



'A' LEVEL

CHEMISTRY

ORGANIC AND

OPTIONS

Table of contents

Chapter	Page
<i>CHAPTER 1</i>	6
ORGANIC CHEMISTRY	6
<i>CHAPTER 2</i>	37
Organic Reactions	37
<u>Functional Groups</u>	37
<u>Oxidation and Reduction</u>	43
<i>CHAPTER 3</i>	56
HYDROCARBONS	56
<u>Reactions of alkanes</u>	59
<u>Combustion reactions</u>	59
<u>Addition reactions of ethene</u>	61
<u>Condensation polymerization</u>	67
<i>CHAPTER 4</i>	74
HALOGEN DERIVATIVES	74
<i>CHAPTER 5</i>	86
HYDROXY COMPOUNDS	86
<i>CHAPTER 6</i>	100
CARBONYL COMPOUNDS	100
<i>CHAPTER 7</i>	111

Organo- Nitrogen Compounds.....	111
<i>CHAPTER 8</i>	128
CARBOXYLIC ACIDS.....	128
<i>CHAPTER 9</i>	144
POLYMERISATION.....	144
<i>CHAPTER 10</i>	157
DISTRIBUTION BETWEEN PHASES	157
Learning outcomes.....	157
<u>Solubility</u>	157
<u>Factors affecting solubility</u>	157
<u>Solvent extraction</u>	159
<i>CHAPTER 11</i>	162
PHASE DIAGRAMS.....	162
<i>CHAPTER 12</i>	173
RAOULT'S LAW AND DISTILLATION	173
2.2 Boiling point-Composition diagram for ideal mixtures.....	176
<u>Theoretical plates</u>	177
<u>Negative deviations</u>	178
<u>Azeotrope mixture</u>	179
Examination Type Questions	183
<i>CHAPTER 13</i>	184
SEPARATION TECHNIQUES FOR ANALYSIS: CHROMATOGRAPHY AND ELECTROPHORESIS	184
<u>Chromatographic methods</u>	184

<u>Electrophoresis</u>	188
<i>CHAPTER 14</i>	190
COMPLEXES	190
<i>CHAPTER 15</i>	204
CHEMISTRY OF TRANSITION ELEMENTS	204

Acknowledgements

I would like to express my gratitude to the members of staff and other external individuals who researched on the contents of this book. I am also grateful to my Secretary **Crystabell Mudzingwa** who typed the manuscript.

We have taken every effort to try and get hold of the copyright holders of any information we have reproduced without acknowledgement. We will appreciate the help from anyone to enable us contact the copyright holders whose permission we have not yet obtained.

S. Madzingira

Director

CHAPTER 1

ORGANIC CHEMISTRY

OBJECTIVES

At the end of this chapter you should be able to:-

Interpret and use the nomenclature, general formulae and displayed formulae of the following classes of compounds;

- alkanes, alkenes, arenes.
- halogenoalkanes and halogenoarenes.
- alcohols: primary, secondary and tertiary, phenols.
- aldehydes and ketones.
- carboxylic acids, esters and acyl chlorides.
- amines, nitriles, amides and amino acids.

Introduction

Organic chemistry is largely the study of carbon compounds. Carbon is unique in that it can use $2s^2 2p^2$ electrons to form strong bonds with other carbon atoms to form long chains and rings (catenate). Carbon can form single, double and triple bonds. Originally it was thought that the compounds came from living organisms. However, this belief was abandoned once it was known that there were man-made carbon compounds like plastics. In organic compounds carbon is almost always combined with hydrogen. You will find that in describing organic molecules various types of formulae are used. We will now discuss these formulae

Empirical Formula

This formula shows the simplest ratio in which atoms are combined.

The formula can be worked out from the composition by mass or by percent.

For example ethene contains; 85,7% by mass of carbon 14,3 % by mass of hydrogen.

85,7% is 0,857

14,3% is 0,143

Expressing these in moles carbon = $\frac{0,857}{12}$ moles = 0,071

Hydrogen = $\frac{0,143}{1}$ moles = 0,143

Dividing by the smallest number;

Hydrogen = $\frac{0,143}{0,071}$ = 2

Carbon = $\frac{0,071}{0,071}$ = 1

Thus the empirical formula of ethane is CH_2
Carbon and hydrogen are combined in the ratio of respectively 1:2.

Molecular Formula

This shows the actual number and type of each atom in a molecule. We can find the molecular formula using the empirical formula, but we must know the empirical formula, but we must know the relative molecular mass (M_r). For example using ethene with a relative molecular mass of 28 and an empirical formula of CH_2 we can calculate the molecular formula of ethane. We use the formula, relative molecular mass (M_r) = empirical formula \times multiple (n);

$$\begin{aligned}28 &= (CH_2)n \\ &= (12 + 2)n \\ 28 &= 14n \\ \therefore 2 &= n\end{aligned}$$

Hence the molecular formula of ethane is
 $(CH_2)_2 = C_2H_4$

General formula

As the name suggests, this formulae is a form of short hand used to express the formula of families of compounds. More complex formulae can be built from simple ones by the repeated addition of the same groups of atoms. For example formulae of higher alkanes can be built up from the simplest (CH_4) by addition of CH_2 . Such compounds are said to form a homologous series. The following shows the alkanes.

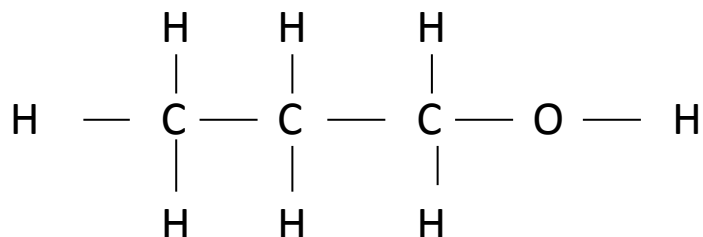
Name	Molecular Formula
<i>Methane</i>	CH_4
<i>Ethane</i>	C_2H_6
<i>Propane</i>	C_3H_8
<i>Butane</i>	C_4H_{10}
<i>Pentane</i>	C_5H_{12}
<i>Hexane</i>	C_6H_{14}
<i>Heptane</i>	C_7H_{16}
<i>Octane</i>	C_8H_{18}

The general formula of alkanes can be expressed as C_nH_{2n+2} where n is the number of carbon atoms. Try to apply this formula to the alkanes listed. We will discuss general formulae of other organic compounds later.

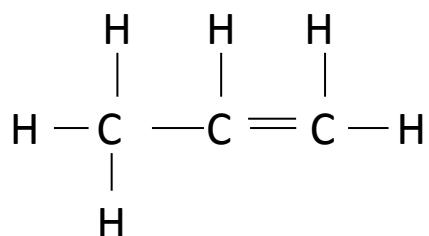
Structural Formula

This formula shows the number type and the way atoms are arranged in a molecule. The types of bonds are also shown. Structural formulae can be shown in various ways. For example propan-1-ol can be shown as $CH_3CH_2CH_2OH$ or as

Displayed formula



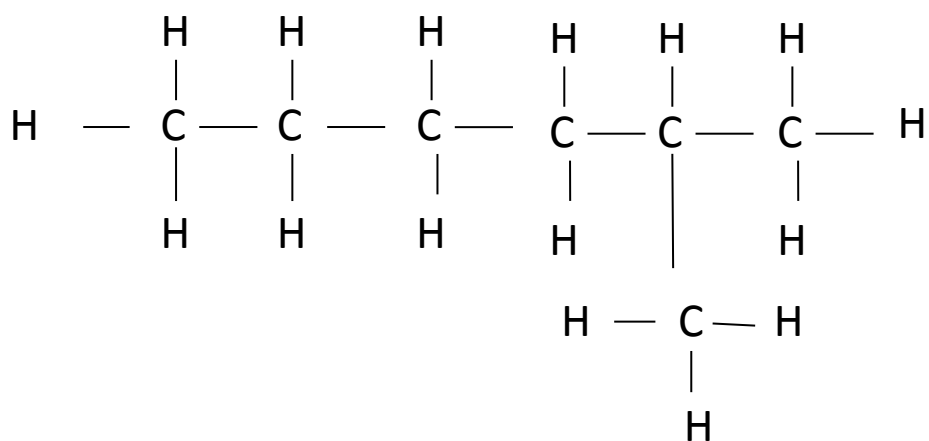
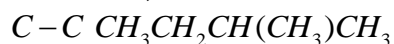
Propene



Displayed Formula

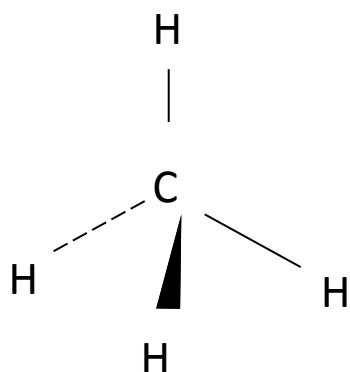
If there are branches in the carbon chains, these are shown in brackets.

For example

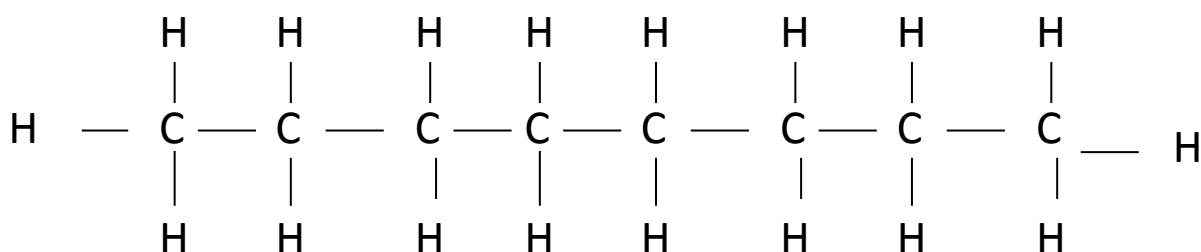


Displayed formula

Structural formula can also be shown in three dimension. For example methane can be show as:



The skeletal form is used to show more complex structures. For example a long molecule like octane

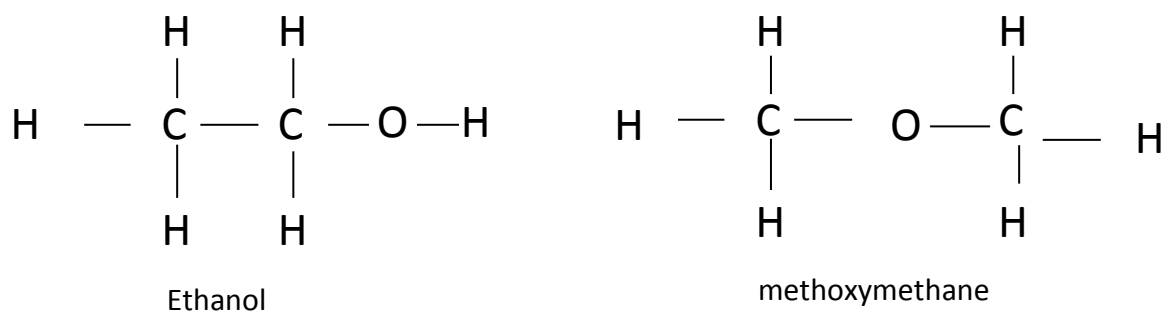


Can be written as



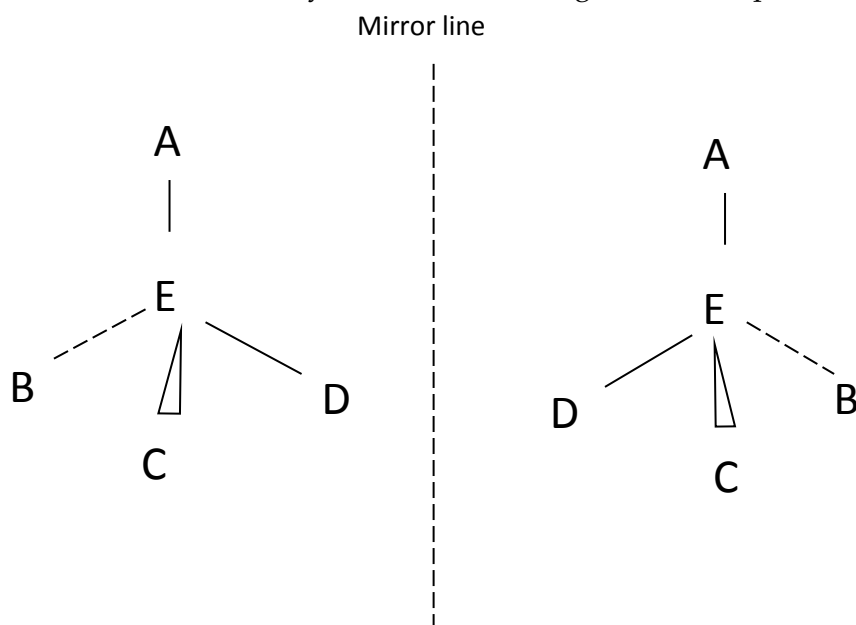
Isomerism

Isomers are molecules with the same molecular formulae but different structural formulae. For example ethanol and methoxymethane have the same molecular formulae C_2H_6O but different structural formulae.



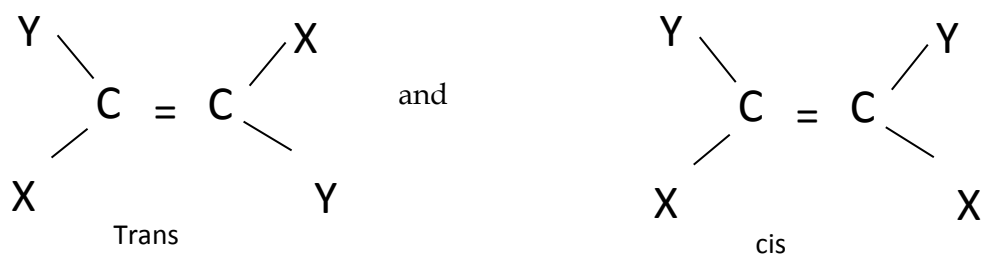
Ethanol and methoxymethane are called structural isomers.

In some cases two isomers may exist as mirror images. For example



Where ABCD represent groups of atoms bonded to the same carbon atom. The above structures represent optical isomers. Such isomers are right and left handed as you can see. They are referred to as chiral for this reason. The carbon atom to which the four different groups are bonded is known as the chiral centre or asymmetrical carbon atom.

Some isomers are produced when four atoms or groups of atoms are bonded to two carbon atoms joined by a double bond. For example,



In the two isomers, rotation about the C=C bond is restricted. These isomers are called cis-trans isomers.

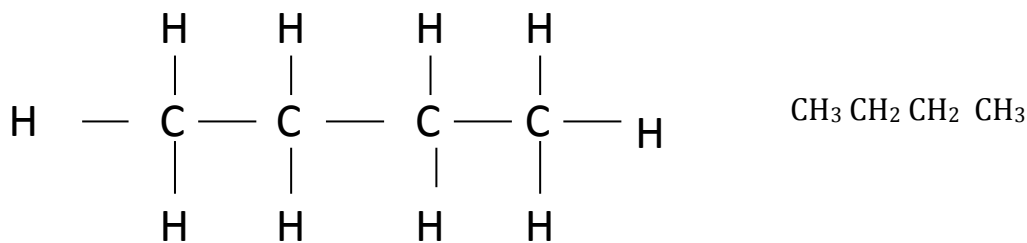
The trans isomer has same type of groups on opposite sides of the C=C double bond.

The cis- isomer has the same type of group on the same side of the C=C double bond.

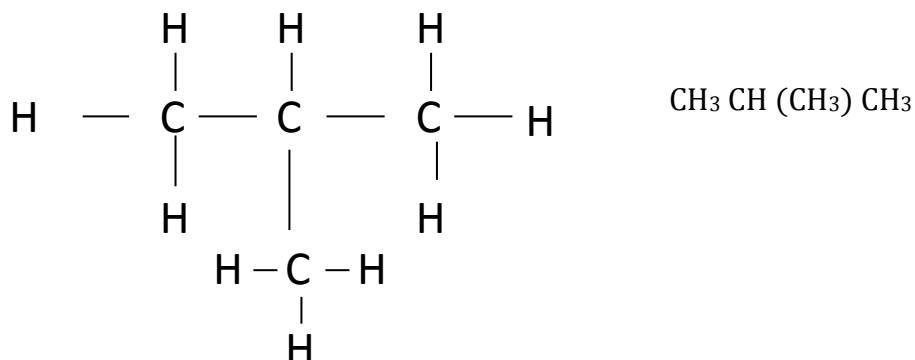
Nomenclature, general formulae and displayed formulae

Alkanes

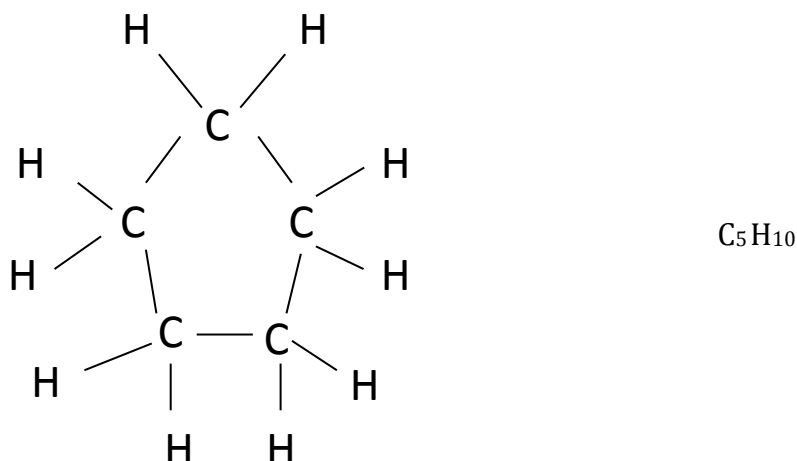
These are hydrocarbons in which there are single C-C bonds and C-H bonds only. Alkanes can be unbranched chains, branched chains and rings. For example butane has an unbranched chain.



