence of air or oxygen, CO_2 and H_2O are produced, just like other aliphatic hydrocarbons

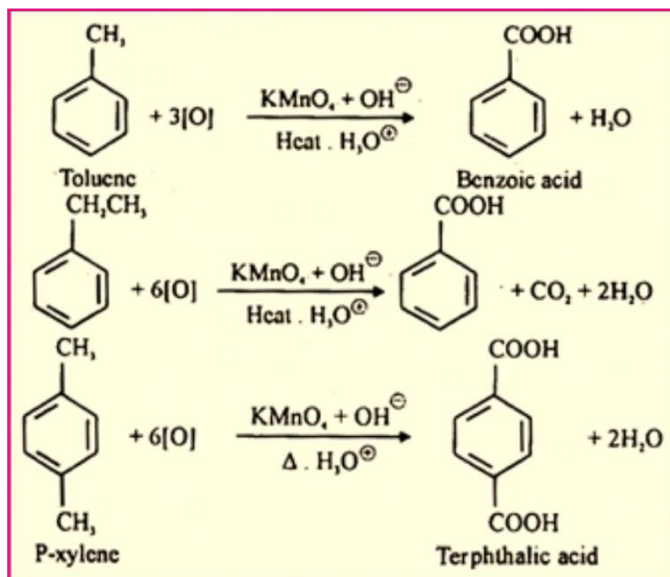


(iii) Ozonolysis:

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. $\text{KMnO}_4 + \text{H}_2\text{SO}_4$
2. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$
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.

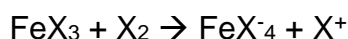
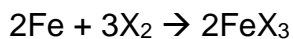
Electrophilic Aromatic Substitution Reactions

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:**

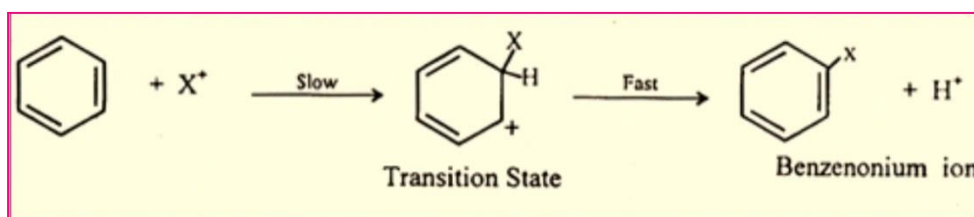
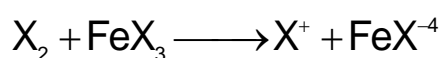
Substitution of halogen in benzene requires iron or corresponding ferric halide as catalyst. It reacts with halogen molecule to produce a powerful electrophile:

1. Formation of a strong electrophile (X⁺)

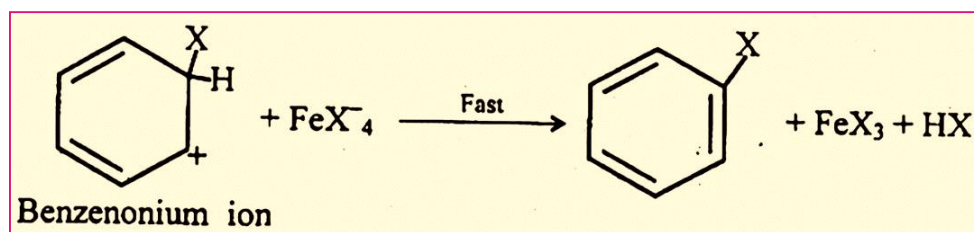
Tetra haloferrate ion (III) Halogenoium ion

2. Attack of electrophile at pi-bond:

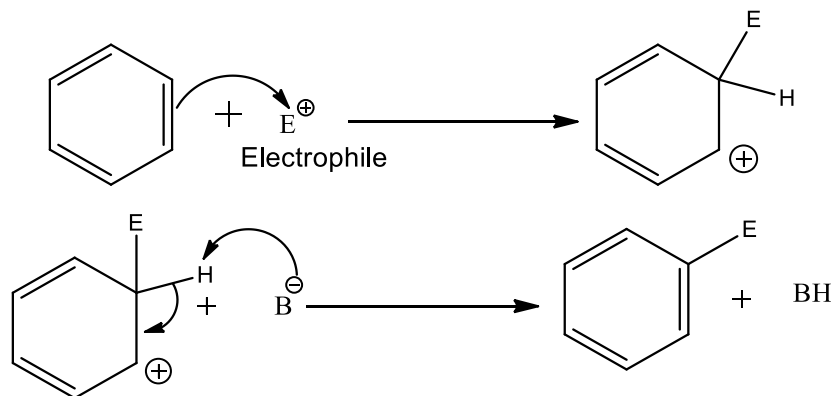
The halogenation ion thus produced attacks as a powerful electrophile on the electrons of benzene ring.



It had benzene unstable. The stability is retained by the removal of H⁺ ion to give substitution product.

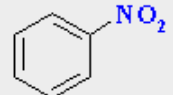
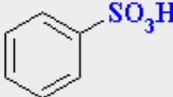
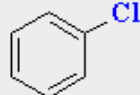
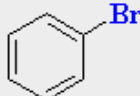
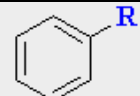
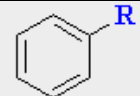
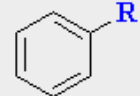
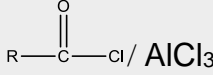
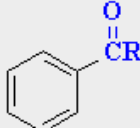
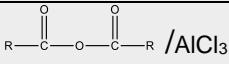
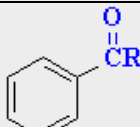
**General Pattern of Substitution**

The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.



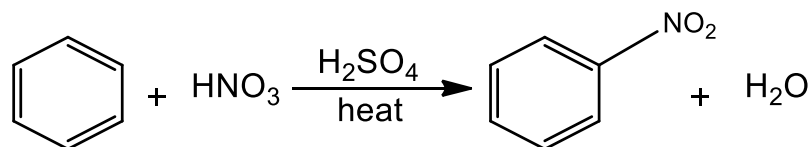
Substitution is preferred over addition in order to preserve the stable aromatic character



Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO ₃ / H ₂ SO ₄	NO ₂ ⁺		E ⁺ formed by loss of water from nitric acid
<u>Sulfonation</u>	H ₂ SO ₄ or SO ₃ / H ₂ SO 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	 / AlCl ₃	RCO ⁺		E ⁺ formed by Lewis acid removing Cl ⁻
	 / AlCl ₃	RCO ⁺		E ⁺ formed by Lewis acid removing RCO ₂ ⁻

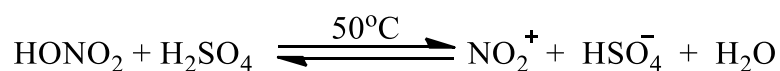
Nitration

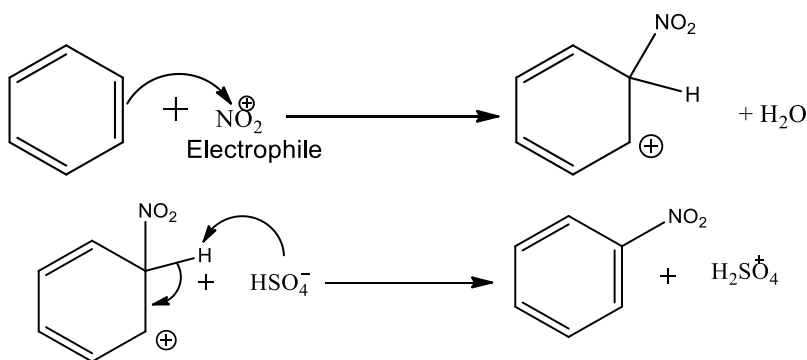
The introduction of – NO₂ group in benzene by substituting hydrogen of benzene ring is called Nitration



Mechanism

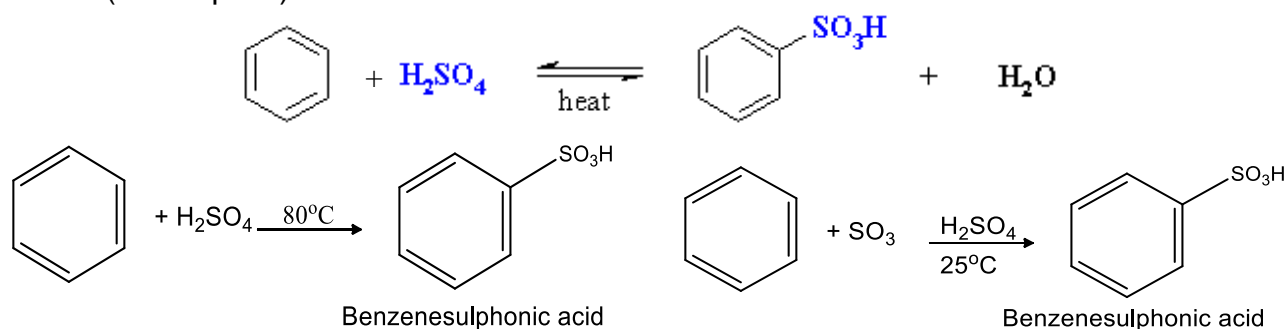
Sulphuric acid reacts with nitric acid to generate nitronium ion.





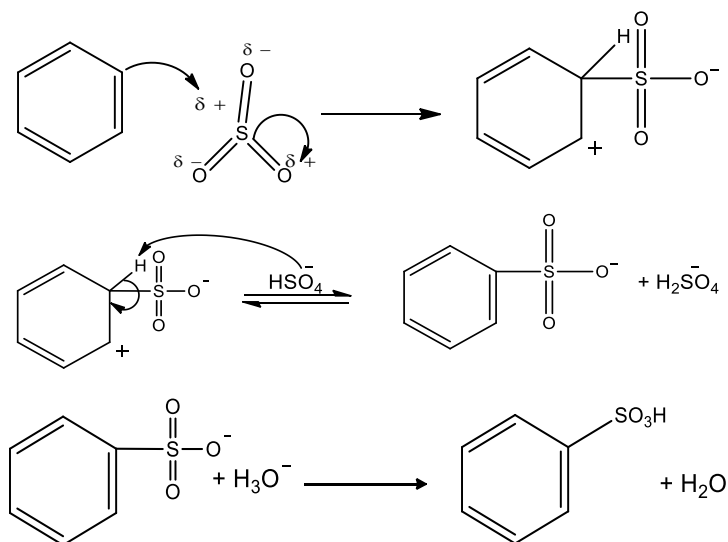
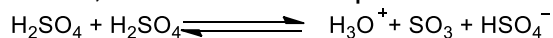
Sulfonation

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_4 has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.



Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3

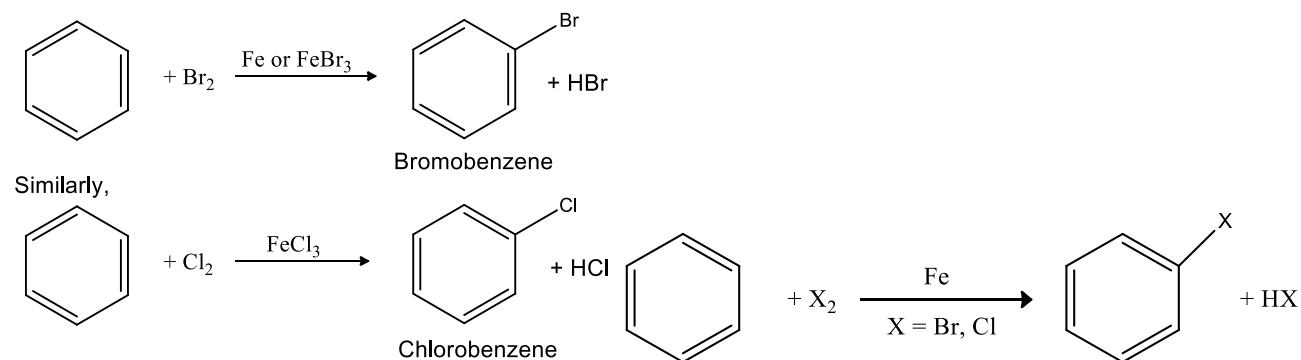


Halogenation

The introduction of halogen in benzene by substituting hydrogen of benzene ring is called halogenation.

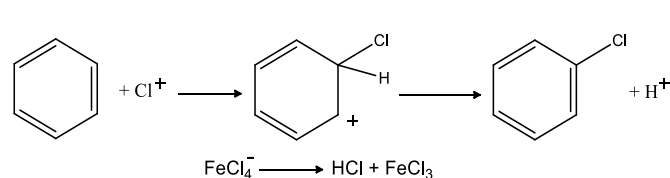
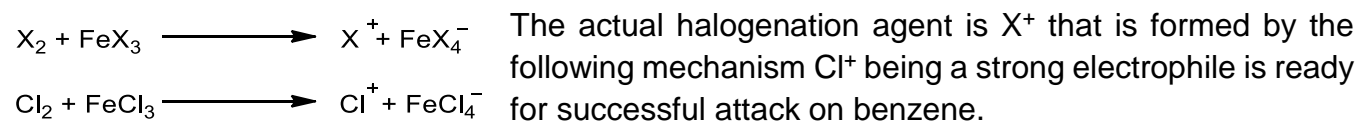


Explanation and Examples:

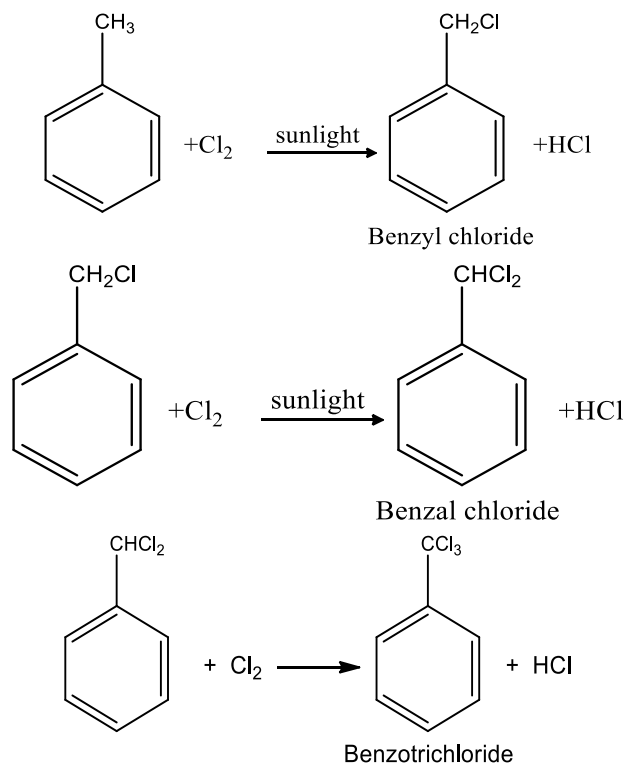


Halogenation of benzene occurs with halogens (X₂) in the presence of a catalyst FeX₃. Chlorination and bromination are normal reaction but fluorination is too vigorous to control. Iodination gives poor yield.

Mechanism:



When alkyl benzenes are treated with chlorine or bromination in the presence of sunlight, only the alkyl groups are substituted.

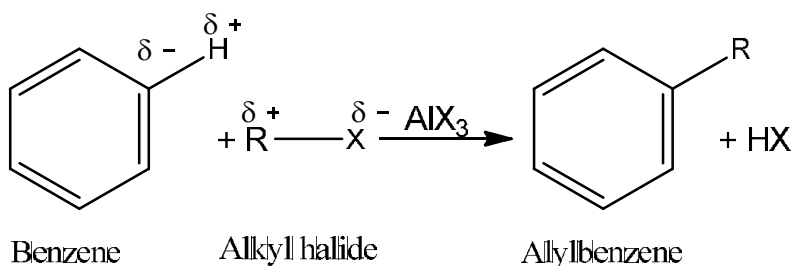




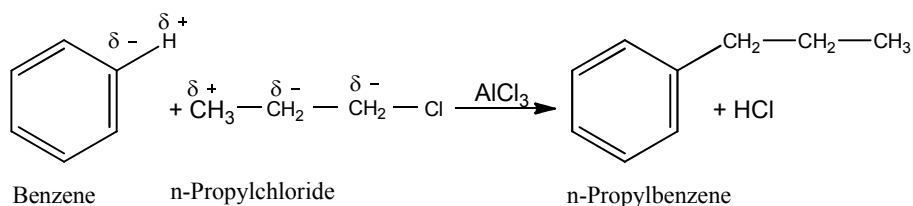
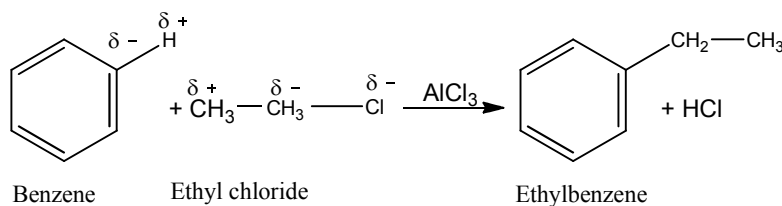
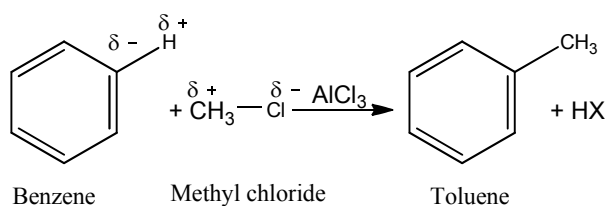
Friedel-Crafts Alkylation

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.

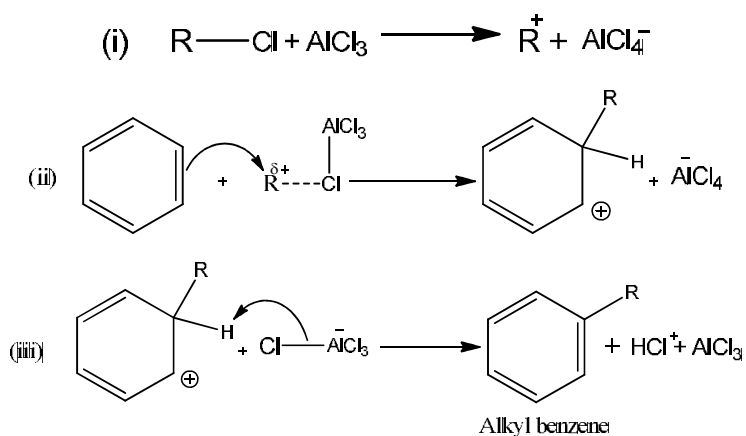
Overall reaction:



Examples:



Mechanism:

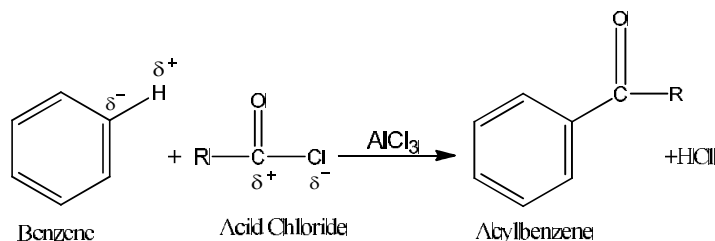




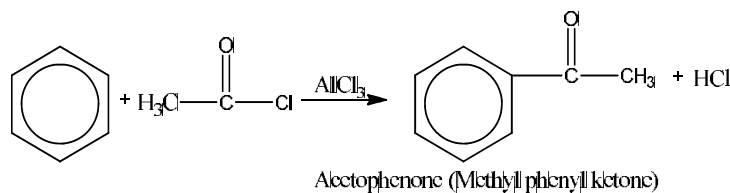
Friedel-Crafts Acylation

The introduction of an acyl group $\text{R}-\text{C}(=\text{O})-$ 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.