Methylpropane has a branched chain



Cyclopentane has a ring structure



Naming alkanes

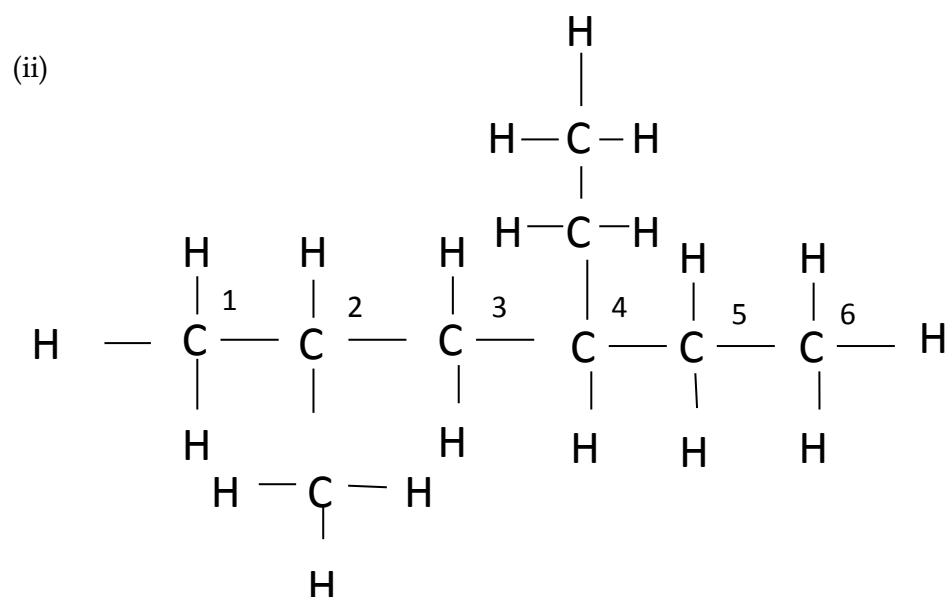
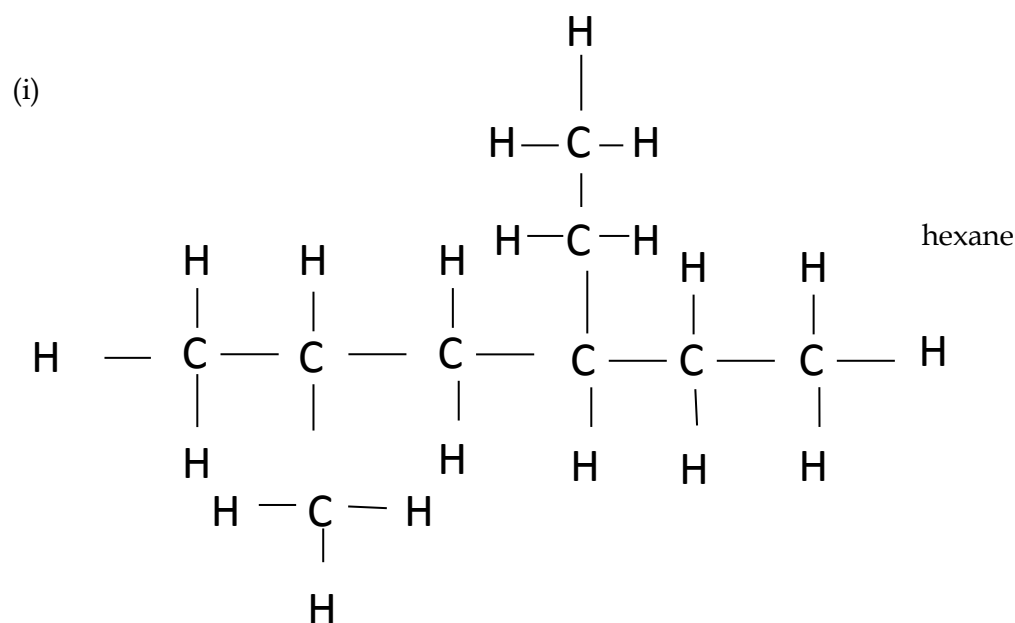
Certain rules should be followed. Make sure you understand the rules so that you can apply them. Naming straight chains is easy.

- a) You identify the root/stem, number of carbon atoms (Meth-eth prop- but, pent-, hex- etc and suffix-ane to give the full name for the alkane.

No. of carbons	Stem	Full name
1	<i>Meth</i> + <i>ane</i> →	<i>Methane</i>
2	<i>eth</i> + <i>ane</i> →	<i>Ethane</i>
3	<i>Prop</i> + <i>ane</i> →	<i>Propane</i>
4	<i>but</i> + <i>ane</i> →	<i>Butane</i>
5	<i>Pent</i> + <i>ane</i> →	<i>Pentane</i>

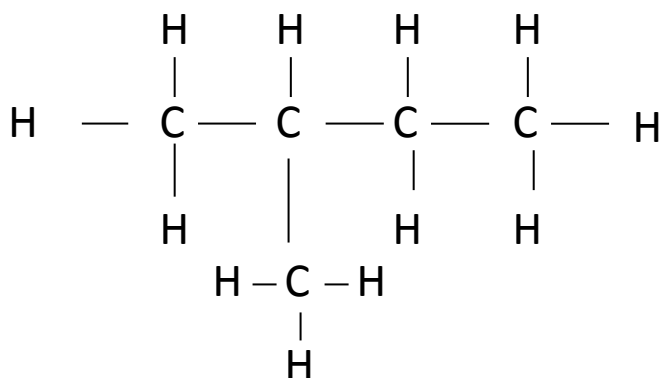
- b) For naming branched chain alkanes you will need to follow the following rules
- i) Identify the parent alkane
 - ii) Number the carbon atoms in the parent alkane
 - iii) Name the branch or substituent using the prefixes, methyl-, ethyl-, propyl-, butyl- depending on the number of carbon atoms.
 - iv) Assign to the substituent the number of the parent carbon atom to which it is attached starting with the smallest
 - v) Arrange the substituents in alphabetical order and name the alkane

Example

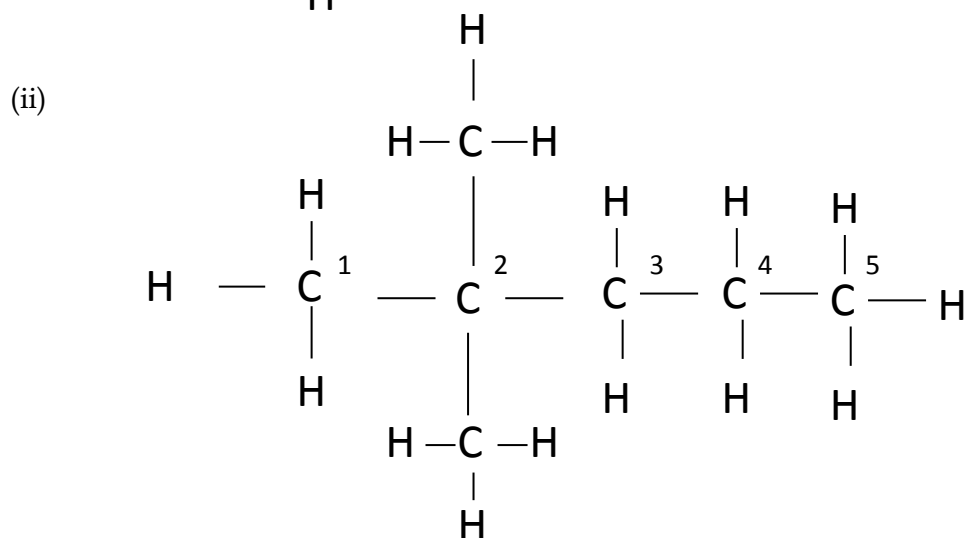
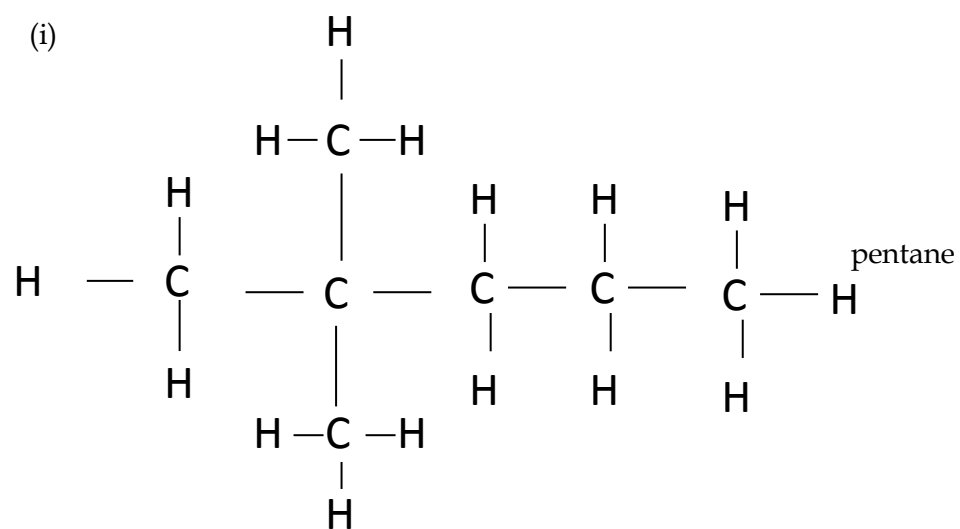


- (iii) Methyl,ethyl-
- (iv) 2-Methyl and 4- ethyl
- (v) 4- ethyl-2- methylhexane

For practice name the following alkane



Sometimes there are two substituent on the same carbon atom. For example.



- (iii) Methyl + Methyl- = dimethyl-
- (iv) 2Methyl + 2 methyl = 2, 2-dimethyl
- (v) Name: 2,2 dimethyl pentane

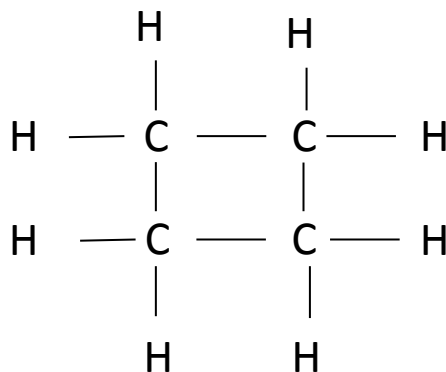
General Formulae of alkanes

The general formula C_nH_{2n+2} applies to all straight and branched alkanes. However, in ring alkanes the formula C_nH_{2n} applies.

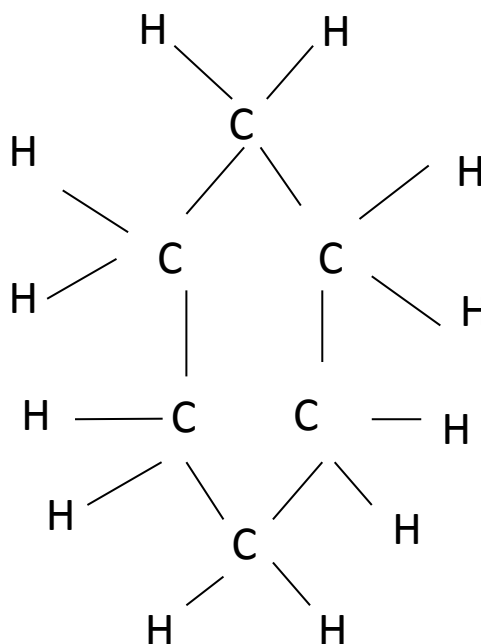
The table shows the molecular formulae, and displayed formulae of straight and branched alkanes based on the general formula C_nH_{2n+2} . You should find the table easy to understand since we have already discussed some aspects of it.

Straight Chain	Formula	Displayed Formula
<i>Methane</i>	CH_4	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array} $
<i>Ethane</i>	CH_3CH_3	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $
<i>Propane</i>	$CH_3CH_2CH_3$	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $

Cyclobutane



Cyclohexane



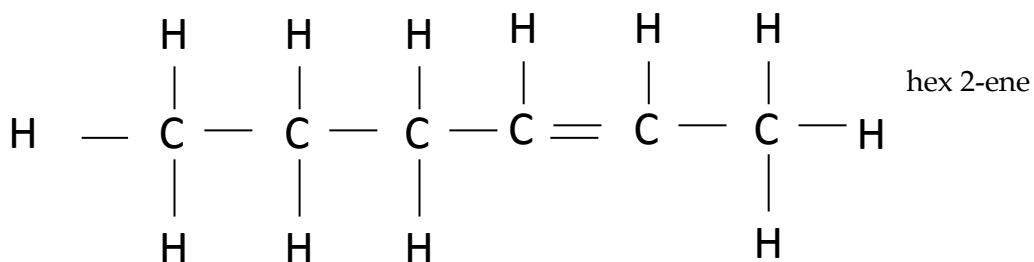
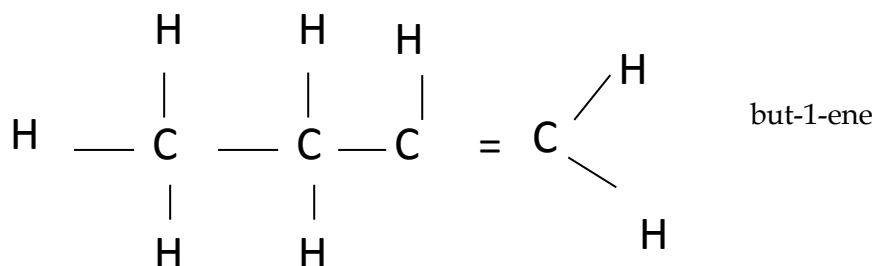
Alkenes

Alkenes are hydrocarbons which contain a, $C=C$, double bond. Their general formula is C_nH_{2n} . You will notice from the formula that they have two less hydrogen atoms than alkanes. For this reason they are said to be unsaturated. Like their alkane counterparts, alkenes can be straight chain, ring or branched chain. For example, ethene and propene are straight chain.

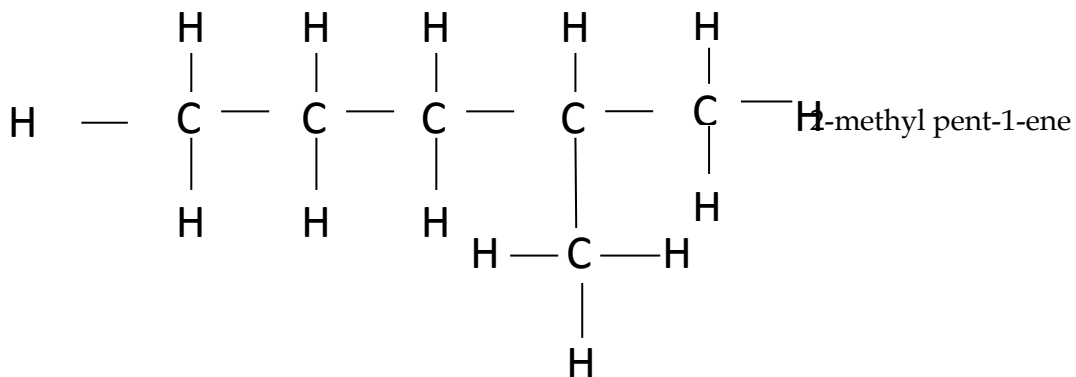
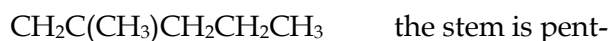
Naming Alkenes

Like in the case of alkanes there are rules to be followed. Refer back to alkanes for these rules. Here the suffix -ene is used instead of -ane for alkanes. You should have noticed this in the introduction to alkenes. Try to follow these examples;

Straight chain

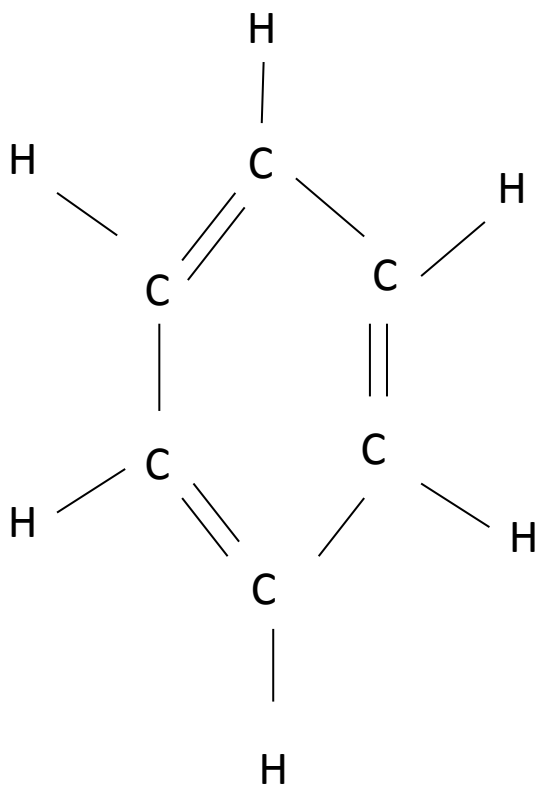


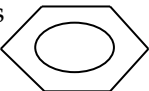
Branched chain



Arenes

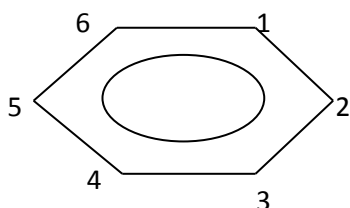
This is another class of unsaturated hydrocarbons based on the molecule of benzene, C_6H_6 . They are also known as aromatic hydrocarbons. The benzene molecule is a ring structure with three pseudo-double bonds.



The π electrons forming the double bonds are delocalized above and below the molecule in the form of rings. This structure is shown as  is also known as the benzene ring.