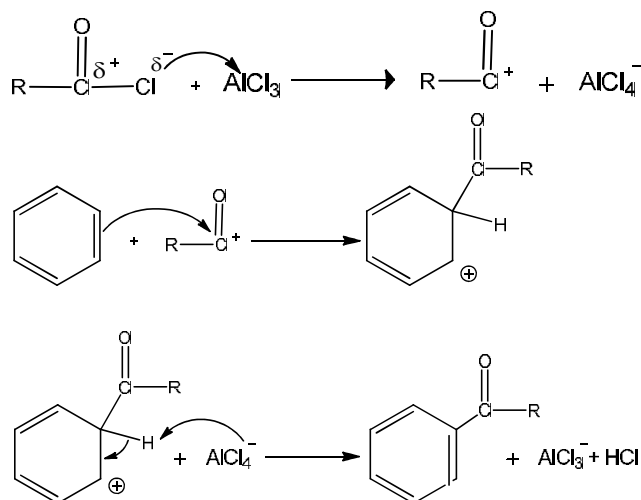
Overall reaction:



Example:



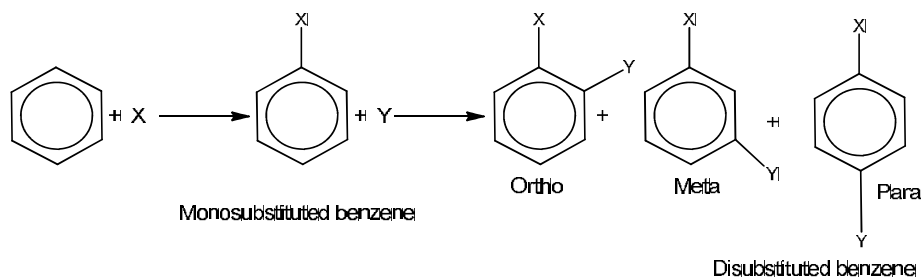
Mechanism:



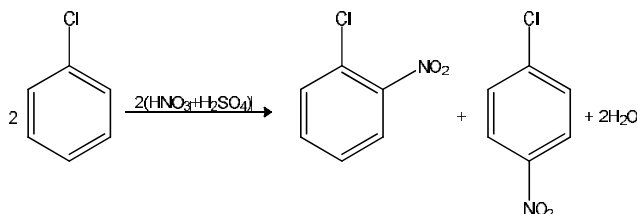
Substituent Effects - (Table of Substituent Effects) and Making Poly-substituted Benzenes

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:

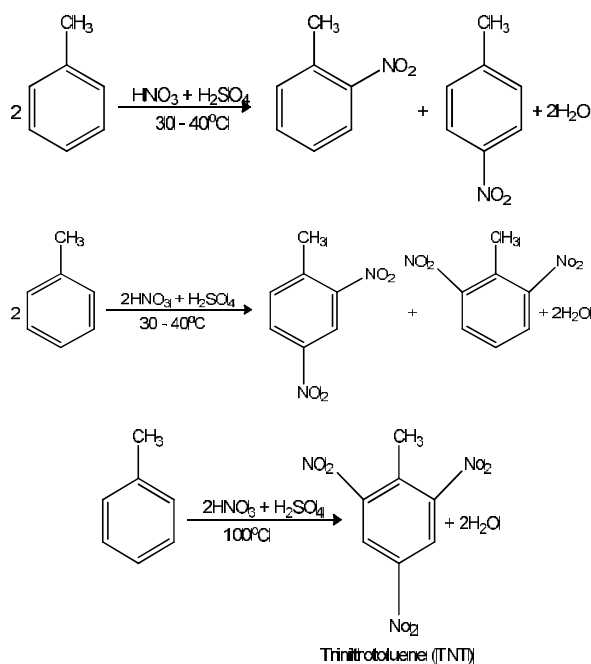
- Ortho- and para- directing groups
- Meta- directing groups

1. Ortho and para directing groups

These groups release electrons towards the benzene ring, at ortho and para positions. Because these positions 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.



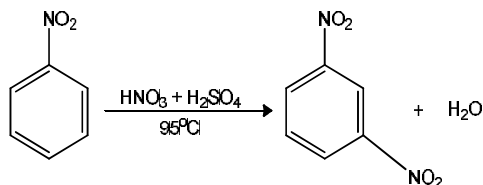


Other examples of ortho and para directing groups are:-

$-\text{N}(\text{CH}_3)_2$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$

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 $-\text{C}\equiv\text{N}$, NO_2 , $-\text{COOH}$, $-\text{CHO}$

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) $-\text{NH}_2$ Nitrogen with greater electronegativity from hydrogen.

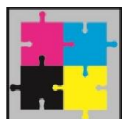
(ii) $-\text{Cl}$ has no other atom hence will have no danger of pulling electrons. Thus it is electron repelling and o, p- directing group. Hence o, p-, directing

i. $\text{—}\overset{\text{O}}{\parallel}{\text{N}^+}\text{—O}^-$ Nitrogen with less E.N from O. Hence meta directing.

ii. In $-\text{SO}_3\text{H}$ 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

- (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.
- 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 some 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

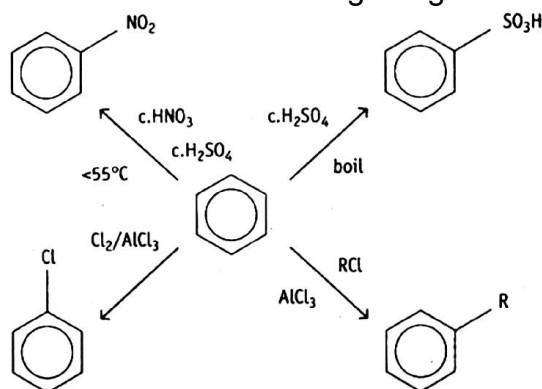


Key Points

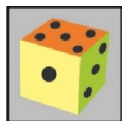
- ❖ Compared to other functional groups, alkanes tend to have low melting and boiling points and very low solubility in polar solvents such as water.
- ❖ Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by sigma bonds. They have a general formula of 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 diagram



- ❖ 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**

- The molecule of ethane posses which hybridization;**
 - sp^3
 - sp^2
 - sp
 - sp^2d
- The sp^2 hybrid orbitals are oriented in space at one angle;
 - 109.5°
 - 180°
 - 100°
 - 120°
- The geometry of acetylene is,
 - angular
 - bent
 - trigonal
 - linear
- Which reaction is used as test for the presence of alkene;
 - reaction of cold diluted alkaline $KMnO_4$
 - Combustion
 - Polymerization
 - Catalytic hydrogenation
- The general formula of alkane is;
 - C_nH_{2n+2}
 - C_nH_n
 - C_nH_{2n}
 - C_nH_{2n-2}
- Sodalime is;
 - $NaOH$
 - KOH
 - Mixture of Na and Ca hydroxide
 - CaO and $NaOH$
- The marsh gas is
 - Ethane
 - Methane
 - Propane
 - Butane
- Acidic hydrogen is present in
 - Acetylene
 - Ethane
 - Benzene
 - Ethene
- The benzene molecule contains:
 - Three double bonds
 - Two double bonds
 - One double bond
 - none of these
- The electrophile in aromatic sulphonation is;
 - H_2SO_4
 - HSO_4^-
 - SO_3
 - SO_4^-
- The conversion of n-hexane into benzene by heating in the presence of Pt is called;
 - Isomerization
 - Aromatization
 - Dealkylation
 - Rearrangement
- Catalyst used for Friedal Craft's reaction is;
 - HNO_3
 - $AlCl_3$
 - $BeCl_3$
 - $FeCl_3$
- Benzene can not undergo
 - Elimination
 - Substitution
 - Oxidation
 - Addition
- Shape of benzene molecule is
 - Pyramidal
 - Liner planar
 - Trigonal
 - Hexagonal planar
- In which one of the following compounds the benzene ring is isolated;
 - Naphthalene
 - Anthracene
 - Phenthrene
 - Diphenyl ethane
- 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
 - identical
 - Position isomers
 - structural isomers
 - stereoisomerism
- the isomers of a substance must have
 - same chemical properties
 - same molecular weight
 - same structural formula
 - same functional groups



18. Ethanol and dimethyl ether are best considered:
(a) structural isomers (b) stereoisomers (c) enantiomers (d) diastereomers
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) if it contains center of symmetry
(c) if it cannot be superimposed on 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 trans 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

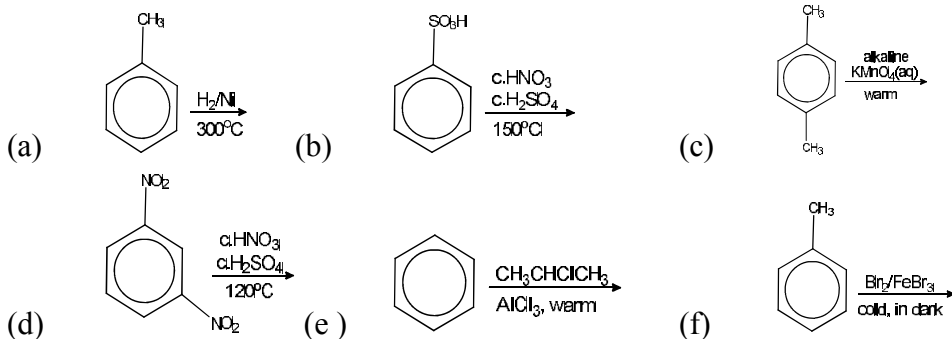
1. Why carbon is sp^3 hybridized in the compounds?
2. How is pi-bond formed in alkenes and alkynes?
3. What is cis-trans isomerism?
4. Why alkanes are relatively chemically inert?
5. Alkenes usually undergo addition reactions while alkanes do not why?
6. What is stereoisomerism?
7. How optical isomers 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

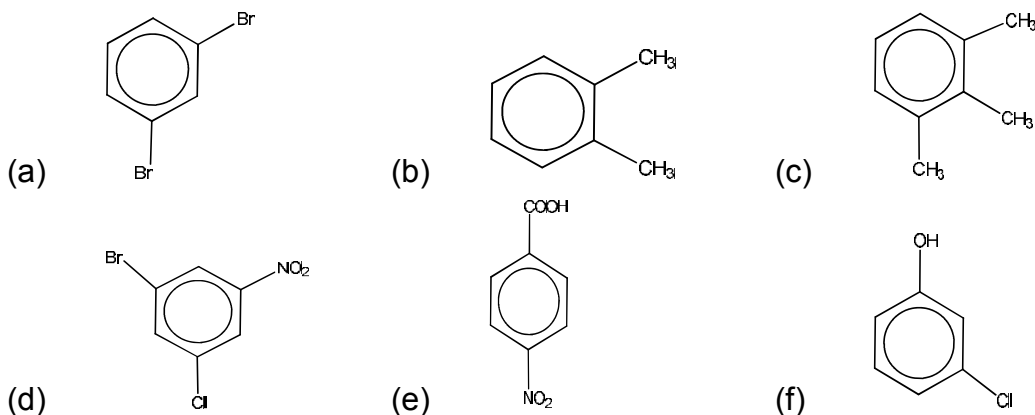
1. What is isomerism? Explain different types of isomerism?



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-methylbenzenesulphonic acid
e) 2-hydroxybenzoic acid
f) 2-chlorophenylamine
8. Predict the major products of the following reactions.



9. Name the following benzene derivatives:





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, SOCl₂ and PX₃ 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 aldehydes, ketones, 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 with RX, reaction with aldehydes, ketones preparations of amides and diazonium salts.
- Describe isomerism in alkyl halides and amines.



Reading

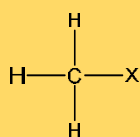
17.1 ALKYL HALIDE

Introduction

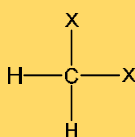
“Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by one halogen atom. They are also known as halogen derivatives of alkanes.”

Types:

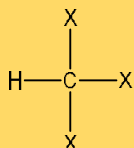
They may be mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides having general formula R-X.



Monohaloalkane



Dihaloalkane

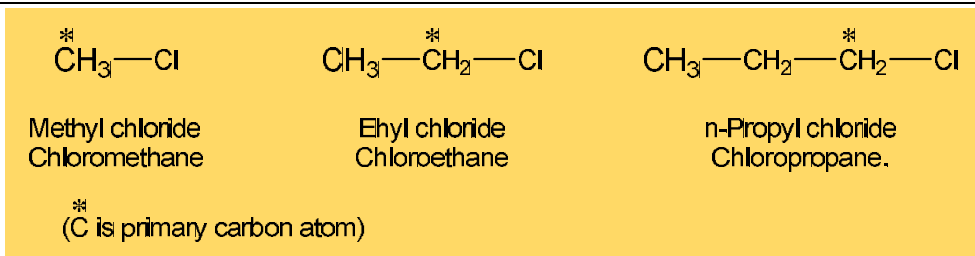


Classification of Alkyl Halides:

Alkyl halides are classified into primary, secondary and tertiary alkyl halides.

(i) Primary Alkyl Halides:

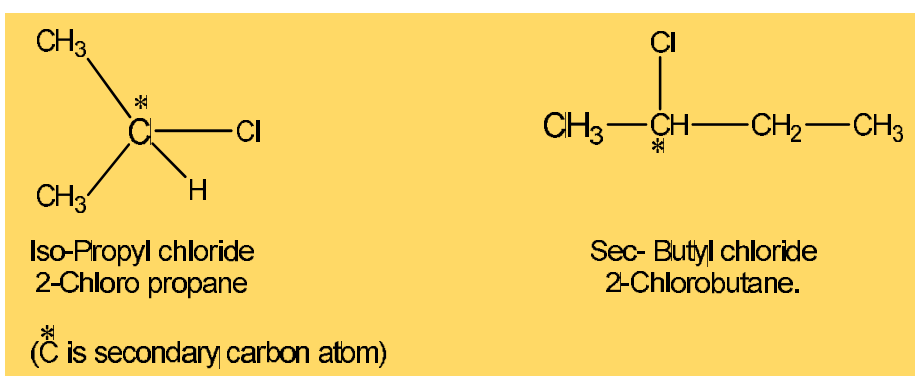
“Alkyl halide in which halogen atom is attached with primary carbon are called primary alkyl halide”. **(Carbon atom attached to one or no carbon atom is called primary C-atom.)**

**(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:

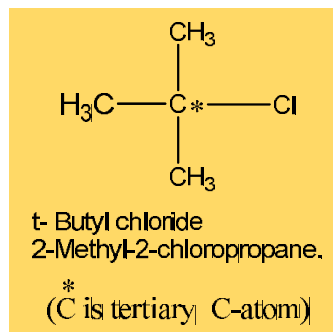
“C-atom, attached to two C-atoms simultaneously is called secondary C-atom.”

**(iii) Tertiary Alkyl Halides:**

“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”.

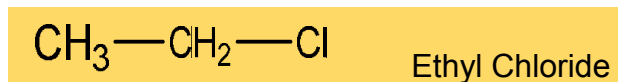
**17.1.1. Nomenclature**

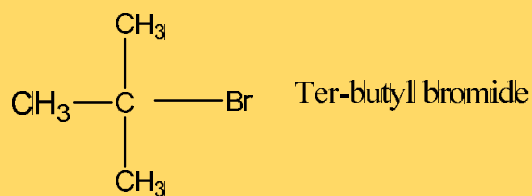
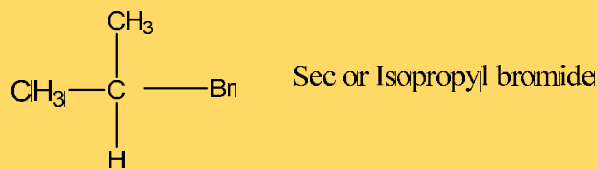
Alkyl halides are named according to the following systems:

- (i) Common System of naming.
- (ii) IUPAC System of naming.

(i) Common System of Naming:

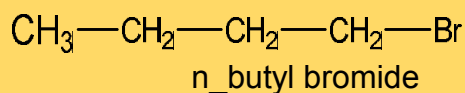
This method consists in first writing the name of alkyl group to which halogen atom is attached and then writing the name of halide ion, e.g.,





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.,

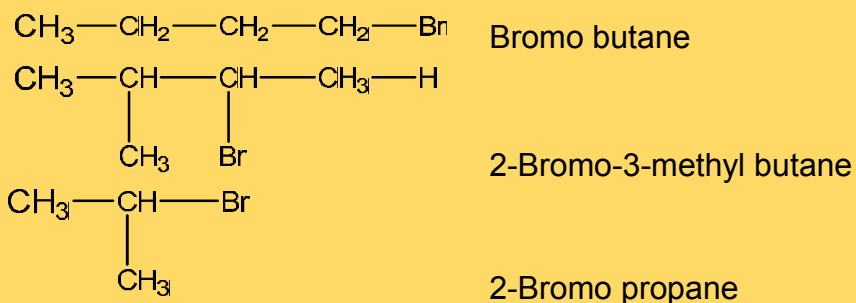
When all the carbons of alkyl group of primary alkyl halides are in a straight chain, the prefix n- is used before the name which indicates 'normal'. e.g.,



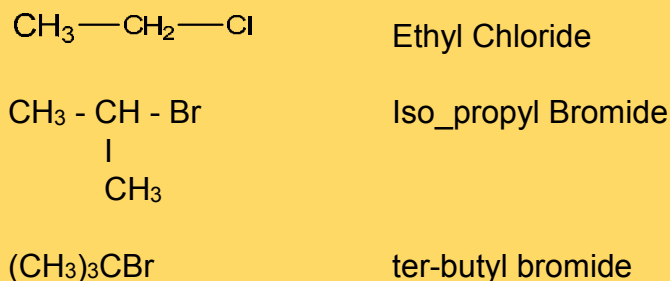
(ii) IUPAC System of naming.

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.,



The names given below are also accepted by the IUPAC



17.1.2. Physical Properties:

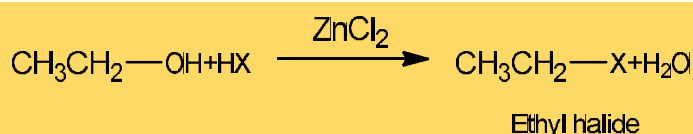
The polar bond creates a molecular dipole that raises the melting points and boiling points compared to alkanes.

**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.

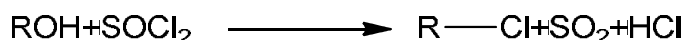
Preparations of Alkyl Halides**17.1.4.1 Reaction of Alcohols with Hydrogen Halides**

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.

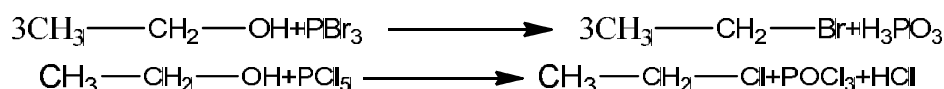
**Reaction of Alcohols with other Halogenating agents ($SOCl_2$, PX_3 , PX_5)**

(a) Alcohols react with thionyl chloride in pyridine as a solvent to give alkyl chlorides.

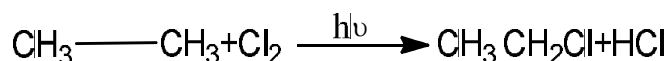
This is the best method because HCl, and SO_2 escape leaving behind the pure product.



(b) Phosphorous trihalides or phosphorous pentahalides react with alcohols to form alkyl halides.

**Halogenation of Alkanes**

By the action of chlorine or bromine, alkanes are converted into alkyl halides. This reaction takes place in the presence of diffused sunlight or ultraviolet light.



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:

- Bond polarity of C-X bond
- Bond energy of C-X bond

1. Bond Polarity

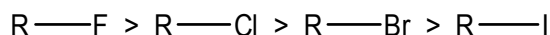
The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C.

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 acquire 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.



2. Bond Energy

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl 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

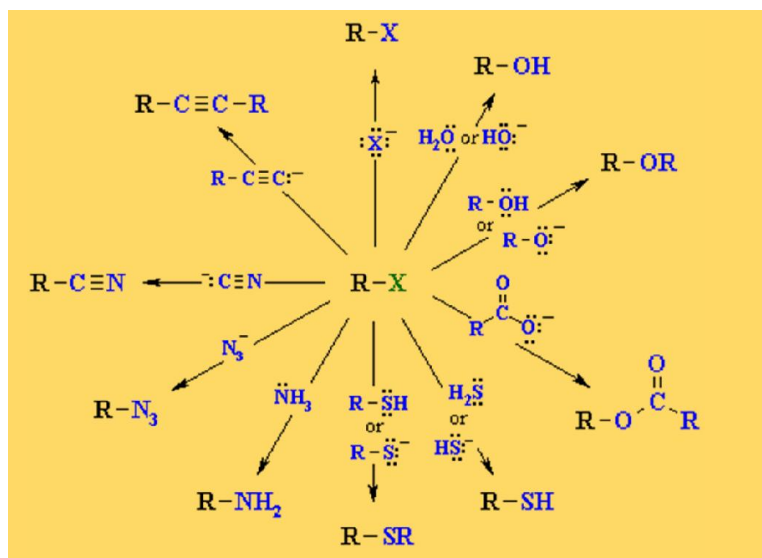
In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