Naming Arenes

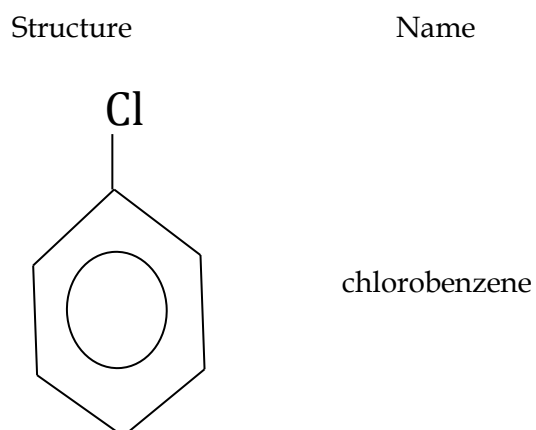
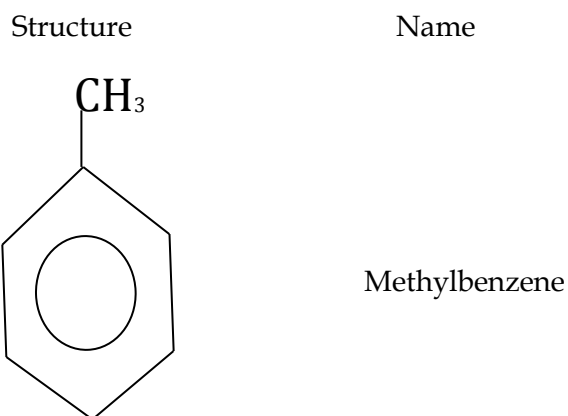
Compounds containing a benzene molecule are called arenes and their names are based on the benzene molecule. Hydrogen atoms on the benzene ring can be replaced by other atoms or groups of atoms. This replacement is called a substitution. As in alkanes and alkenes the carbon atoms in the ring are assigned numbers one to six.

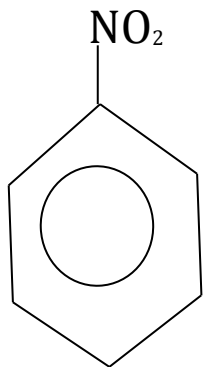


In the naming of the compounds these numbers are used to indicate the carbon atoms where the hydrogen atoms have been substituted. The following are some substituting groups.

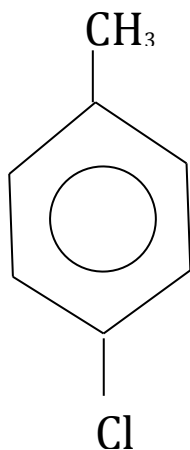
Group	Name
$-CH_3$	<i>Methyl</i> –
$-NO_2$	<i>Nitro</i> –
$-Cl$	<i>Chloro</i> –
$-OH$	<i>Hydroxy</i> –
$-NH_2$	<i>Amino</i>
$-CO_2^-$	<i>Carboxyl</i>

Structure of arenes





Nitrobenzene



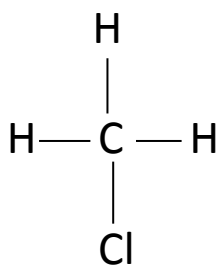
Methyl- 4-chlorobenzene

Halogenoalkanes

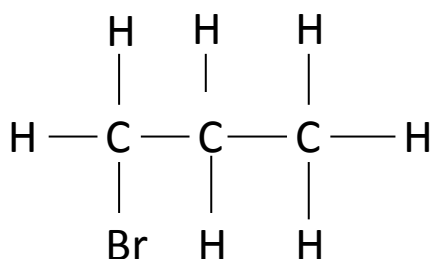
In these compounds some of the hydrogen atoms in alkanes have been substituted by halogens *F, Cl, Br, I*. The prefixes used are:

<i>F</i>	<i>Fluoro</i> –
<i>Cl</i>	<i>chloro</i> –
<i>Br</i>	<i>Bromo</i>
<i>I</i>	<i>iodo</i> –

These prefixes follow the name of the parent alkane. The rules used in naming branched alkanes apply.

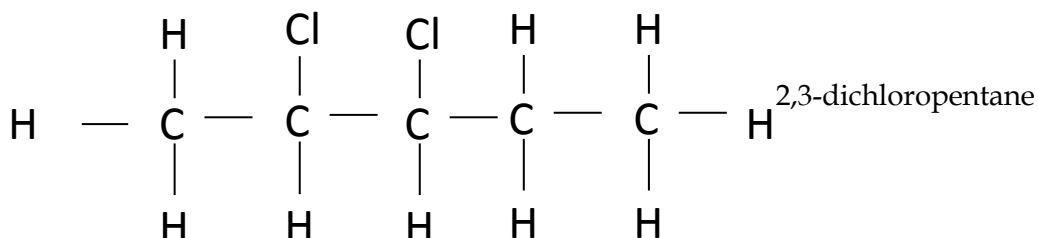
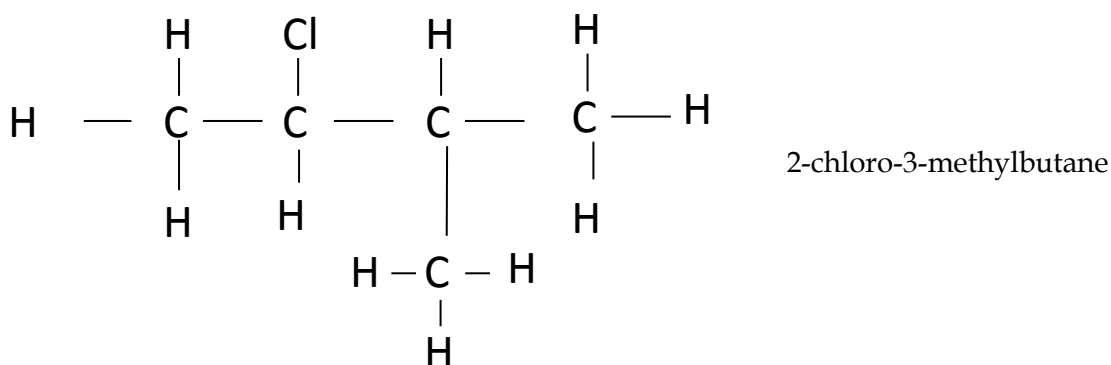
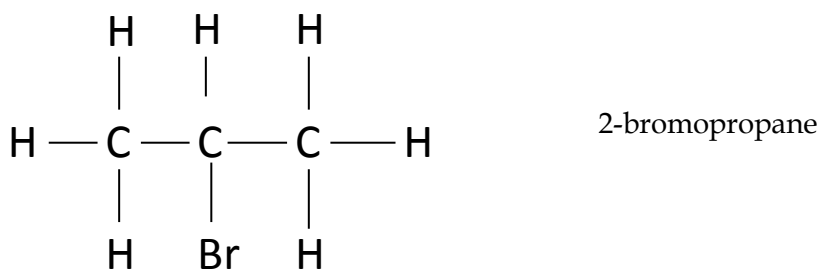


Chloromethane



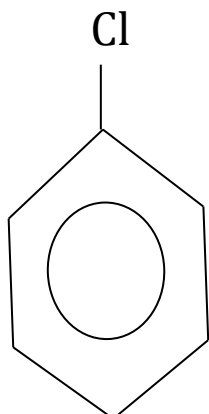
1-bromopropane

The position of the substituent in the chain is identified by the number on the carbon atom.

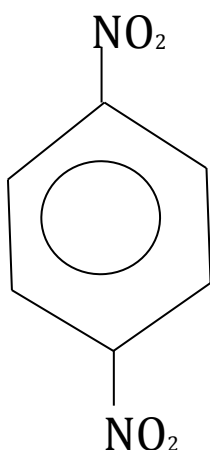


Halogenoarenes

The hydrogen atoms on the benzene ring are substituted by the halogens, the positions of substituents' being identified by numbers on the ring carbon atoms. The prefixes fluoro-chloro-bromo, iodo- are used.



Chlorobenzene

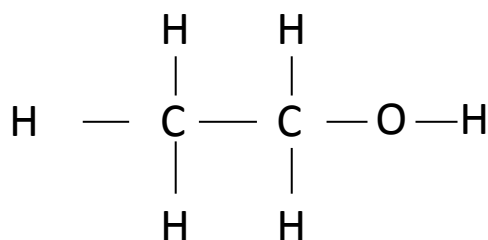


1,4-dinitrobenzene

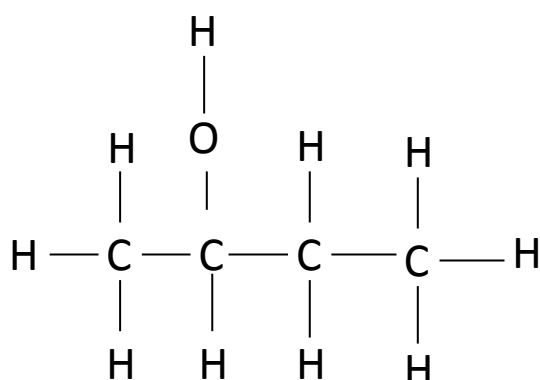
Alcohols

These are compounds which contain the hydroxyl group. In naming alcohols the suffix *-ol* is used preceded by the stem of the parent alkane. Alcohols can be straight chain or branched chain.

Straight Chain



ethanol

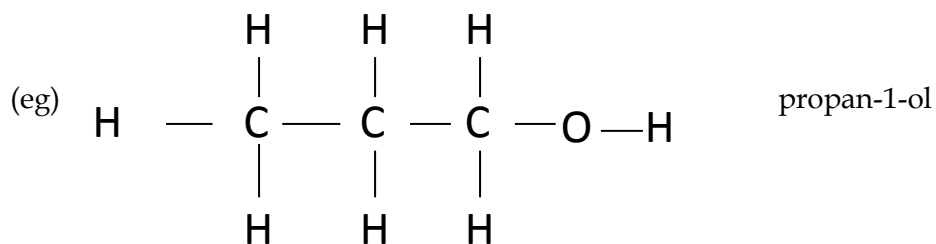


butan -2-ol

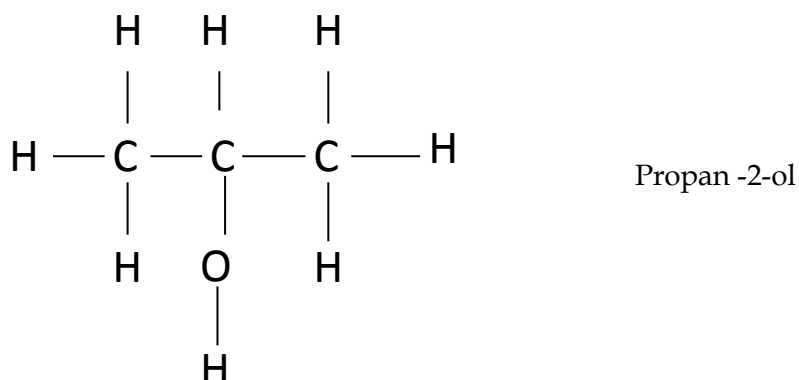
Classification

Alcohols are classified as primary (1°) secondary (2°) and tertiary (3°)

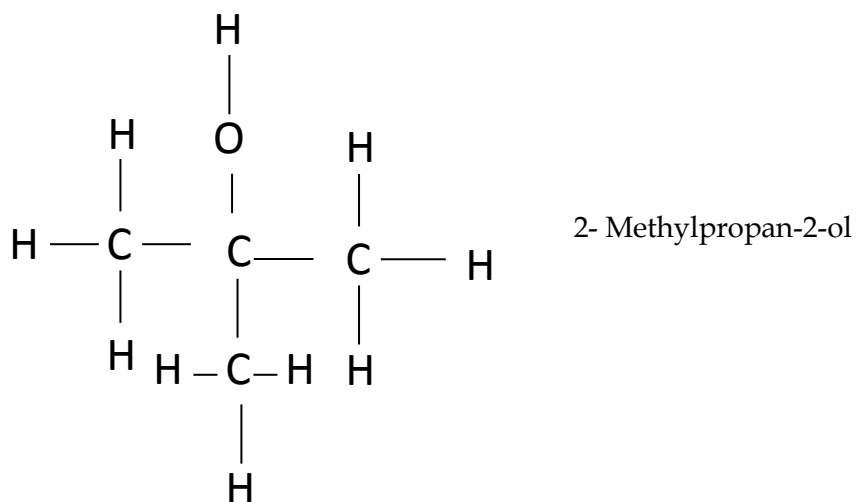
In a primary alcohol (1°) the carbon atom bonded to the $-\text{OH}$ group is bonded directly to one other carbon atom.



In a secondary alcohol (2°) carbon atom bonded to -OH group is bonded directly two other carbon atoms.



In a tertiary alcohol (3°) carbon atom bonded to -OH group is directly bonded to three other carbon atoms.



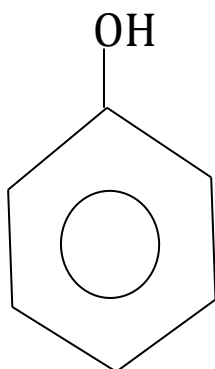
General formula

In alcohols one of the hydrogens on alkane molecule has been replaced by the -OH group.

The general formula becomes $C_nH_{2n+1}OH$

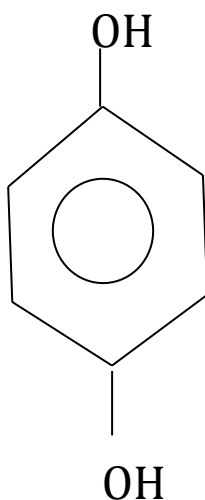
Phenols

In this group of compounds the OH group is attached directly to the benzene ring.



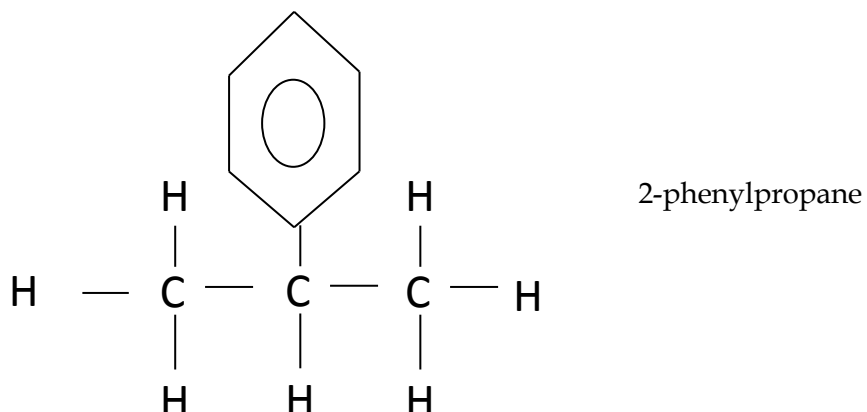
Phenol

When two -OH groups are attached to the ring the suffix -diol is used, but when there is only one OH on the ring the name phenol is retained.



Benzene 1, 4- diol

When the benzene ring is a substituent the prefix phenyl is used.

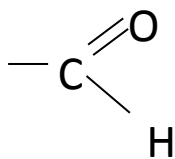


2-phenylpropane

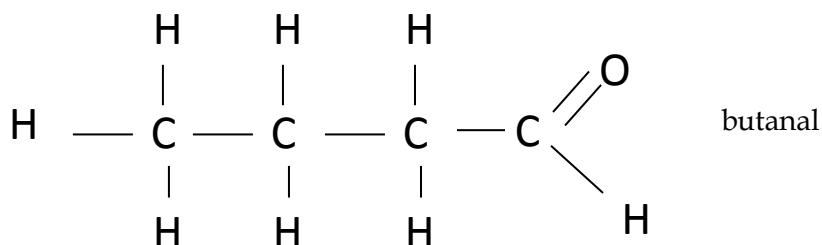
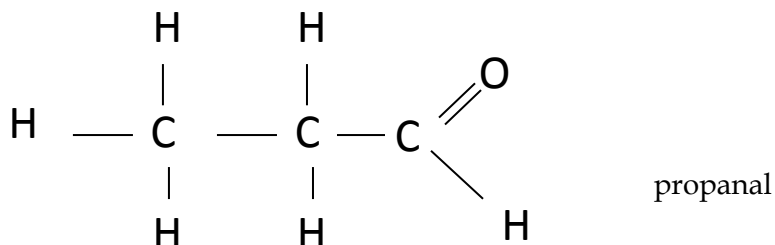
Aldehydes and ketones

Aldehydes

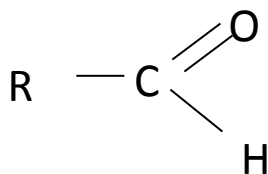
These compounds contain the carbonyl group at the end of the chain.



In Aldehydes the suffix-al is used after the stem of the parent alkane, the carbon in $-\text{CO}(\text{H})$ being counted as part of the chain.



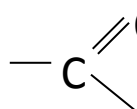
The general formula of aldehydes is



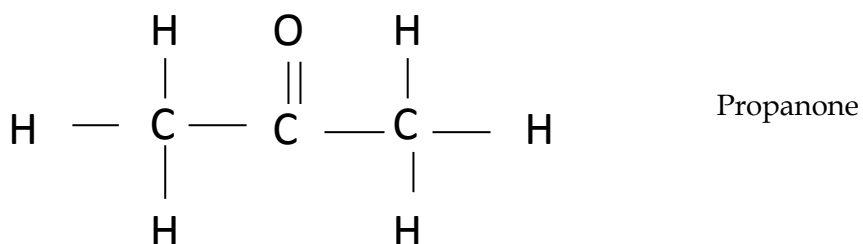
where R is the alkyl chain or aryl group or hydrogen.

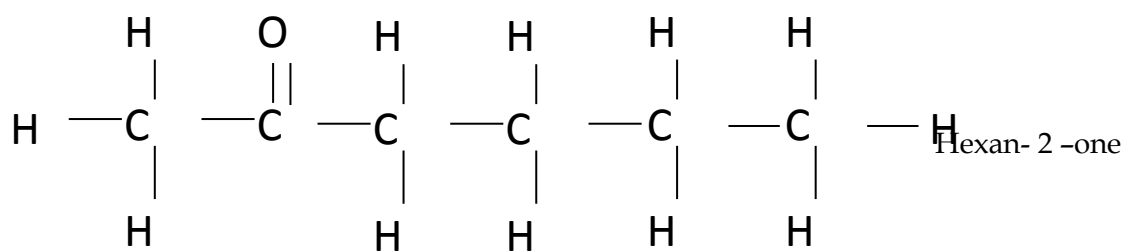
Ketones

In Ketones the $\text{C}=\text{O}$ is inside the chain rather than at the end. The suffix- one is

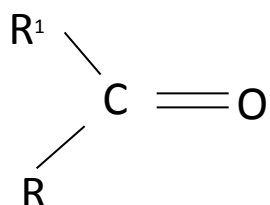


placed after the stem of the parent alkane.