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

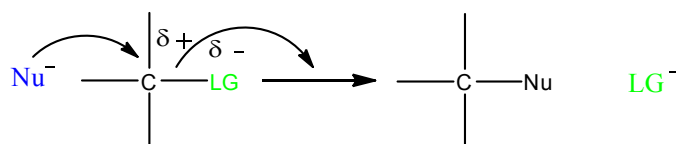
Nucleophilic Substitution Reactions



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:

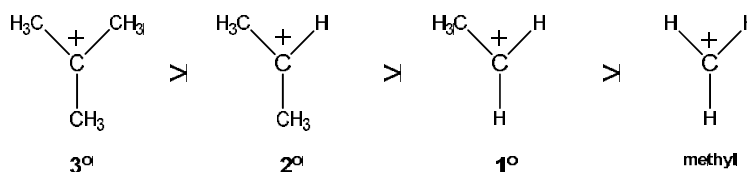
- Bond breaking to form a carbocation precedes the formation of the new bond : SN_1 reaction
- Simultaneous bond formation and bond breaking : SN_2 reaction

Important Concepts

Carbocations and their Stability

Stability:

The general stability order of simple alkyl carbocations is: (most stable) $3^\circ > 2^\circ > 1^\circ >$ 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
$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thio cyanate ion	$\ddot{\text{N}}\text{H}_3$	Ammonia
$\text{H}_2\ddot{\text{O}}:$	Water		



Substrate and Leaving Group

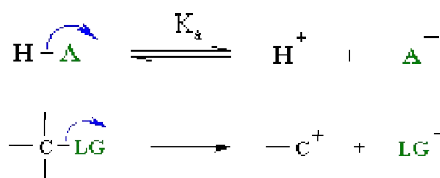
Substrate Molecule:

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 $\text{S}_{\text{N}}1$ type reaction.

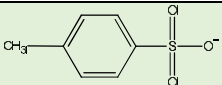
Note the similarity of the two equations: both show heterolytic cleavage of a sigma bond to create an anion and a cation.

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 stabilization of a LG^- .

Here is a table classifying some common leaving groups that we will eventually meet.....

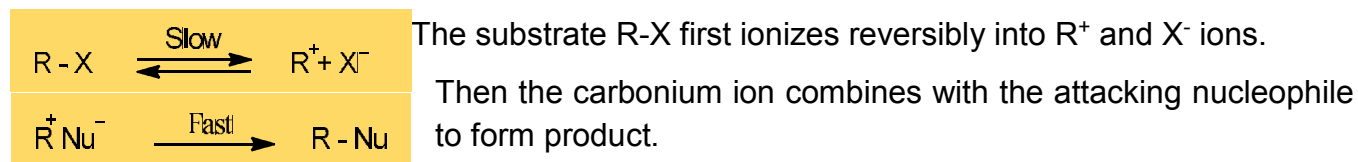
Excellent	 , NH_3
Very Good	I^- , H_2O
Good	Br^-
Fair	Cl^-
Poor	F^-
Very Poor	HO^- , NH_2^- , RO^-

But water itself, is a good leaving group, since it is the conjugate base of H_3O^+ .

$\text{S}_{\text{N}}1$ Mechanism

"It is substitution nucleophilic unimolecular two step reaction."

Explanation:





Mechanism:

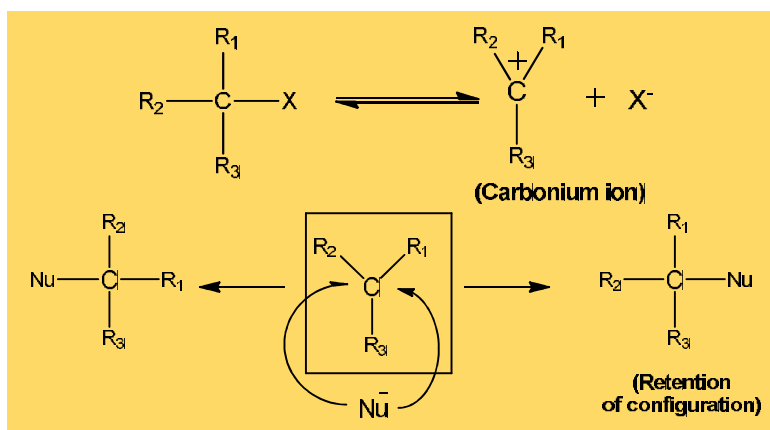
Since only one molecule is undergoing a change in covalency in rate determining step, this two step nucleophilic substitution reaction is unimolecular and is called S_N1 reaction. The brief mechanistic picture of S_N1 reaction base upon the following evidences:

1) Kinetic Evidence:

The rate of an S_N1 reaction depends upon the concentration of alkyl halide only. The change in concentration of attacking nucleophile has no effect on the rate

$$\text{Rate} = k[\text{R-X}]$$

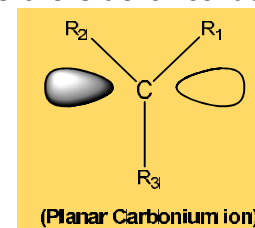
It is because the nucleophile combines with the carbonium ion in the second step. for the same reason, the rate of an S_N1 reaction does not depend on the nature of attacking nucleophile.



2) Stereo Chemical Evidence:

Experiments have shown that S_N1 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 racemic mixture. However, the partial racemization 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



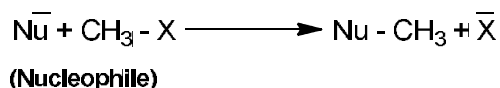
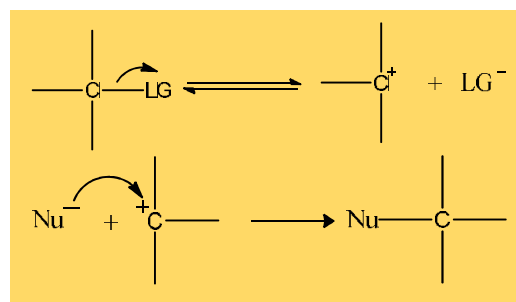
Therefore, the product has some optical activity.

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

S_N2 Mechanism

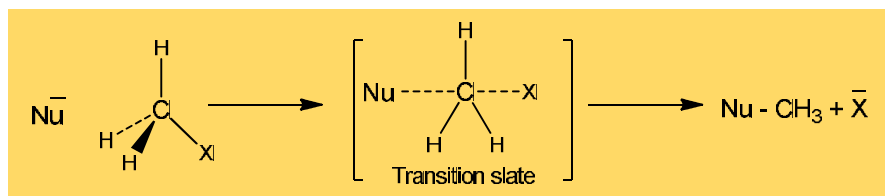
"It is substitution nucleophilic bimolecular reaction. It occurs in one step".





Mechanism:

The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step.

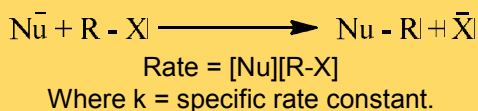


This is rate-determining step because the bond breaking and bond making processes occur simultaneously. Since two molecules are undergoing change in covalency in rate

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 S_N2 reaction depends upon the concentration of nucleophile as well as the concentration of alkyl halide. The rate expression for the reaction can be written as

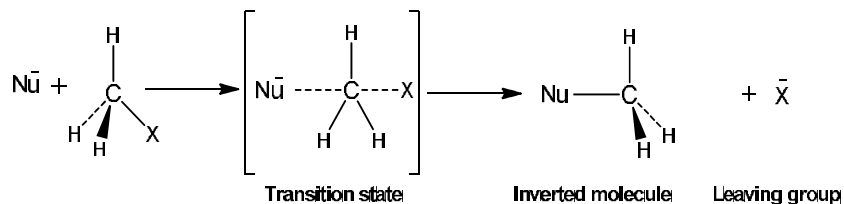


This means that the rate of reaction will be double if the concentration of any of the two is double e.g., the rate of increases when Cone of either OH^- or $\text{CH}_3\text{-Br}$ is increased.



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 and the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.



Comparison of S_N1 and S_N2 Mechanism

Sr. No.	S_N1	Sr. No.	S_N2
(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% retention of configuration takes place.	(6)	100% inversion of configuration takes place.
(7)	Rate = K[R-X]	(7)	Rate = [Nu][R-X]

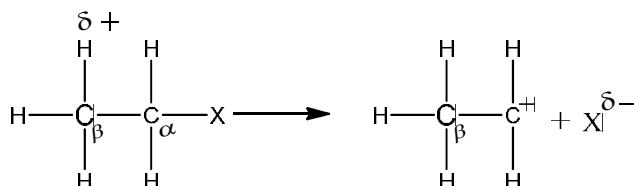
17.1.7 1,2 Elimination Reactions

Definition of Elimination Reaction:

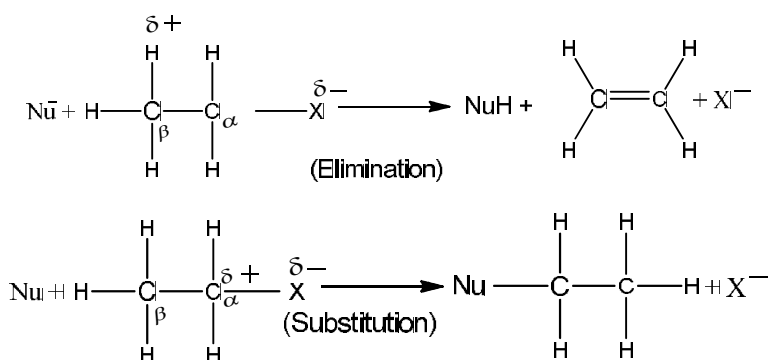
“The chemical reaction in which two groups are eliminated from two adjacent atoms is called elimination reaction”. Since β -hydrogen is necessary for eliminations, it is also called β -elimination.

Explanation:

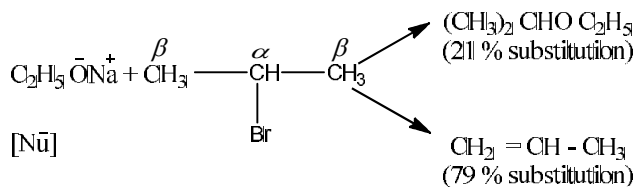
β -hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen.



The attacking nucleophile can either attack α -carbon to give substitution product or β -hydrogen to give elimination reaction.



Strong bases such as OH^- , OR^- , NH_2^- cause elimination in preference to substitution. Highly polarizable nucleophile and weak bases such as I^- , RS^- etc. give substitution reactions.



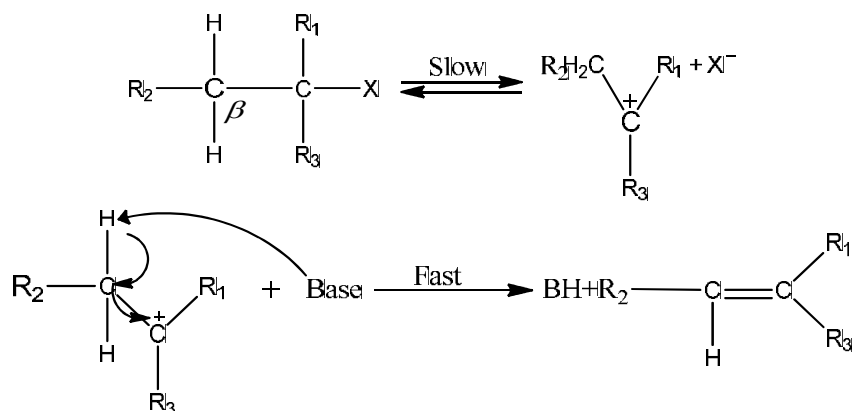
E_1 mechanism

“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

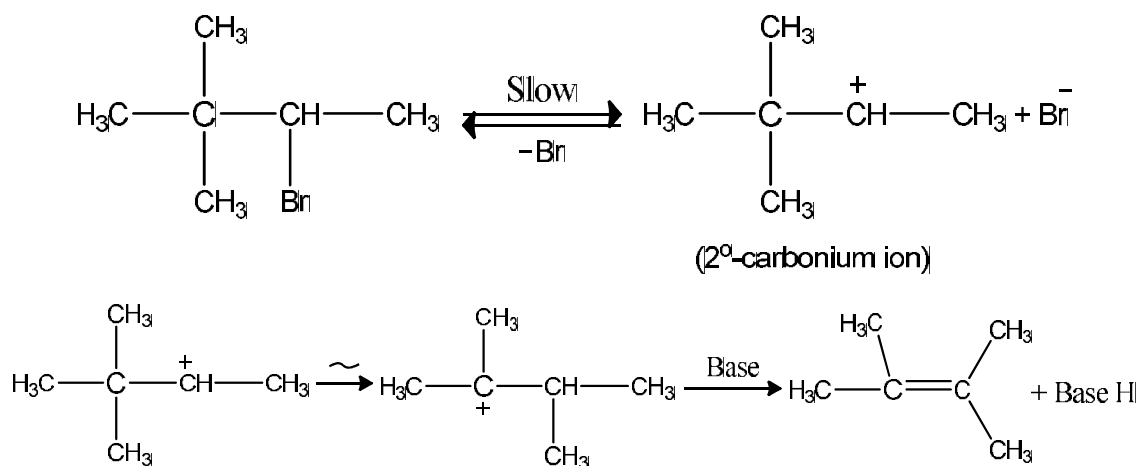


Since only one molecule is undergoing a change in the rate determining step, i.e., first step, this is two step unimolecular elimination reactions.

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.

$$\text{Rate} = k[\text{R-X}]$$

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.

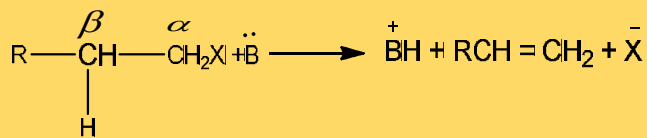


E_2 mechanism

“It is bimolecular one step elimination reaction”.

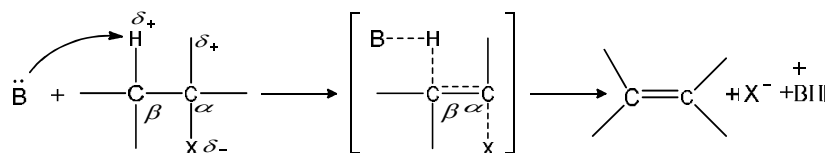
Explanation:

Consider the reaction,





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.

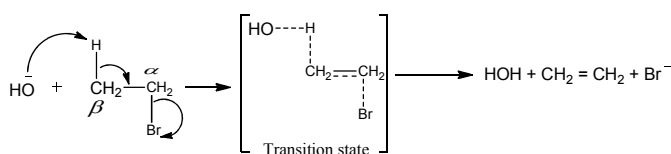


This is rate determining step because bond breaking and bond making processes are taking place simultaneously.

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

$$\text{Rate} = k[\text{R}-\text{X}][\text{B}]$$

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

$$\text{Rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$$

17.1.8 Substitution versus Elimination Reactions

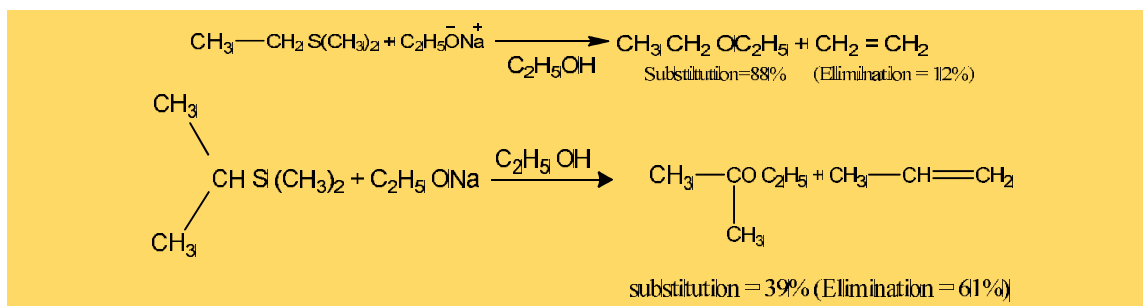
Though substitution and elimination reaction lead to different products, there is always a competition between them because of close resemblance in their mechanism. Since substitution is more favorable energetically it is the dominant reaction in the substitution-elimination reaction.

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:

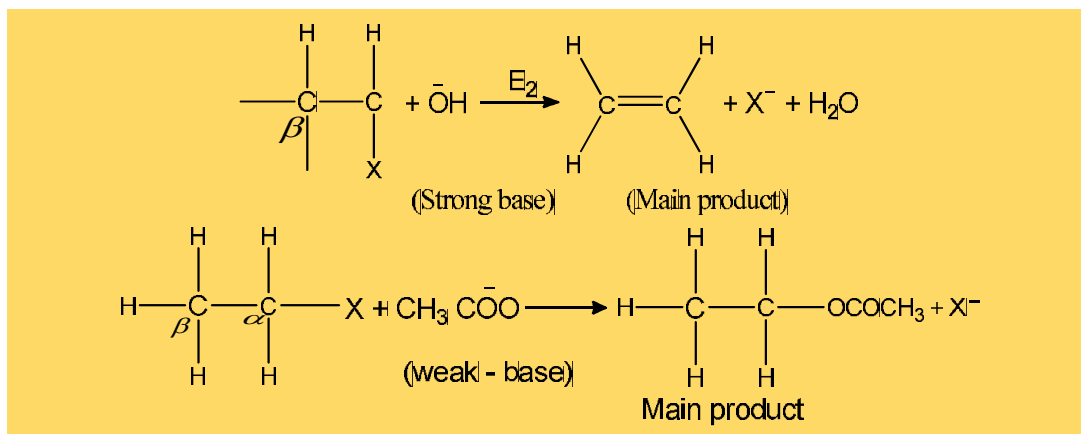
Crowding within the substrate favors elimination over substitution because the approach of the nucleophile to α -carbon is difficult for substitution. However, the elimination is favorable because the removal of β -H atom by base from tertiary planar carbonium ion is easy, e.g.,





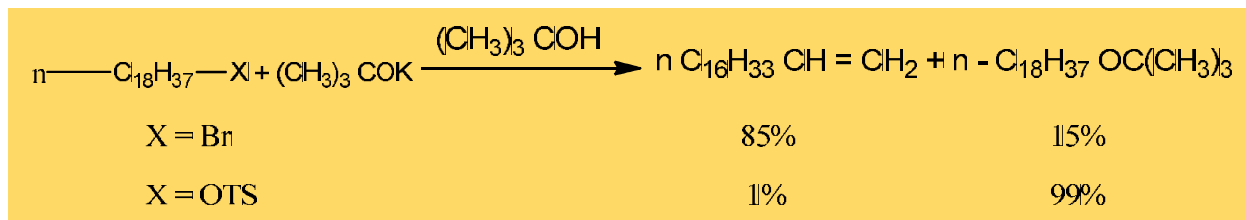
(ii) Nature of Base:

When the electron pair donor is a strong base, e.g., OH^- , OR^- 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 E_2 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.,

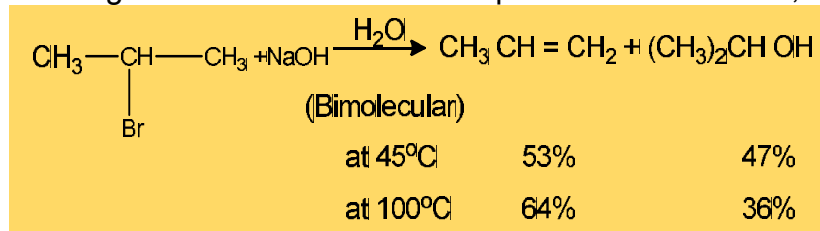


(iv) Nature of Solvent

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. E_1 is favored by polar solvents like SN_1 reaction. In non-polar solvents, the reaction will follow E_2 -mechanism.

(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.,



**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 polarity.
7. Define bond energy.
8. What is nucleophile?
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



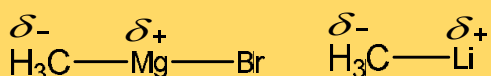
Magnesium metal cut into small pieces is added to a solution of an alkyl halide or aryl halide in only dry ether. The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.

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.