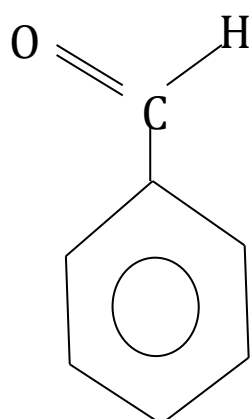
The general formula of Ketones is



(Where R¹ and R are alkyl or aryl or hydrogen)

Aromatic aldehydes and Ketones

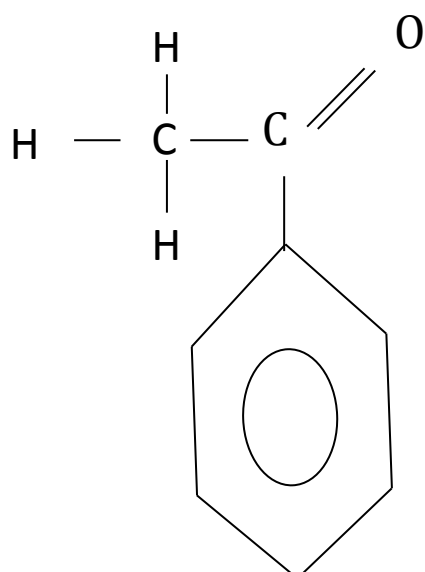
Here the carbonyl group is attached to the benzene ring .



Benzaldehyde

Ketone.

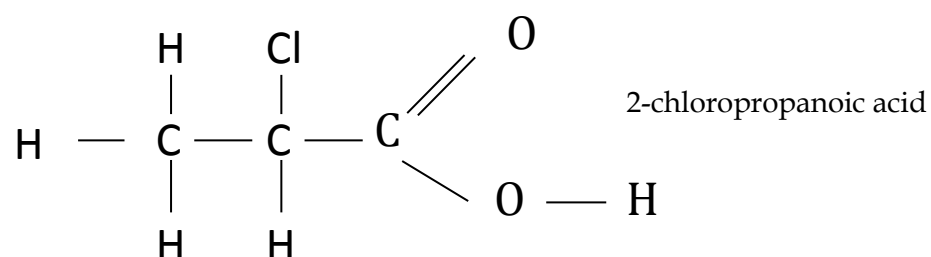
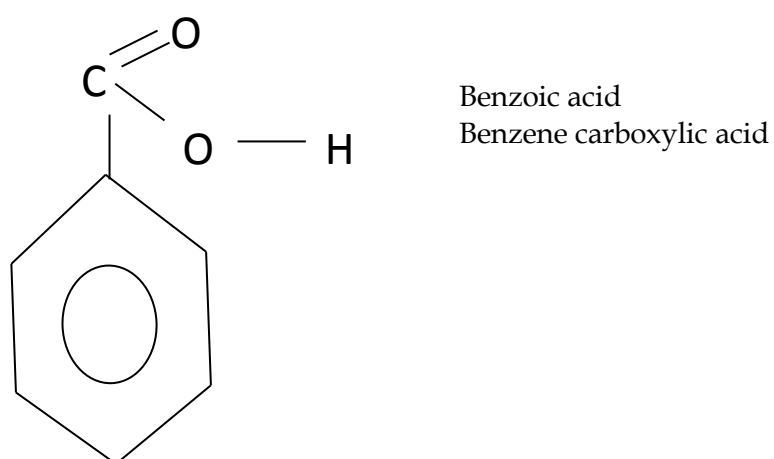
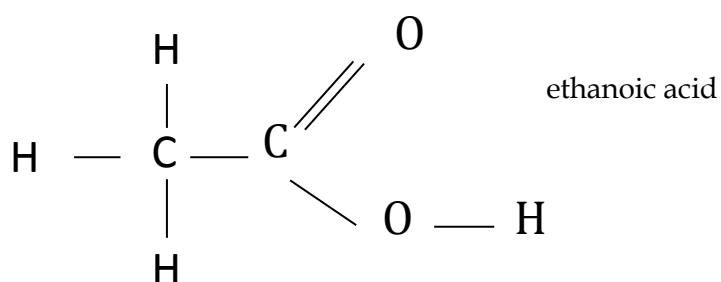
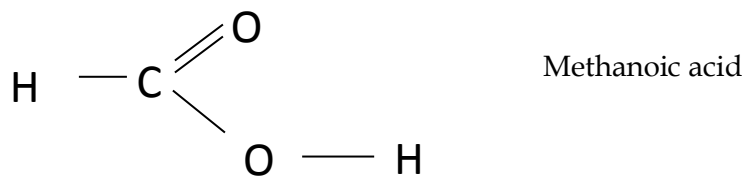
The carbonyl group is attached to the benzene ring.



Phenyl ethanone

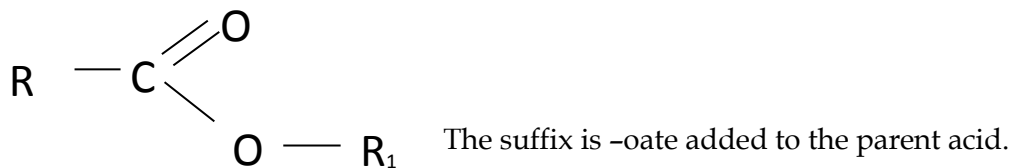
Carboxylic acids

These contain the carboxyl group -COOH and their general formula is R COOH where R can either be an alkyl group, hydrogen as an aryl group. The suffix -oic acid after the stem of the parent alkane. The carbon atom on the carboxyl group is included.



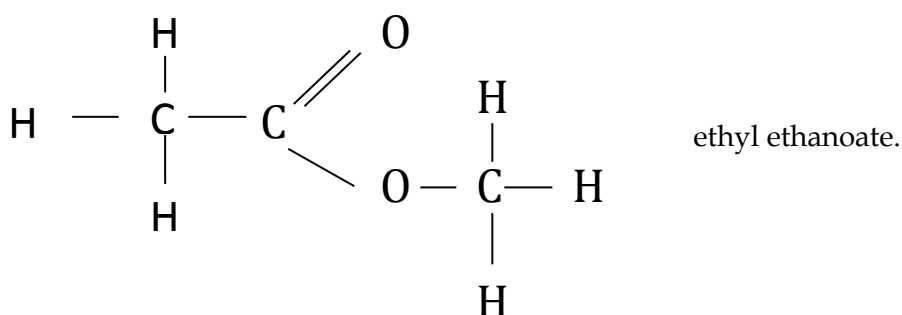
Esters

Esters are formed when carboxylic acids react with alcohols. They have the general formula



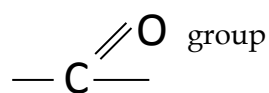
Parent acid ethanoic R₁ methyl group.

Name: methyl ethanoate

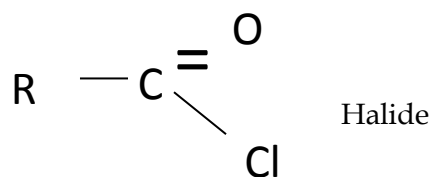


Acyl chlorides

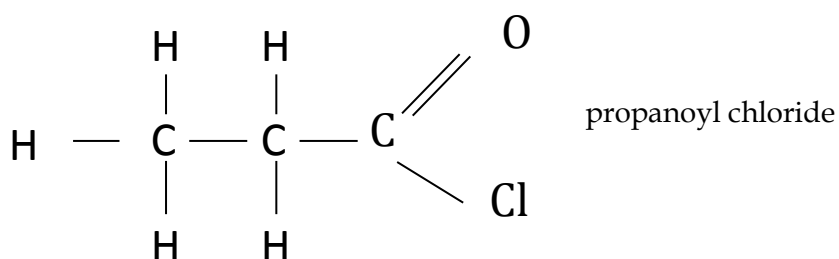
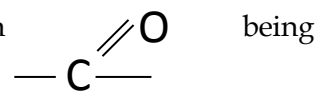
In these compounds the chlorine atom is attached to the



The general formula of acyl halides is

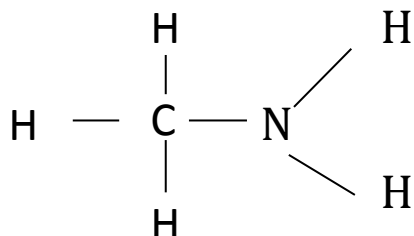


The suffix is oyl after the stem of the parent group. The carbon on

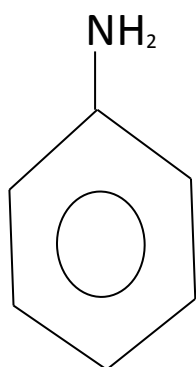


Primary amines

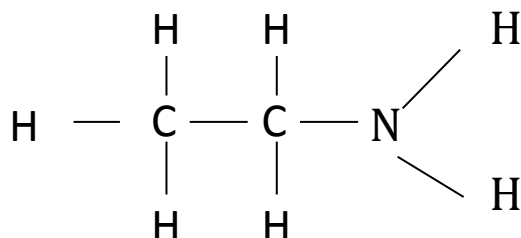
These compounds have the general formula $R-NH_2$ where R can be an alkyl or aryl group. The suffix is amine to the parent stem:



methylamine

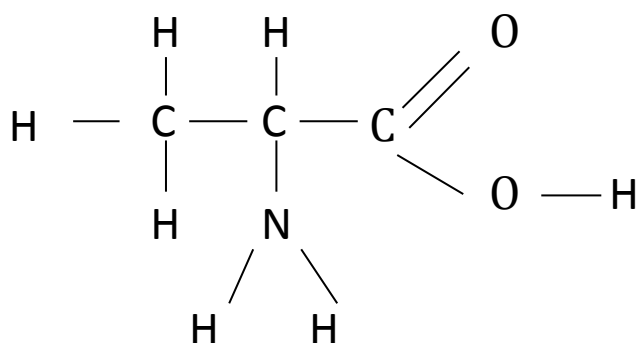


Phenylamine



Ethylamine

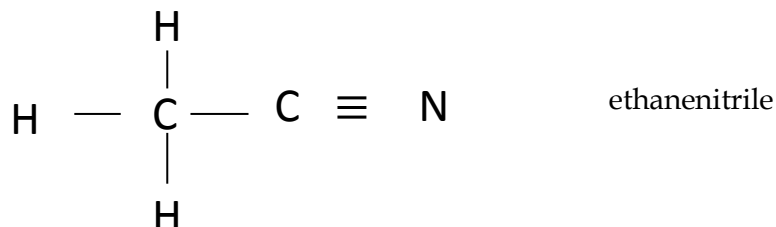
If the amine is a substituent the prefix amino is used.



2- Aminopropanoic acid

Nitriles

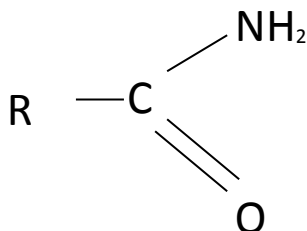
These are cyano compounds containing the group $-C \equiv N$. The suffix -nitrile is added to the parent stem. The carbon in $-C \equiv N$ is included in the stem.



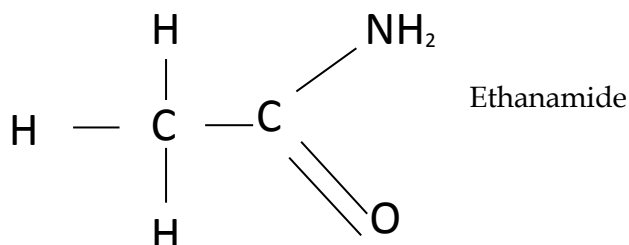
The general formula is $R-C \equiv N$

Amides

These have the general structure

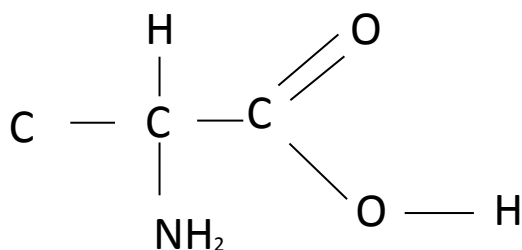


The suffix -amide is attached to the stem of the parent molecule. Thus if in the above general formula R is replaced with CH_3 The molecule becomes;

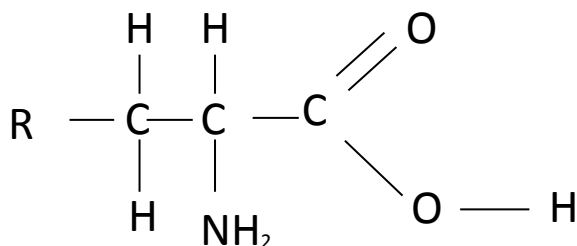


Amino acids

The molecules contain the $-NH_2$ groups and the $-C_{OH}^O$ group. Their general Formula is



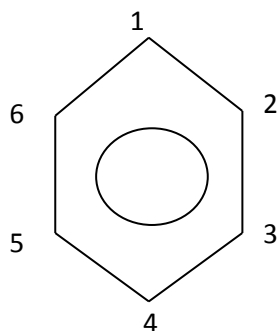
If R is replaced with CH_3 the molecule becomes.



2-amino-propanoic acid.

Summary

- a) The empirical formula shows the simplest ratio in which atoms in a compound are combined.
- b) The general formula of alkanes is C_nH_{2n} . Alkanes form a homologous series
- c) Isomers are molecules with the same molecular formula but different structural formulae.
- d) In naming alkanes the following are taken into account:
 - (i) Parent alkane.
 - (ii) Number of carbon atoms in the alkane.
 - (iii) Substituents are identified with prefixes methyl- ethyl- etc.
 - (iv) Substituents are arranged in alphabetic order.
- e) i) Alkenes carry a double bond, $C=C$.
 ii) Their general formula is C_nH_{2n}
 iii) They are unsaturated hydrocarbons..
 iv) The suffix -ene is used in their names. Arenes are based on the benzene ring;



f) Substituent occupy carbon atom 1-6

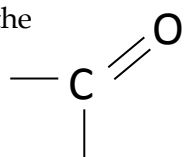
g) Alcohols contain the -OH group. Their general formula is $C_nH_{2n+1}OH$

h) Arenes which carry an -OH group bonded directly to the benzene ring are called phenols.

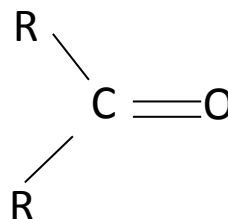
i) Aldehydes contain the carbonyl group $-C_H^O$. Their general formula is

$$\begin{array}{ccc}
 & & \text{O} \\
 & & // \\
 \text{R} & - & \text{C} \\
 & & \backslash \\
 & & \text{O} - \text{H}
 \end{array}$$

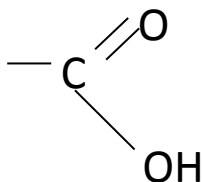
j) Ketones contain the



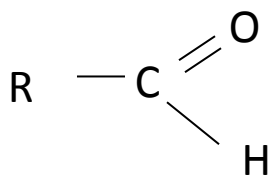
group. Their general formula is



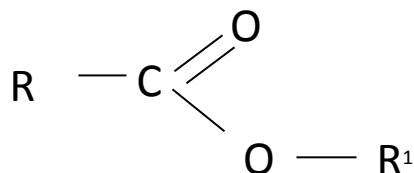
k) Carboxylic acids contain the group



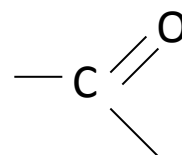
Their general formula is



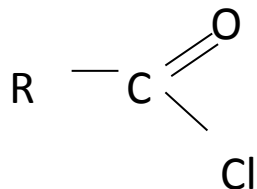
l) Esters have a general formula of



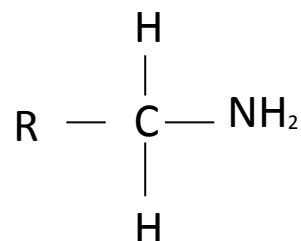
m) In acyl chlorides the chlorine atom is bonded to the group



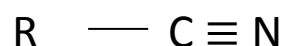
The formula is



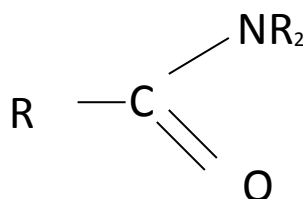
n) Primary amines contain the --- NH_2 group. They have a general formula of



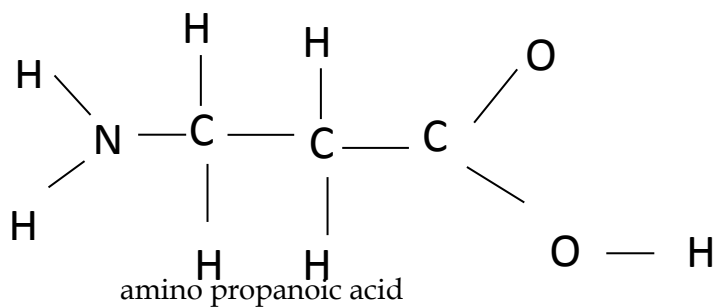
o) Nitriles contain the $\text{--- C} \equiv \text{N}$ group. The general formula is .



p) Amides have a general formula



q) Amino acids contain the — NH_2 group and the — COOH group.