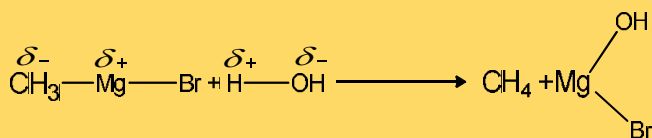
17.2.2. Reactivity



Organo metallic compounds are nucleophile because of partial negative charge on the carbon of alkyl group



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.,

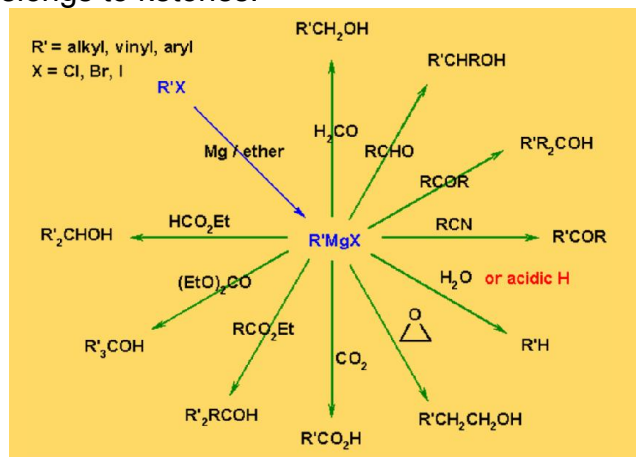


The following reaction supports the electrophilic character of organic metallic compounds;



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.



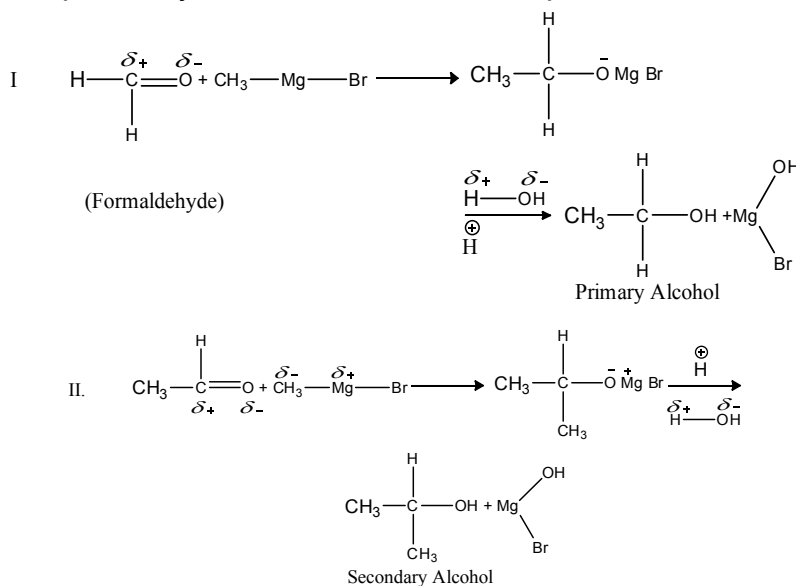
Classification of Monohydric Alcohols:

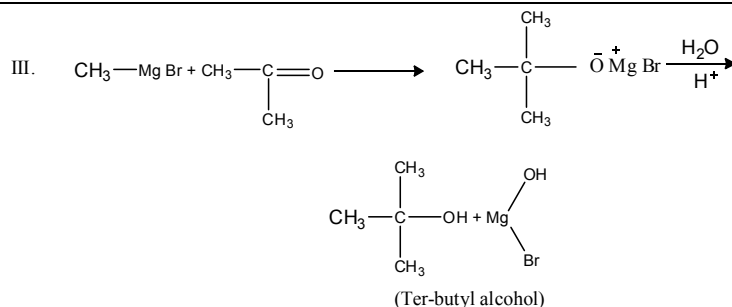
Monohydric alcohols are classified into the following three families:

- (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.

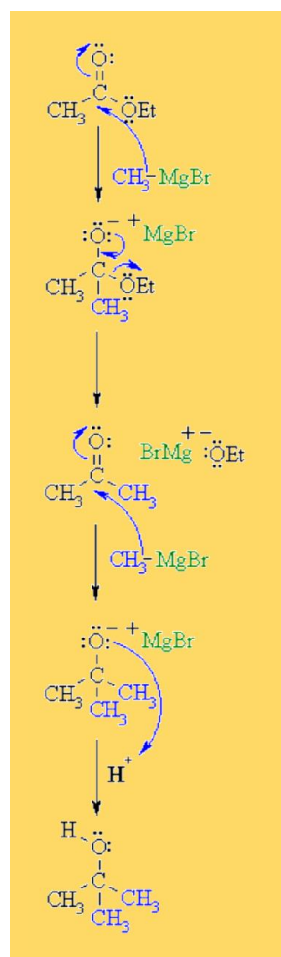
Reaction type: Nucleophilic acyl substitution then nucleophilic addition





1. Carboxylic esters, $\text{R}'\text{CO}_2\text{R}''$, 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 $\text{C}=\text{O}$ 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 $\text{C}=\text{O}$ 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.

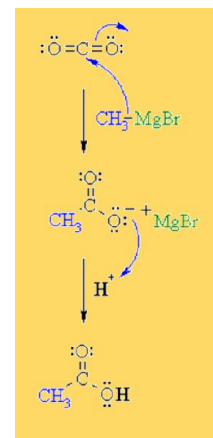


With CO₂ (Carbonylation of Grignard Reagents, RMgX)

NUCLEOPHILIC ADDITION OF RMgX TO CARBON DIOXIDE

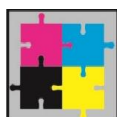
Step 1:

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 CO₂?
5. Write the formula of Grignard Reagent.

17.3 AMINES

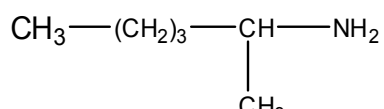
17.3.1 Nomenclature:

1. Common System of Naming

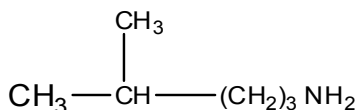
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals.



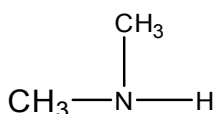
Ethyl amine



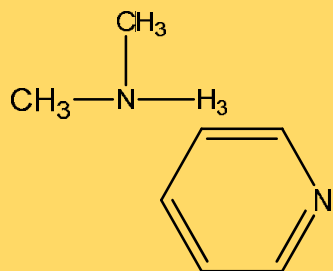
Sec-hexyl an



Iso-hexyl amine
(a primary amine)



Dimethyl amine (a sec-amine)

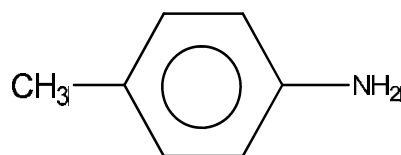


Trimethylamine (a ter-amine)

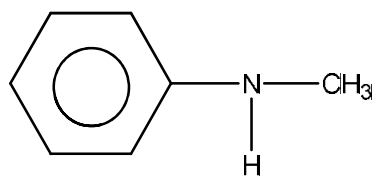
Pyridine (a ter-amine)

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. If there are two substituent on N, it is repeated twice,

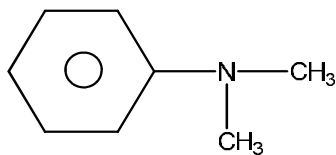
2. IUPAC System of Naming



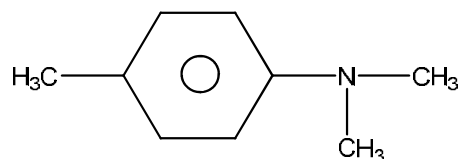
p-Toluidine



N-methyl aniline

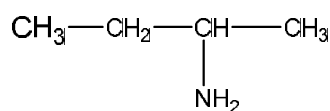
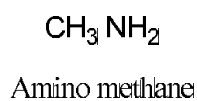


N, N-dimethyl aniline

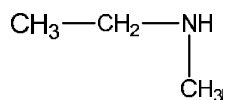
N, N-dimethyl
p-toluidine

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.

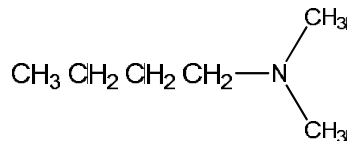
Secondary and tertiary amines are named by using a compound prefix that includes the names of all but the largest alkyl group.



2-Aminobutane



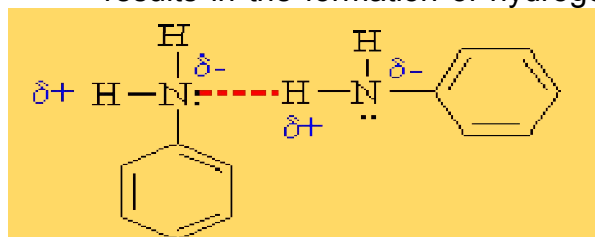
Methyl amino ethane



(Dimethyl amino butane)

17.3.2. Physical Properties:

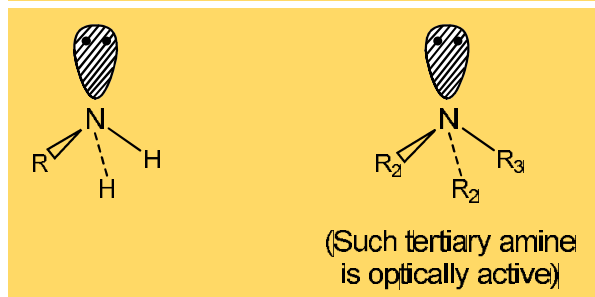
- The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules, see below, or other H-bonding systems (e.g. water). The applications of this are:



intermolecular H-bonding in amines

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



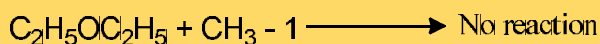
17.3.3 Structure:

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 $\text{CH}_3\text{-I}$,



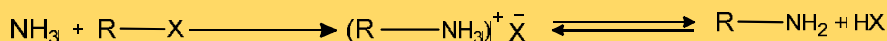
are more basic than alcohols and ethers and they are also more nucleophilic, e.g., ether does not react where as at the same temperature amines gives addition product with $\text{CH}_3\text{-I}$,

17.3.5 Preparation of Amines

Alkylation of Ammonia by Alkyl Halides



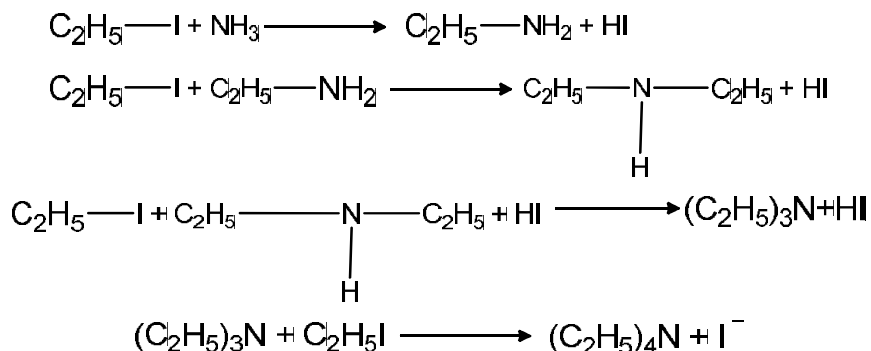
When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of prim-, sec-, ter- amines and a quaternary ammonium salt is obtained. The reaction occurs with nucleophilic displacement of halide by ammonia of amines,





This reaction is further alkylated, e.g., accompanies by the following reactions

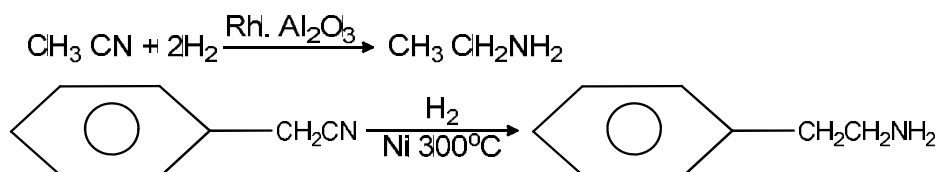
At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts but the quaternary salt is unaffected. The three amines are separated by fractional distillation. Over alkylation can be avoided by using excess of ammonia but the yield is low.



Reductions of nitrogen containing functional groups:

Reduction of Nitriles

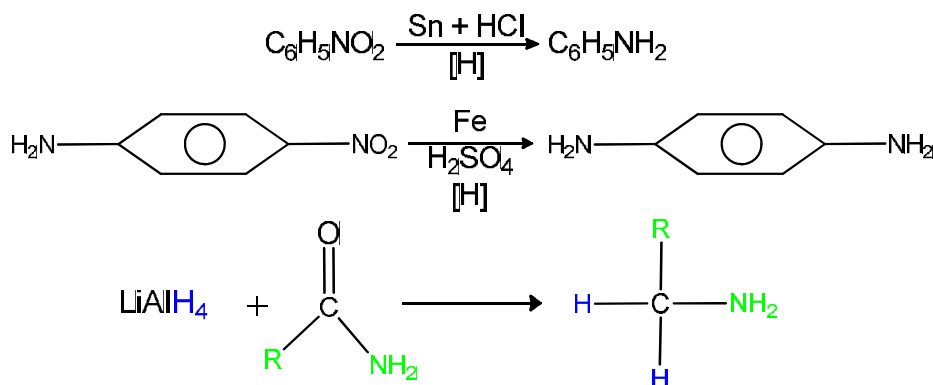
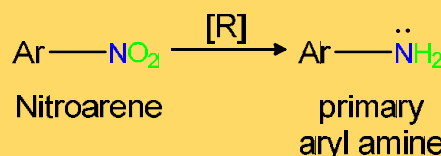
Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by LiAlH_4 , or sodium in ethanol. Catalytic hydrogen with $\text{Rh-Al}_2\text{O}_3$, Pt or Raney nickel may also be employed to get primary amines



Reduction of Nitro Compounds

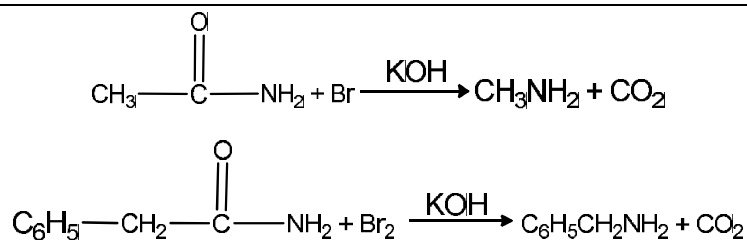
Nitro compounds on catalytic or chemical reduction produce primary amines

- Nitroarenes can be reduced to primary aryl amines.
- Typical reducing agents include, Fe / H^+ , Sn / H^+ or catalytic hydrogenation (e.g. H_2 / Pd)



Reduction of Amides

An amide on treatment with Bromine in the presence of KOH yields primary amines. The reaction occurs through rearrangement.

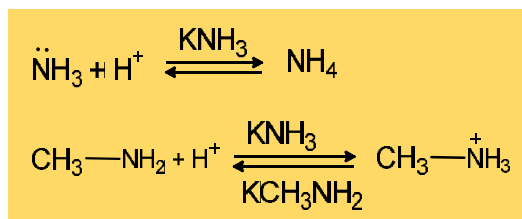


17.3.6 Reactivity:

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 $\text{p}K_b$, i.e., $\text{p}K_b = -\log K_b$

For ammonia and methyl amine, the $\text{p}K_b$ values are $\text{p}K_{\text{NH}_3} = 4.76$; $\text{p}K_{\text{CH}_3\text{NH}_2} = 3.38$



Since $\text{p}K_{\text{NH}_3} < \text{p}K_{\text{CH}_3\text{NH}_2}$ methyl amine is a stronger base than ammonia. It can be explained as under:

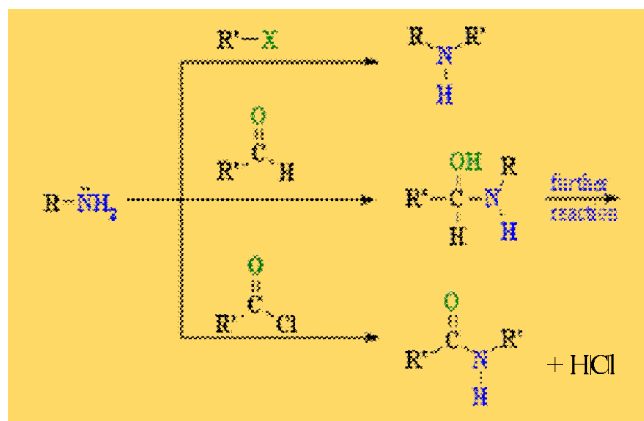
In ammonia, the pair of electron attracted by s-orbitals of hydrogen atoms where as in CH_3NH_2 , sp^3 -orbital of carbon pushes electrons towards nitrogen.

Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia. The methyl ammonium ion, CH_3NH_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 solvation, 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



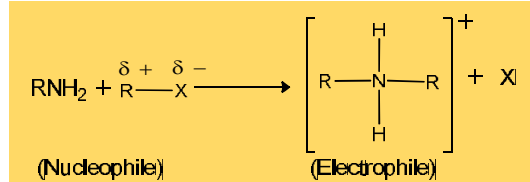
The important organic reactions of amines (nucleophiles) are with the common electrophiles:

- 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,"

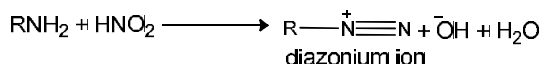
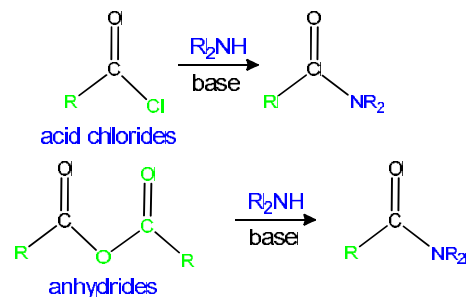
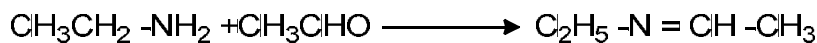
$R_2NH_2^+$ loses a proton with a base to give a free amine.

**Reactions of Primary Amines with Aldehydes and Ketones**

Aldehydes and ketones react with primary amines to form Schiff's base

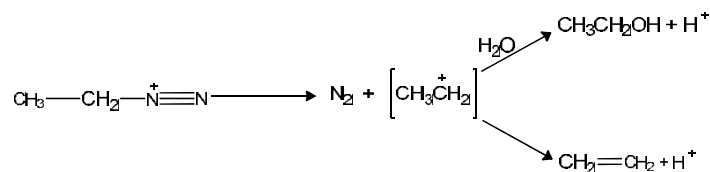
Preparation of Amides**Preparation of Diazonium Salts**

When amines react with nitrous acid, diazonium compounds are formed.



The diazonium group, is rather unstable. In case of ethyldiazonium 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 $10^\circ C$.

**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 chloroquine, is antimalarial drug.
- Vanadocene acetylacetonate has potential in preventing HIV transmission.
- $Ru(\eta^6-C_6H_6)Cl_2(DMSO)$ has been shown to inhibit topoisomerase II, an important target in chemotherapy.

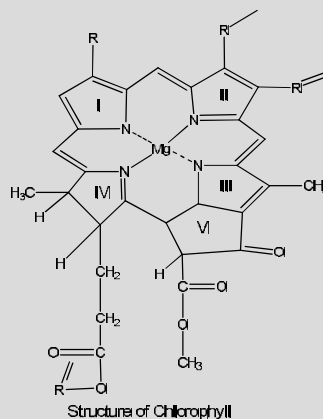
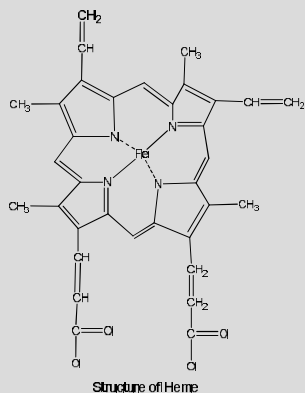
Do You Know?

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.

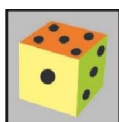
1. Hemoglobin is a porphyrin ring with iron while chlorophyll is a porphyrin ring with magnesium while chlorophyll is a porphyrin ring with magnesium.
2. Hemoglobin is the red pigment in the blood while chlorophyll is the green pigments in green plants, algae, and certain organism.
3. Hemoglobin is involved in oxygen transport while chlorophyll functions as a receptor of light energy during photosynthesis.





Key Points

- ❖ Monohalo derivatives of alkanes are called alkyl halides.
- ❖ The general formula of alkyl halides is $C_nH_{2n+1}X$.
- ❖ 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 a very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of a 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 reactions show first-order kinetics, whereas SN_2 reactions show second-order kinetics.
- ❖ Nucleophilic substitution reactions take place simultaneously with elimination reactions 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 an elimination reaction. Like nucleophilic substitution, β -elimination reactions also take place in two distinct ways: E_2 and E_1 .
- ❖ A nucleophile is an 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 an alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
- ❖ Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centers to give 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.

- 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
- 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. RCI 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 reagent 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 substitution 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?