Questions

1. Give the (i) displayed formula and (ii) names of the following compounds:

- i. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
- ii. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
- iii. CH_3OCH_3
- iv. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- v. $\text{CH}_3\text{CH}_2\text{COOH}$
- vi. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})\text{CH}_3$
- vii. $\text{C}_6\text{H}_5\text{Br}$
- viii. $\text{C}_6\text{H}_5\text{OH}$
- ix. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
- x. $\text{CH}_3\text{CH}_2\text{COOCH}_3$

REFERENCES

1. Mc Murray J.
Organic Chemistry
Cornell University USA
ISBN-0534-01204-3
2. Hill GC and Holman JS; Chemistry in Context
Nelson and Sons
Surrey UK
3rd Edition
3. Lister T and Renshaw J
Understanding Chemistry
Stanley Thornes (Publishers) Ltd
Cheltenham England
1994 Edition

CHAPTER 2

Organic Reactions

By the end of this chapter you should be able to:

- a) interpret and use the following terminology associated with organic reactions.
 - (i) functional group.
 - (ii) homolytic and heterolytic fission.
 - (iii) free radical, initiation, propagation and termination.
 - (iv) nucleophile and electrophile.
 - (v) oxidation and reduction.
- bi) describe the shapes of the ethene, ethane and benzene molecules.
- ii) predict the shapes of other related molecules.
- c) explain the shapes of the ethane, ethene and benzene molecules in terms of carbon-carbon bonds.
- d) describe cis-trans isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of C=C bonds.
- f) explain what is meant by a chiral centre and that such a centre gives rise to optical isomerism.
- h) deduce possible isomers for organic molecules by known molecular formulae.
- i) identify chiral centres and/or cis-trans isomerism in a molecule of a given structural formula.

Introduction

In this chapter we will focus on types of reaction that take place in organic compounds. These reactions form the basis of synthesis of most organic compounds that we use in everyday life. It is therefore important that you understand the principles underlying these reactions. You will also meet these reactions when you study selected classes of organic compounds. The reactions will include the following;

- functional groups
- free radicals
- homolytic and heterolytic fission
- nucleophiles and electrophiles
- addition, substitution, elimination and hydrolysis
- oxidation and reduction.

Functional Groups

Before we examine organic reactions in detail, it is important to note that the whole molecule does not always take part in a reaction. It is only part of the molecule which is involved. This reaction part of the molecule is known as a functional group. A functional group

behaves the same way despite the size of the molecule to which it is attached. Groups of compounds containing the same functional are known as a homologous series. Remember we met the term homologous when we discussed alkanes. The table shows some functional groups.

Functional Group	Homologous Series	Name and Formula
-OH	alcohols	ethanol CH_3CH_2OH
— NH ₂	amines	ethylamine $CH_3CH_2NH_2$
— COOH	carboxylic acid	propanoic acid $CH_3CH_2CO_2H$
C = C	alkene	ethene $H_2C = CH_2$
-Hal	organohalogens	chloromethane CH_3Cl
$\begin{array}{c} O \\ \\ -C - O - \end{array}$	esters	methyl ethanoate CH_3COCH_3
$\begin{array}{c} O \\ // \\ -C \\ \backslash \\ H \end{array}$	aldehydes	propanal CH_3CH_2COH
$\begin{array}{c} O \\ \\ -C - \end{array}$	Ketones	Propanone CH_3COCH_3

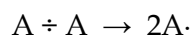
Homolytic and Heterolytic Fission

Use of Curly arrows

As you are aware, bonds are broken and new ones made during a chemical reaction. This involves rearrangement of electrons. Curly arrows are often used to show this movement of electrons. The tail of the arrow represents the source of the electron pair and the head of the arrow represents the new position of the electrons. Movement of single electrons is represented by half curly arrows

Homolytic Fission

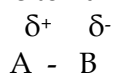
This is the breaking of a covalent bond in which the bond electron pair is shared equally. This is because the bond electrons are attracted equally. For example in a molecule represented by $A\dot{}A$ (where A is an atom and the dots indicate the shared bond pair) each atom carries away one bond electron.



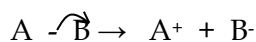
The atom $A\cdot$ or molecule carrying an unshared electron is called a free radical. Free radicals are very reactive and can start a series of chain reactions. We will discuss these reactions later.

Heterolytic Fission

This is the bond fission in which one of the atoms or groups of atoms carries away both bond electrons. This leaves the other atom or group deficient of electrons. For example in a molecule represented by $A\delta^+ - B\delta^-$ where B is more electronegative than A the bond pair is more towards B. This gives B a slight negative charge and A a slight positive charge.



When the bond breaks B carries both bond electrons as shown.



Chain Reaction

In the presence of light, hydrogen and chlorine react very fast to give hydrogen chloride. The reaction starts with the homolytic fission of the chlorine molecule.



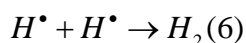
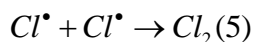
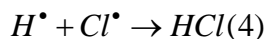
The free radical $Cl\cdot$ then attacks the hydrogen molecule releasing a hydrogen free radical



The H· can in turn attack another chlorine molecule.



Two possibilities can arise here. Either the Cl· reacts with another Cl· or H· to form neutral molecules.



The reactions (1) to (6) constitute a chain reaction. Reaction (1) is called a chain initiation reaction. Reaction (2) and (3) where more free radicals are generated to continue the reaction are called chain propagation reactions. Reactions (4), (5) and (6) where free radicals react without producing some more are called chain termination reactions.

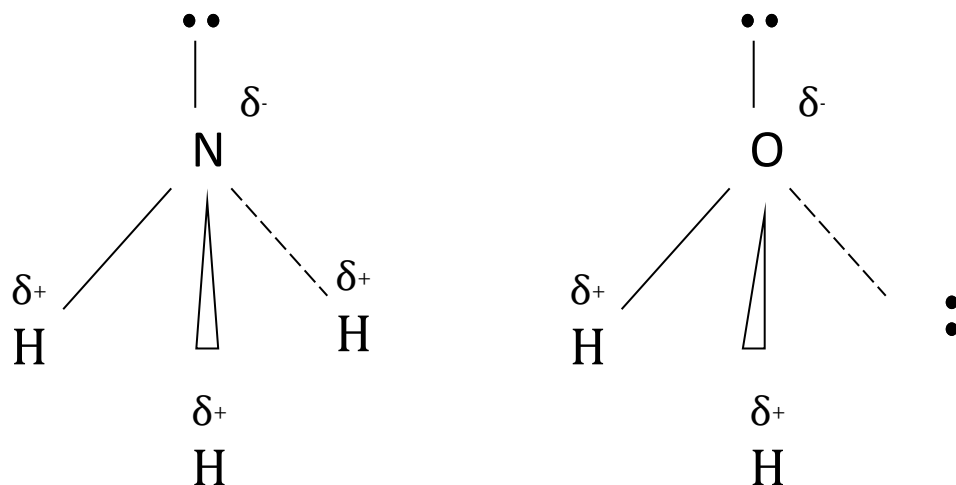
Nucleophiles

These are molecules or ions which carry lone electrons or negative charges.

Examples are:

NH ₃	OH ⁻	Cl ⁻	H ₂ O
ammonia	hydroxyl ion	chloride ion	water molecule

One atom in a molecule may be more electronegative than other atoms. This atom will tend to attract bond electrons leaving the rest of the atoms electron deficient. In ammonia and water molecules the charge distribution is shown.



Nucleophiles can combine with other electron deficient groups by forming a dative bond using the lone pair of electrons. Generally nucleophiles are represented by :Nu or Nu (where Nu is a short for nucleophile). You will learn more about reactions involving nucleophiles later.

Electrophiles

These are molecules or ions that are electron deficient. Hence they carry a positive charge or are polar. They react by attacking molecules that are electron rich. Some of the common electrophiles are H^+ , NO^+ . Generally, electrophiles are represented by E^+ or E (where E is a short for electrophile). Electrophiles as indicated above are electron deficient and therefore they will be expected to receive electrons from nucleophiles to form bonds during chemical reactions.

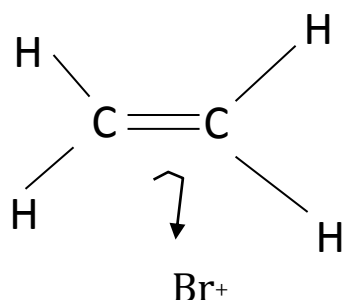
Reactions involving electrophiles are important and so you will need to know the above information in order to understand the reactions in which electrophiles take part.

Addition Reactions: Nucleophilic/Electrophilic

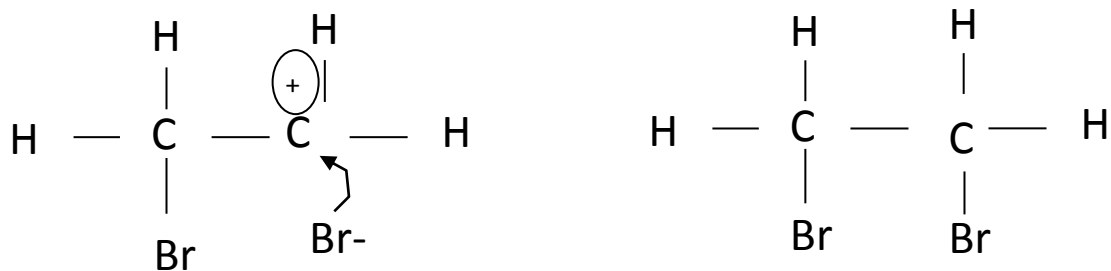
As the name suggests, molecules combine to form larger ones due to the involvement of nucleophiles. These are also called nucleophilic addition reactions. An example of this type of reaction is the addition of a bromine molecule to ethene.

The reaction starts with the heterolytic fission of a Br – Br bond to form a bromonium ion.

Notice that the ion Br^+ is an electrophile. In the presence of ethene, the ion receives an electron pair from the double bond to form a dative bond.



One of the carbon atoms becomes electron deficient and therefore acquires a positive charge. This ion is also called a carbocation. The carbocation is then attacked by the nucleophile: Br^-

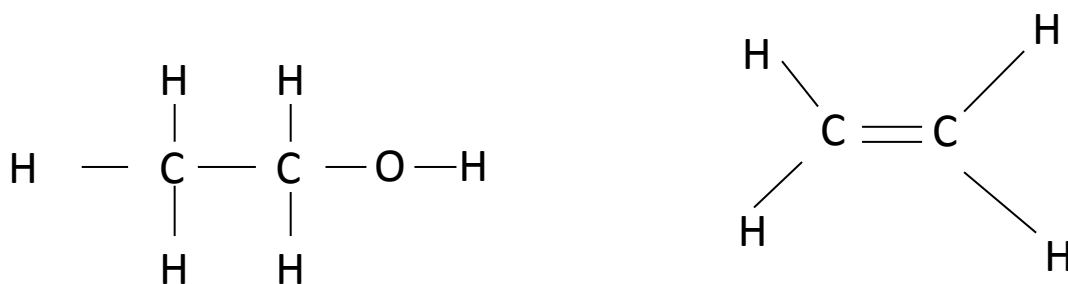


The new addition compound formed is 1,2-dibromo ethane.

Do you realize that the reaction involved the addition of an electrophile (Br^+) and a nucleophile ($:\text{Br}^-$) to the ethene molecule? The reaction above is however called an electrophilic addition one because initially, the Br^+ electrophile attacked the electron-rich double bond to initiate it.

Elimination Reaction

This is the type of reaction in which a smaller molecule is removed from a larger one. For example when ethanol is heated with concentrated sulphuric acid, a water molecule is removed from the ethanol molecule to form ethene.

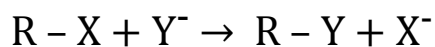


Ethanol

ethene

Substitution Reaction

In this reaction one group, the leaving group is replaced by another incoming group in a molecule.

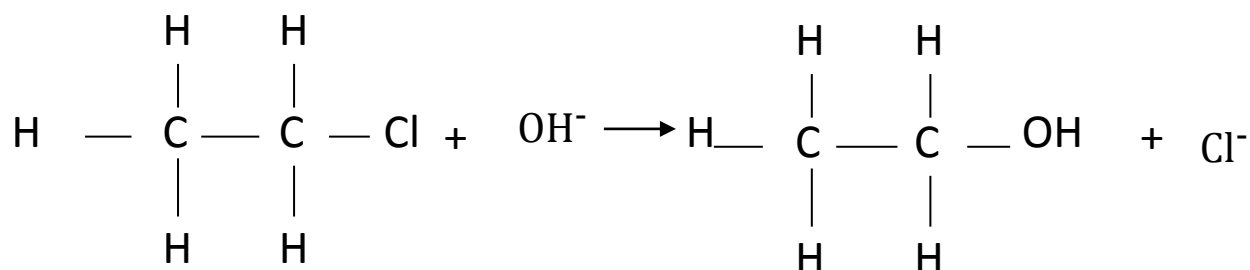


For example in a generalized reaction

Incoming	leaving
Group	group

Notice that the incoming group is a nucleophile

Another example;

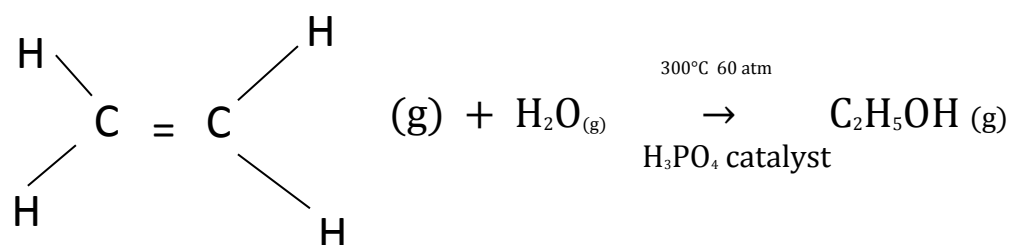


In this reaction the Cl⁻ has been substituted by the :OH⁻ group since the incoming group OH⁻ is a nucleophile the reaction is also called a nucleophilic substitution reaction.

Hydrolysis Reaction

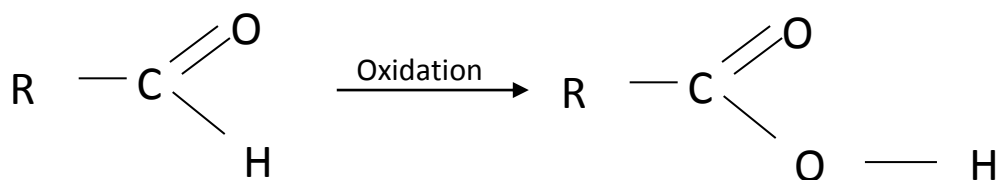
As the name suggests this involves addition of a water molecule to another molecule which carries a double bond.

For example



Oxidation and Reduction

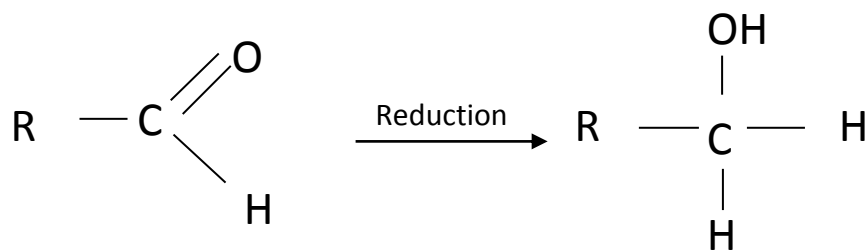
Oxidation is the addition of oxygen to a molecule or atom. For example an aldehyde can be oxidized to a carboxylic acid.



Aldehyde

carboxylic acid

On the other hand reduction is the addition of hydrogen to a molecule. For example an aldehyde can be reduced to an alcohol by addition of hydrogen.



Aldehyde

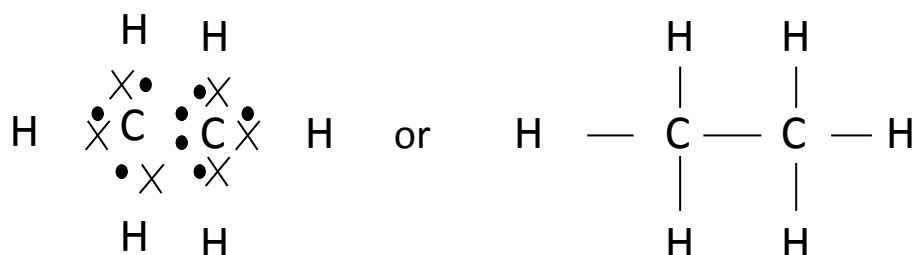
alcohol

Shapes of molecules

Ethane, CH₃CH₃

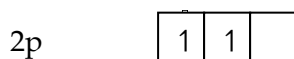
Before we consider the structure of a molecule of ethane we will discuss bonding between carbon atoms.

We will start with the electronic structure of a carbon as $1s^2 2s^2 2p^2$. Simply the four electrons in the 2s and 2p sublevels of each carbon atom form C-H and C-C covalent bond. These bonds are also referred to as sigma (σ) bonds. The ethane molecule can be represented as:



We will now consider in some detail how bonding involving a carbon atom occurs. We start with the arrangement of electrons in a carbon atom which is shown.

Sub level

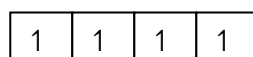


The two electrons in 2s uncouple and one is promoted to the 2p sublevel. The atom is said to be in the excited state.



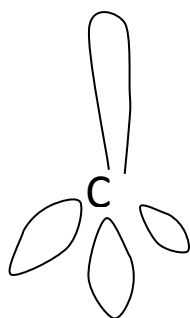
excited state

s^1 p^3



hybridised

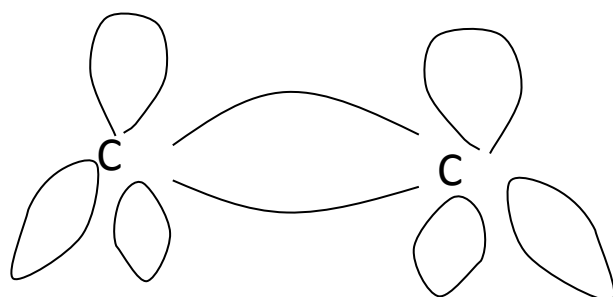
The 2s electron and three 2p electrons have their energy equalized. In other words all the four electrons have equivalent energy. These electrons are said to be hybridized and are now called $s^1 p^3$ electrons. It is these four electrons that form σ bonds (C-C and C-H). The distribution of these electrons can be represented as electron clouds orbitals, an orbital being the volume of space where there is a high probability of finding an electron.



s^1p^3 Orbitals

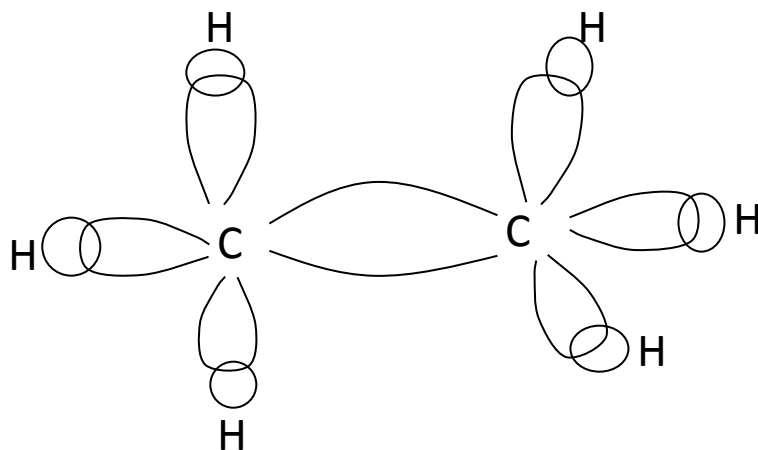
When a carbon atom forms a σ bond with another carbon atom there is an orbital overlap which is the covalent or sigma bond.

σ bond

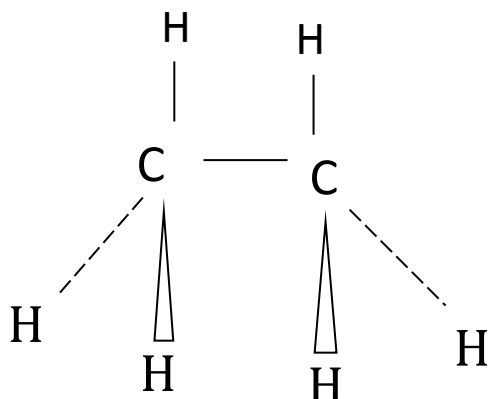


$s^1p^3-s^1p^3$

The rest of the electrons on each carbon overlap with those of hydrogen atoms.



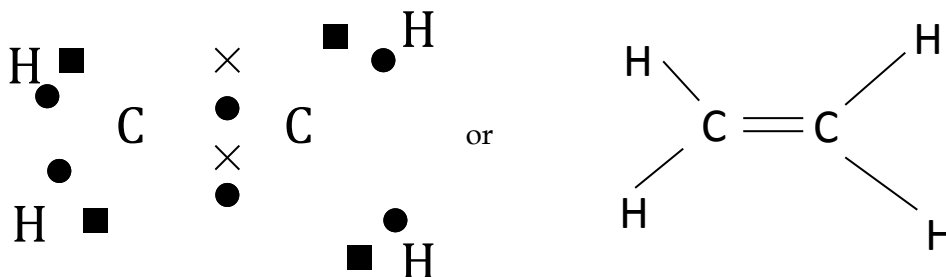
Space orientation of the bonds is shown



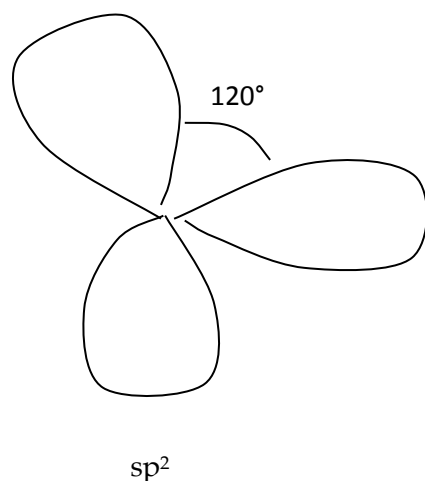
The H - C - C - CH₃ bond angle is the expected tetrahedral angle of 109.5°. In the ethane molecule the CH₃ groups can rotate about the C-C sigma bond giving several orientations or conformations.

Ethene C₂H₄

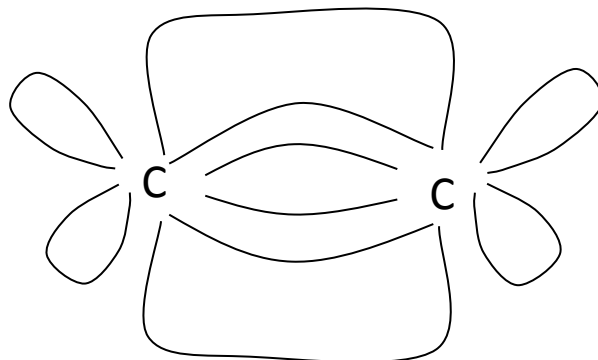
The ethene molecule can be represented electronically as shown.



In the formation of ethene, one of the 2p electrons remains unhybridised so that the C-H and C-C π bonds are formed from three sp^2 hybridised orbitals on each carbon atom. The space orientation of the sp^2 orbitals is shown with an orbital angle of 120°

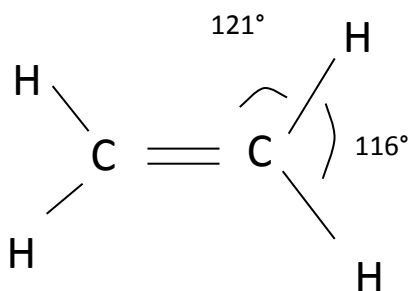


The sp^2 orbitals from each carbon atom overlap to form a strong C-C, C-H σ bonds. What do you think happens to each of the unhybridised 2p orbitals in each carbon atom? These overlap sideways to form a 2p-2p π bond. Hence the two carbon atoms are linked by an sp^2 - σ bond. These two bonds form a double bond between the carbon atoms. The space orientation of the bonded orbitals is shown.



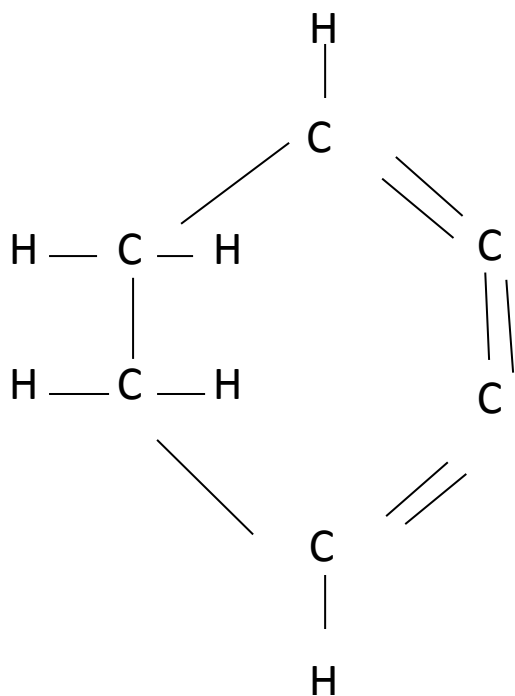
π bond

We can deduce from the orientation of the orbital that the molecule of ethene is flat with H-C-H and H-C-C bond angles of 120° theoretically. However, there are slight distortions due to orbital-orbital repulsion resulting in the decrease in the H-C-H bond angle to 115° and an increase in the H-C-C bond angle to 121° . The molecule can be represented as shown.

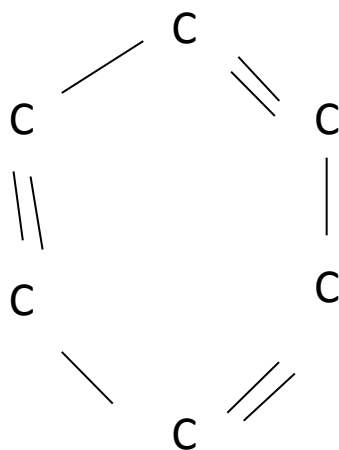


The Benzene Molecule

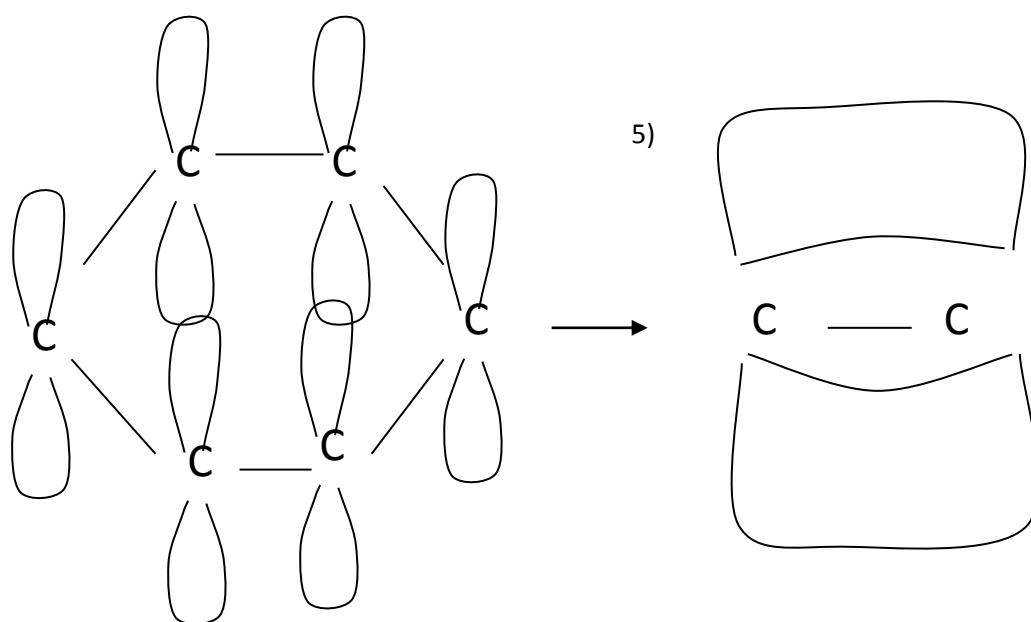
The structure of the benzene molecule presented challenges until Kekule came up with a structure that more or less fitted the behaviour of the molecule. He proposed a cyclic structure with three double bonds.



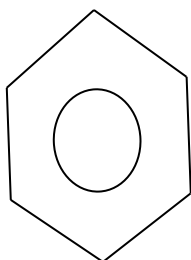
He later proposed another similar structure but with double bonds at alternative positions.



It is now known that the actual structure of the benzene molecule is a hybrid of the two Kekulé structures. As is evident from the structures, the molecule is in the form of a regular hexagon with a C-C-C bond angle of 120° . You saw in the ethene molecule that the sp^2 orbitals overlapped to form a sigma σ bond while the unhybridised p orbitals formed a pi (π) bond. The same principle applies to the benzene molecule. The six unhybridised orbitals are delocalized above and below the C-C bonds forming two circular rings above and below the regular hexagon.



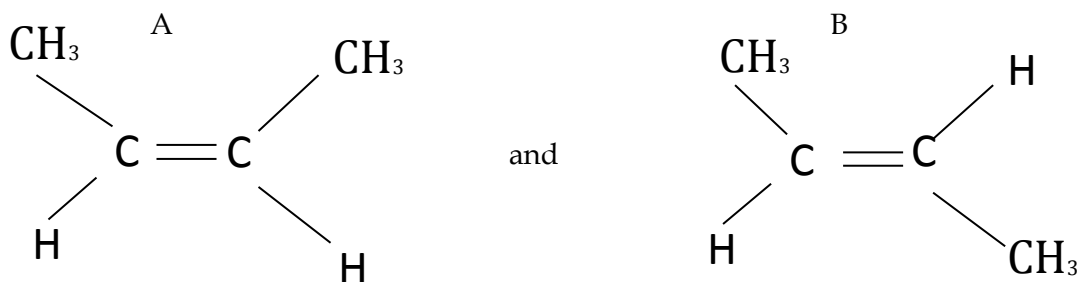
In order to make the structure simpler, the benzene molecule is shown as a regular hexagon with a circular ring inside.

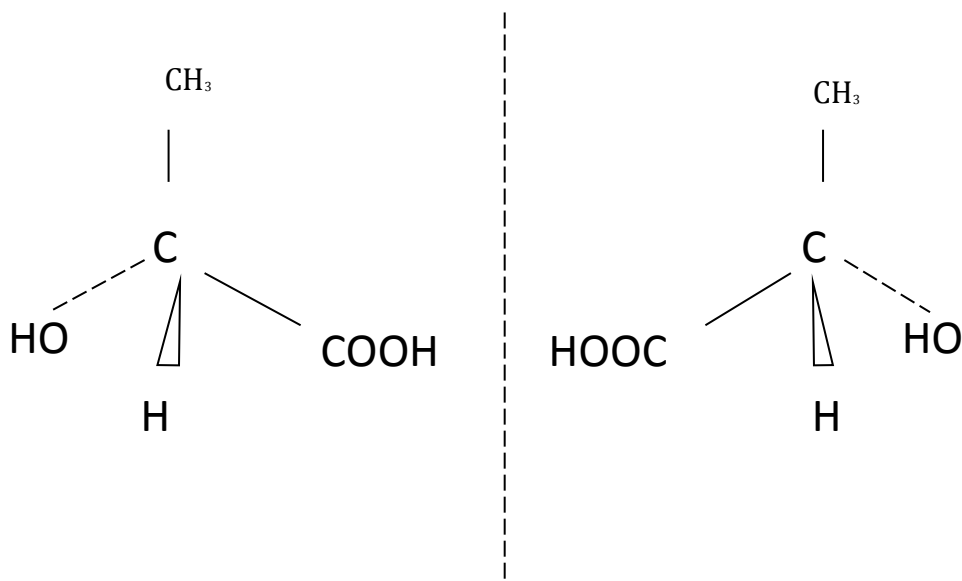


What does the circular ring represent?

Isomerism

As we have seen earlier in the last chapter, isomers are molecules with the same chemical formula but different structural formulae. Take for example but-2-ene. Its molecular formula is C_4H_8 . However its structure can be represented as:





One important property of optical isomers is that they turn the plane of polarized light either to the right or left. For this reason they are said to be optically active.

Summary

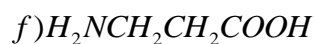
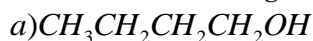
1. A functional group in a molecule is a part which takes part in a reaction.
2. In homolytic bond fission each atom carries away one of the covalent bond electrons.
3. In heterolytic bond fission only one of the atoms carries away both bond electrons.
4. A free radical is an atom or group of atoms carrying an unbonded electron.
5. A nucleophile is a molecule or ion which carries a lone pair of electrons or a negative charge.
6. An electrophile is a molecule or ion that is electron deficient.
7. During an addition reaction, molecules combine to form larger ones.
8. In an elimination reaction a smaller molecule is removed from a larger one.
9. A substitution reaction is a reaction in which a leaving group is replaced by an incoming group.
10. Hydrolysis is the addition of a water molecule to another molecule.
11. Oxidation is the addition of oxygen to a molecule and reduction is the removal of oxygen or addition of hydrogen to a molecule.
12. In a reaction involving a carbon atom the sp electrons/orbitals are hybridized to form sp^3 orbitals. The sp^3 orbitals form sigma (σ), bonds with other atoms in ethane .

The unhybridised p orbital forms pi (π) bonds while sp^2 orbitals form sigma σ bonds in ethene.

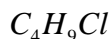
13. The benzene molecule is hexagonal with two circular rings of delocalized electrons above and below the hexagon.
14. Isomers are molecules with the same chemical/molecular formula but different structural formulae.
15. Stereoisomers are due to restricted rotation about the C=C bond and can be cis- or trans.
16. Optical isomers are mirror images of each other and are non-superimposable. Such isomers are said to be chiral.

Examination Type Questions

1. To which of the homologous series does each of the following belong?



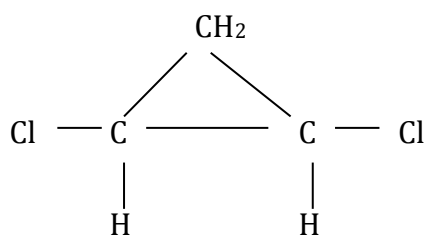
2. Write displayed structures of all isomers of the following molecular formulae.



- b) State the type of isomerism shown by each.
- c) Name the isomers.

3. Write the molecular formulae and displayed formulae of the following.

- a) 1, 2- dimethylcyclopentane.
- b) 2,2,3-trimethylpentane.
- c) Hex-1-ene.
- d) 2-methylpent-2-ene.
- e) 1,2-dichlorocyclopropane.



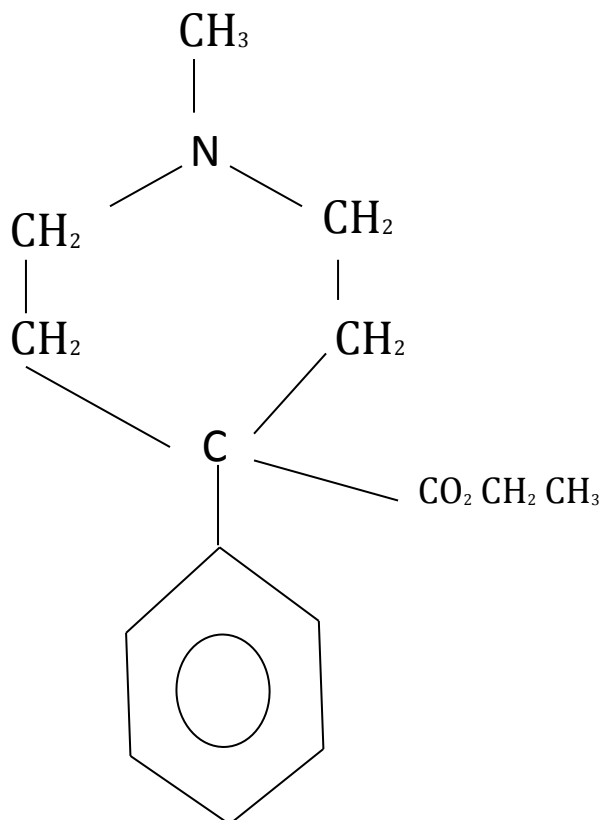
has cis and trans isomers.

Draw the two isomers and explain why there are cis and trans isomers.

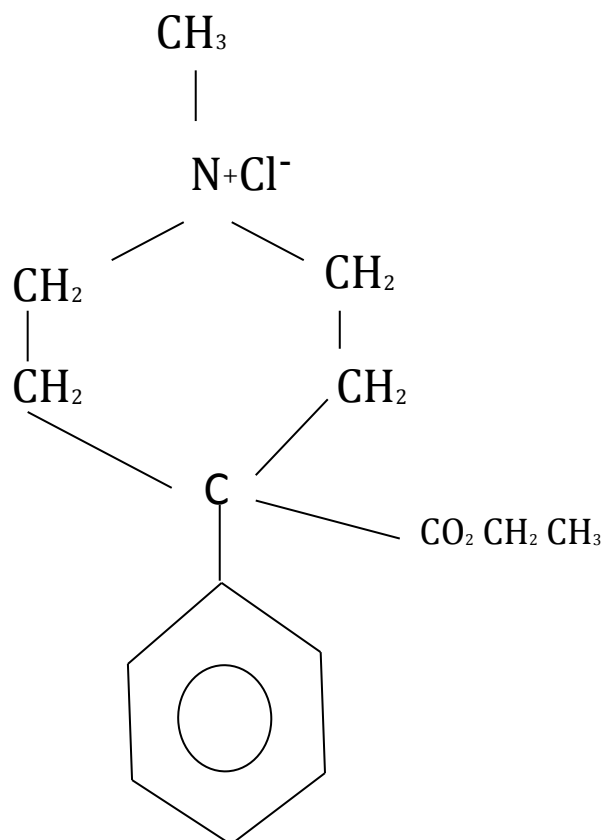
4) Chlorine reacts with methane (CH_4) in the presence of light: (a) Explain using free radicals how the reactions occur.

b) Indicate the following stages: chain initiation, chain propagation and chain termination.

5) Pethidine is a powerful pain killer



The pethidine molecule contains two functional groups one of which reacts with cold dilute hydrochloric acid to produce the following compound.



- What type of reaction is this and what type of functional group does it show the pethidine molecule to contain?
- Name the other functional group in the molecule. State the type of reaction taking place and give the displayed formulae of one product when pethidine reacts with sodium hydroxide.

References

1. Hill G and Holman J
Chemistry in Context
Thomas Nelson and Sons Ltd
Surrey, U.K
3rd Edition
2. Lister T and Renshaw J
Understanding Chemistry
Stanely Thornes Ltd
Cheltenham U.K.
1994 Edition
3. Murray J.
Organic Chemistry
Cornell University
Brooks/Cole Publishing Company, Monterey, California USA
ISBN 0-534-01204-3.
4. Cambridge A Level Past Paper 3
5. Cambridge A Level Chemistry Syllabus.
6. Zimsec A Level Chemistry Syllabus

CHAPTER 3

HYDROCARBONS

At the end of this chapter you should be able to:

- a) describe the general unreactivity of alkanes, including towards polar reactants.
- b) describe the chemistry of alkanes as shown by the reactions of ethane:
 - i) combustion.
 - ii) substitution by chlorine and by bromine.
- c) describe the mechanism of free radical substitution at methyl groups with reference to initiation, propagation and termination reactions.
- d) describe the chemistry of alkenes as exemplified where relevant by the following reactions of ethene.
 - (i) addition of hydrogen, steam, hydrogen halides and halogens.
 - (ii) oxidation by cold, dilute manganate (viii) to ions to form diols.
 - (iii) oxidation by hot concentrated manganate (viii) ions leading to the rupture of the carbon to carbon double bond in order to determine the position of alkene linkages in larger molecules.
 - (iv) polymerisation.
- (e) describe the mechanism of electrophilic addition in alkenes using bromine-ethene as an example.
- f) explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons.
- g) suggest how "cracking" can be used to obtain more useful alkanes and alkenes of lower M_r from larger hydrocarbon molecules
- h) describe and explain how combustion reactions of alkanes lead to their use as fuels in industry, in the home and in transport.
- i) describe the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal.
- j) describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene.
 - i) substitution reactions with chlorine and with bromine.
 - ii) nitration.
 - iii) oxidation of the side chain to give a carboxylic acid.
- k(i) describe the mechanism of electrophilic substitution in arenes, using the mono-nitration of benzene as an example.
- ii) describe the effect of the delocalisation of electrons in arenes in such reactions.
- l) predict whether halogenations will occur in the side chain or aromatic nucleus in arenes depending on reaction conditions.
- m) apply the knowledge of positions of substitution in the electrophilic substitution of arenes.

Introduction

As the name suggests hydrocarbons are compounds of carbon and hydrogen. Hydrocarbons appear as branched chains, unbranched chains, and rings. Thus carbon is capable of forming literally millions of compounds.

The reasons for carbon forming such a large variety of compounds are that:-

- a) The carbon atom has the ability to expand its bonding electrons to four

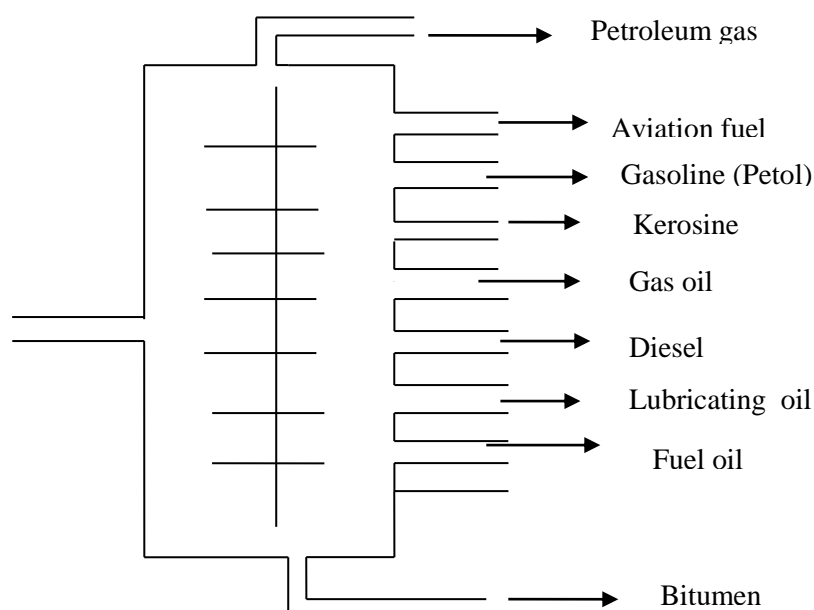
b) The carbon atom can form stable C-C bonds and C-H bonds. It is also able to form multiple bonds with other carbon atoms. As discussed earlier carbon can bond with other carbon atoms to form chains and rings (catenation).

Alkanes

This is a class of hydrocarbons whose molecules do not have double bonds. They are also referred to as saturated hydrocarbons. Alkanes are obtained from crude oil, a dark thick liquid mixture which was formed from plant and animal remains millions of years ago.

Extraction of alkanes

Crude oil is subjected to fractional distillation during which the components are separated. The diagram represents the fractionating column.



The table shows the composition and uses of the products of fractional distillation of crude oil.

Fraction	Number of Carbon atoms	uses
Petroleum gas	C ₁ - C ₄	heating and Synthesis of other Hydrocarbons
Aviation fuel	C ₅ - C ₆	Light air-craft engines
Gasoline (petrol)	C ₅ - C ₁₂	Internal Combustion Engines
Kerosine	C ₁₂ - C ₁₈	domestic heating Fuel engine

The alkanes are heated in the presence of silicon dioxide and aluminum oxide to about 500°C. Here the cracking occurs at a lower temperature than steam cracking because of the presence of a catalyst mixture of silicon dioxide and aluminum oxide because $C_{10}H_{22}$ can be cracked to give octane C_8H_{18} , a fuel and ethene, C_2H_4 which is used to make plastics.

Reactions of alkanes

Due to the fact that all four available electrons in the carbon atom are used to form strong $C-C$ bonds and $C-H$ bonds, alkanes are unreactive. Also because the $C-C$ bonds and $C-H$ bonds are non-polar, alkanes will therefore not react with polar reagents. However, alkanes will take part in only two types of reactions, combustion and substitution by the halogens, chlorine and bromine. We will consider these two reactions in detail using ethane.

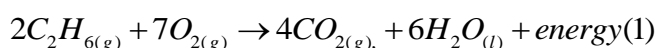
Combustion reactions

In all combustion reactions $C-C$ and $C-H$ bonds are broken and energy is released. For example when one mole of $C-C$ bonds are broken 348kJ of energy are produced. Also when one mole of $C-H$ bonds are broken 412kJ of energy are produced. You can imagine the amount of energy produced from one mole of a multiple bond molecule like C_5H_{12} .

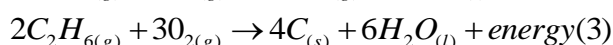
This is the basis for the use of alkanes as fuels. Various conditions determine the nature of products and the amount of energy produced. The following reactions occur when ethane burns in oxygen.

Burning ethane

When ethane burns in excess oxygen the products are CO_2 and H_2O and energy.



However, when ethane is burnt in a limited supply of oxygen, the following reactions occur.



Most heat energy from ethane is obtained from reaction (1), the energy decreasing in (2) and (3).

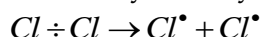
As shown above you notice that other than water, CO_2 , CO , and C are produced. As you know all these products are environmental pollutants. Carbon dioxide is a green house gas carbon monoxide is an extremely poisonous gas and carbon in the form of smoke is an atmospheric pollutant. Other pollutants are oxides of nitrogen whose production and catalytic removal was discussed in detail in inorganic chemistry.

Reaction of Ethane with Chlorine and Bromine

Though ethane does not react with polar reagents as we have seen with all alkanes, it can be attacked by free radicals to form a series of compounds. We will now consider the reactions with chlorine and bromine.

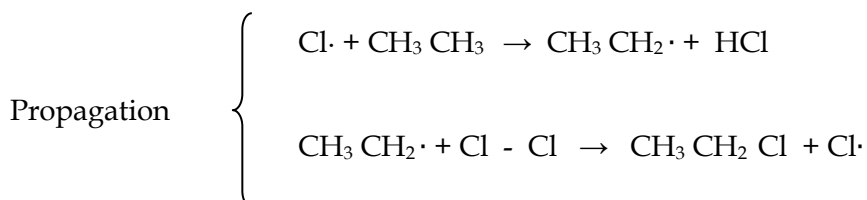
Reaction with chlorine

This reaction occurs in the presence of light which initiates the formation of chlorine free radicals by homolysis of the $Cl - Cl$ bond



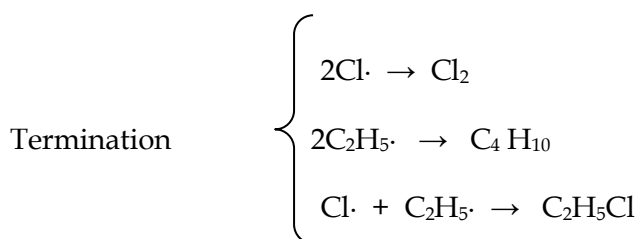
This is the initiation step.

The Cl^{\bullet} radical then attacks the methyl group removing hydrogen and releasing another free radical

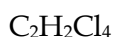
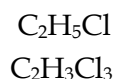


Reaction (2) and (3) can be repeated several times and if there is sufficient chlorine all the hydrogens in the methyl groups are replaced by chlorine. Reactions (2) and (3) are the chain propagation steps.

The following reactions are also possible.



You will notice that no new free radicals are generated. (4) (5) and (6) are the chain termination steps. What do you think will be in the mixture at the end of the reaction other than chlorine. A whole series of substitution products and hydrogen chloride will be formed. Considering the step by step substitution of hydrogen in the methyl groups these are the possibilities.



The same reaction between bromine and ethane occurs when a mixture of the two is exposed to ultraviolet light.

Alkenes

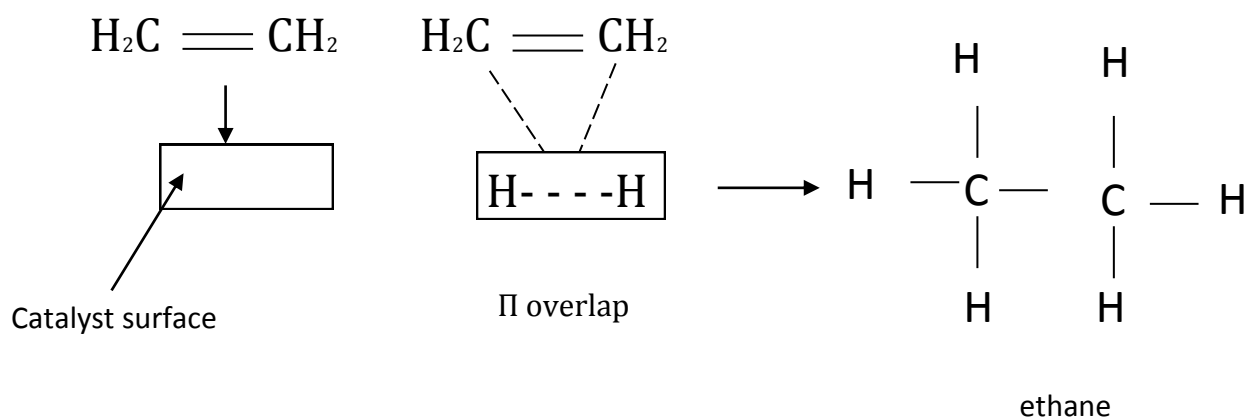
These are unsaturated hydrocarbons containing $C = C$ double bonds. Their general formula as we saw earlier is C_nH_{2n} . We will now consider reactions of this group of hydrocarbons with specific reference to ethene.

Addition reactions of ethene

Before we study these reactions you will need to familiarise yourself with the terms nucleophile, carbocation, addition and electrophile which we have already discussed.

Addition of Hydrogen

The addition of hydrogen across the π bond in ethene occurs in the presence of a catalyst which could be nickel, platinum or palladium. As it happens in reactions catalysed by solid catalysts, the process involves the overlap of metal orbitals with the π electrons of the ethene double bond forming a complex on the catalyst surface. Hydrogen is incorporated into the π bond.

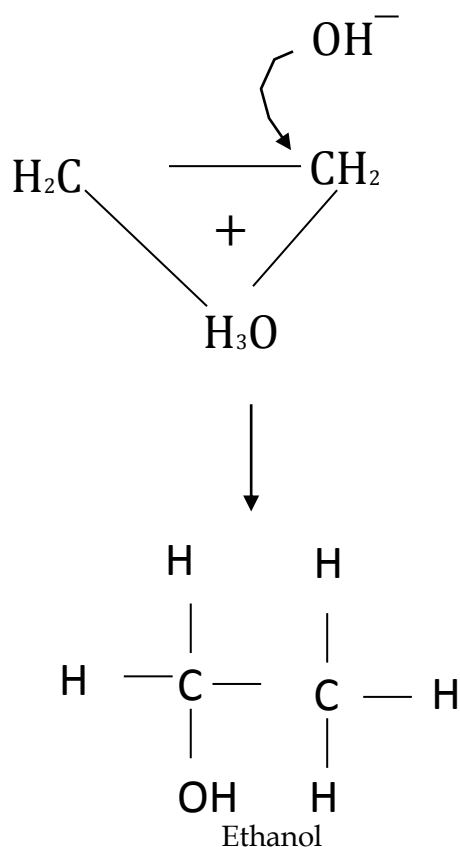


This reaction is used to convert vegetable oils into margarine.

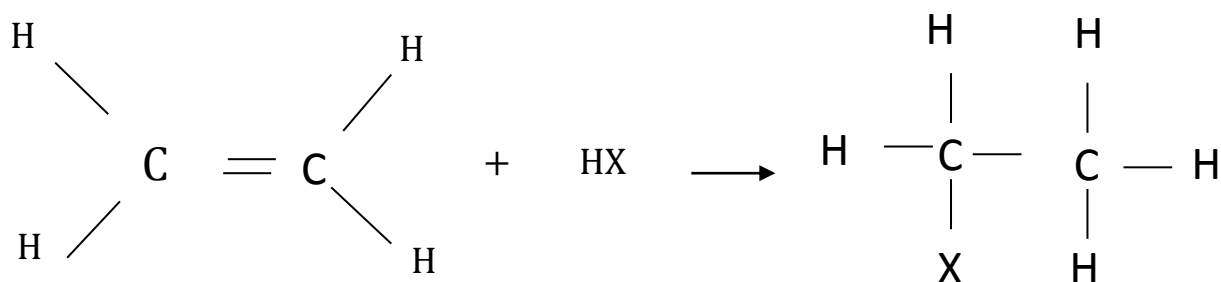
Reaction of Ethene with Steam

In this reaction a water molecule is added to ethene to produce ethanol. This is a reaction of industrial importance as it is used to manufacture ethanol on a large scale. The reaction involves subjecting a mixture of steam, ethene and phosphoric acid to 60 atmospheres at 330°C . The reaction starts by protonation of the water molecule by phosphoric acid which acts as a catalyst to give a hydronium ion.

H_3O^+ which acts as the electrophile receives electrons from the double bond. The rest of the reaction proceeds via the carbocation as shown.

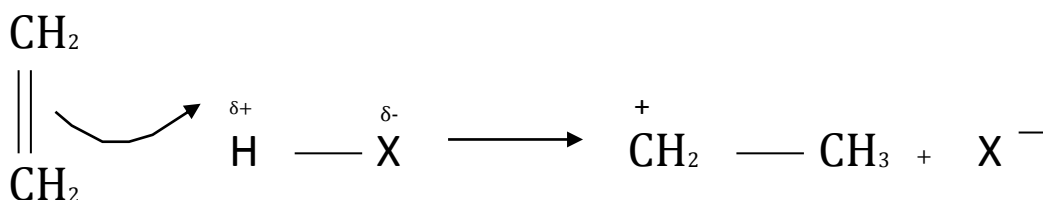


Reaction of ethene with a hydrogen halide. The general reaction occurs as shown

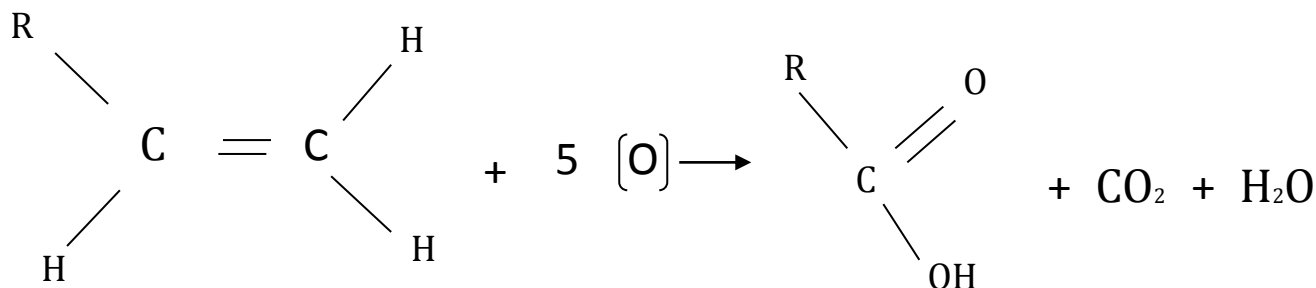


where X is a halogen atom.

The hydrogen halide molecule is polar. Since the double bond on the ethene molecule is a nucleophile due to the presence of π electrons it attacks the hydrogen halide molecule on the hydrogen end releasing a halide ion.



The second carbon atom becomes electron deficient. This atom is called a carbocation which acts as an electrophile. The carbocation then receives electrons from the halide ion forming an alkyl halide.



The products in this reaction are an indicator of the position of the double bond in an alkene molecule.

Activity

Write equations for reactions that occur when a) cold b) hot concentrated Manganate (vii)

ions react with
 (i) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
 (ii) $(\text{CH}_3)_2\text{C}=\text{CH}_2$

Polymerisation

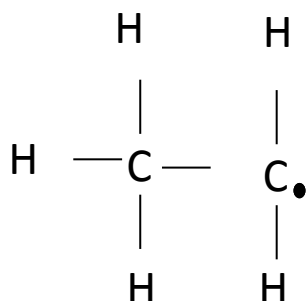
Polymerisation is the joining of small molecules called monomers to form long chains of very large relative molecular masses. Polymers can be formed from both natural and synthetic monomers.

There are two main types of polymers classified according to the nature of reactions producing them. We will now discuss these reactions.

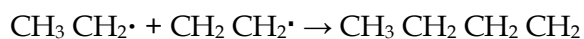
Addition polymerisation.

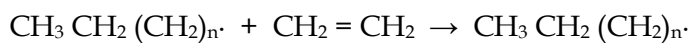
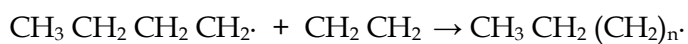
Here monomers are joined together to form long chains. A simple example is polythene formed from ethene monomers. The reaction is initiated by an anion or cation or a free radical. The free radical uses the π bond electrons in the $\text{C}=\text{C}$ double bond. In the process another free radical is produced from the ethene molecule.

The radical R^\bullet bonds with π electrons



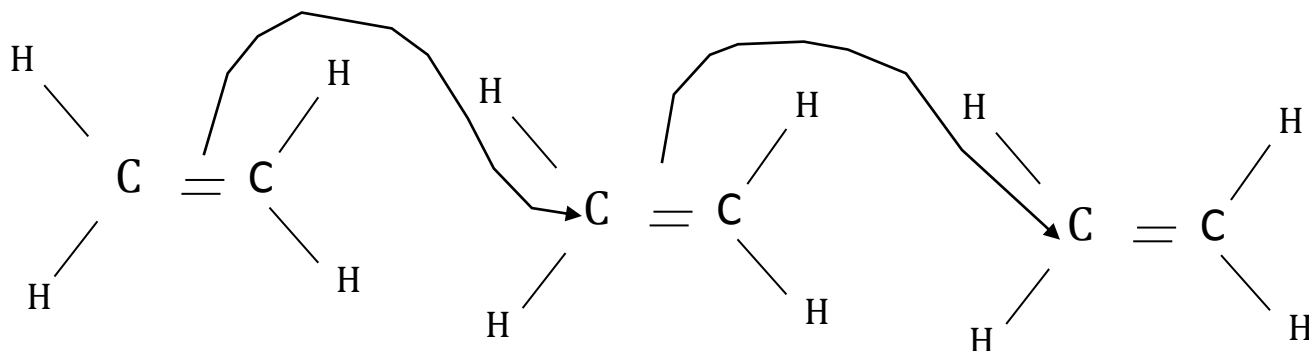
Ethene radical





Repeat several times

The reaction can also be represented as

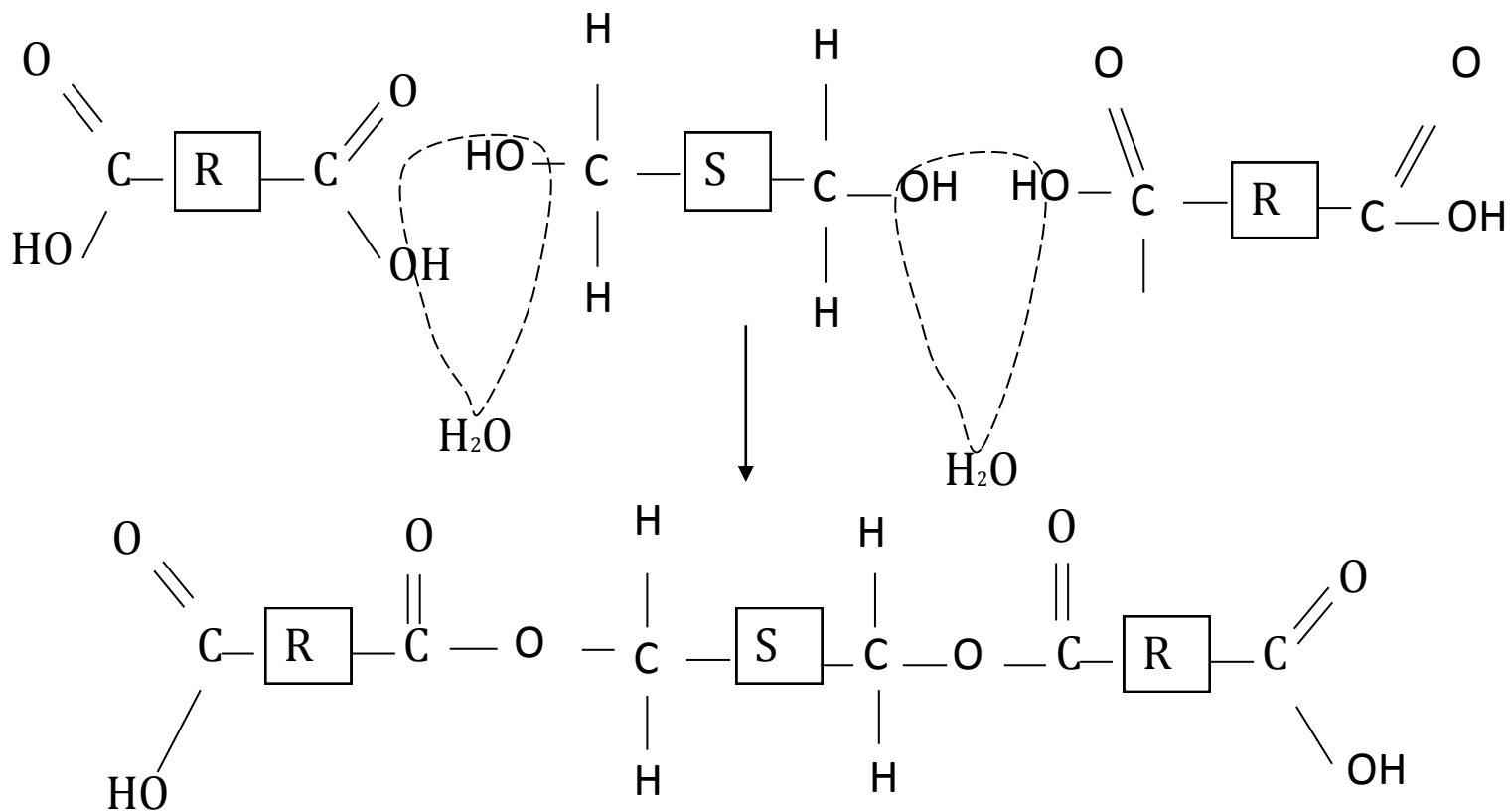


The table shows some of the common polymers, their monomers and some of their uses.

<u>NAME OF POLYMER</u>	<u>MANOMER</u>	<u>USES</u>
Poly (ethene) (polythene)	$\text{CH}_2 = \text{CH}_2$	- Plastic bags, - Toy-making - Kitchenware - Food boxes - Bowls, buckets
Poly(propene)	$\text{CH}_3\text{CH} = \text{CH}_2$	- ropes - Packaging
Poly(chloroethene) (PVC)	$\text{CH}_2 = \text{CHCl}$	- building material - electrical insulation - shoe-making - plumbing
Poly(tetrafluoro-ethene) (PTFE, Teflon)	$\text{CF}_2 = \text{CF}_2$	- non-stick frying pans
Poly(ethyl-ethanoate) (polyvinylacetate) (PVA)	$\begin{array}{c} \text{CH}_3\text{CO}_2 \\ \\ \text{CH} = \text{CH}_2 \end{array}$	- used in emulsion paints

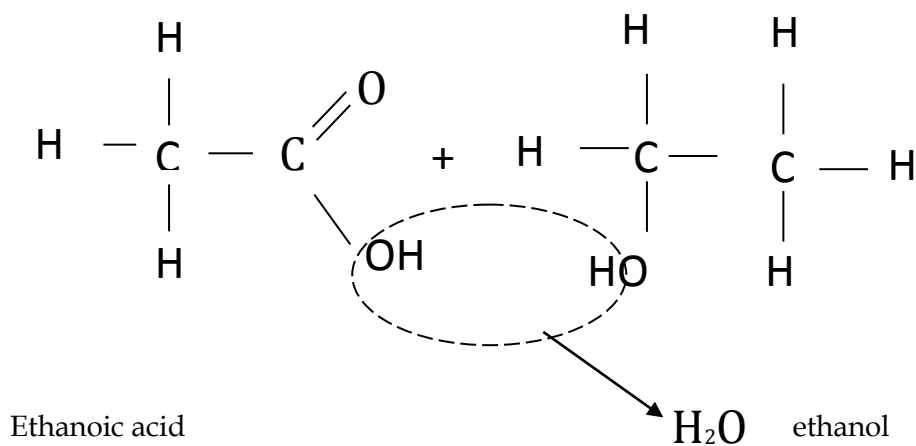
Condensation polymerization

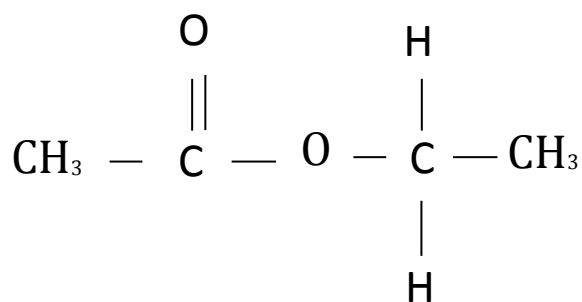
In this type of polymerisation the joining of monomers is accompanied with the elimination of a small molecule usually water. The reaction can be represented generally as the joining of two monomers R and S.



You will notice that the monomers are different

A simple example is the reaction between ethanoic acid and ethanol.





Ethyl ethanoate

Ethyl ethanoate is called an ester. Several of the ester monomers can be joined to form polymers called polyesters.

Arenes

This is a large group of aromatic compounds based on the benzene molecule. Do you still remember the structure of a benzene molecule? Refer back to the shapes of molecules in the previous chapter. In this topic we will discuss some reactions that involve the benzene molecule. These reaction will include:

- substitution reactions with chlorine and bromine
- nitration
- side chain reactions

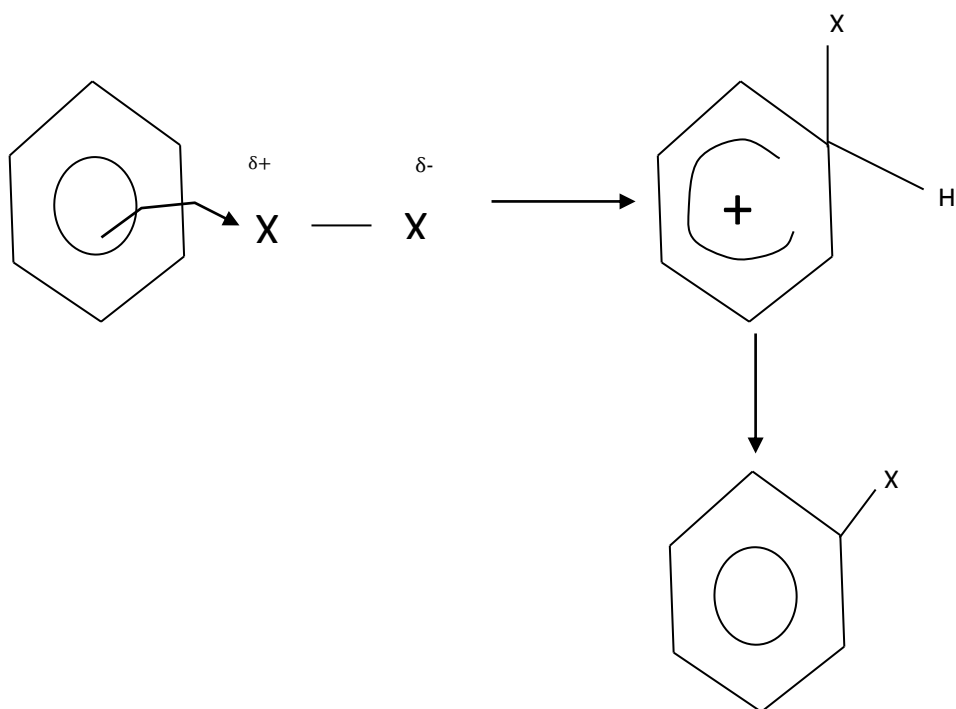
Substitution reactions

As the name suggests the reactions involve replacing an atom or group with another.

Substitution with a halogen

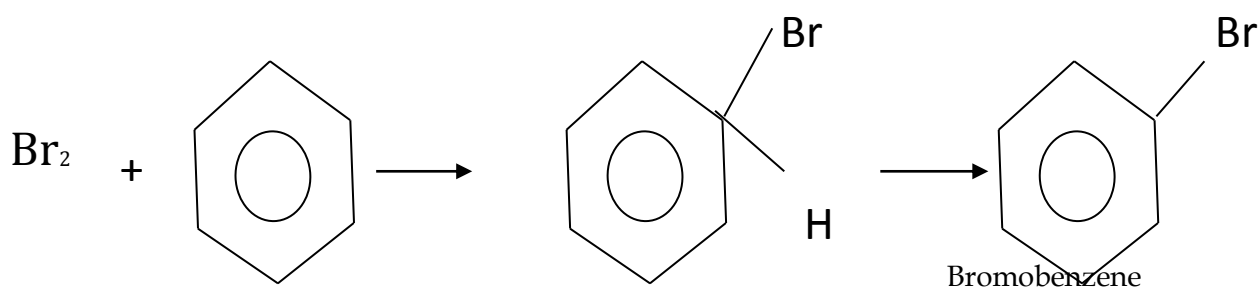
As you have already learnt a halogen molecule (X-X) is polarised. This means that they can behave as electrophiles in their reaction with electron rich molecules. You saw how this happened in the reaction between ethene and halogens.

If you can remember the benzene molecule is electron rich due to delocalized π electrons above and below the ring. In the presence of a catalyst usually iron filings or aluminum chloride ($AlCl_3$) the X - X accept electrons from the benzene ring and in the process replace the less reactive hydrogen atom. The reaction mechanism is shown.

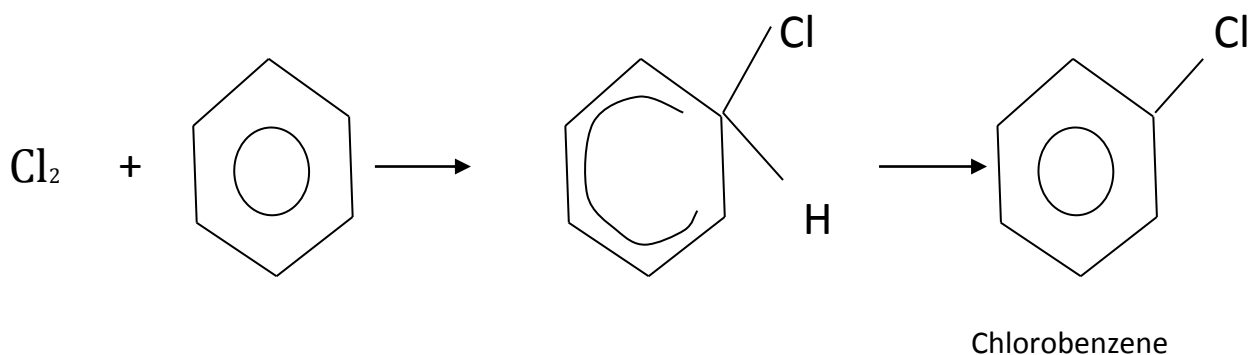


The reaction goes through a complex in which the ring acquires a partial positive charge. In this case the X is the incoming group while H is the outgoing group.

More specific examples with chlorine and bromine are shown below.



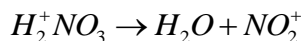
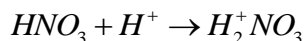
Chlorine



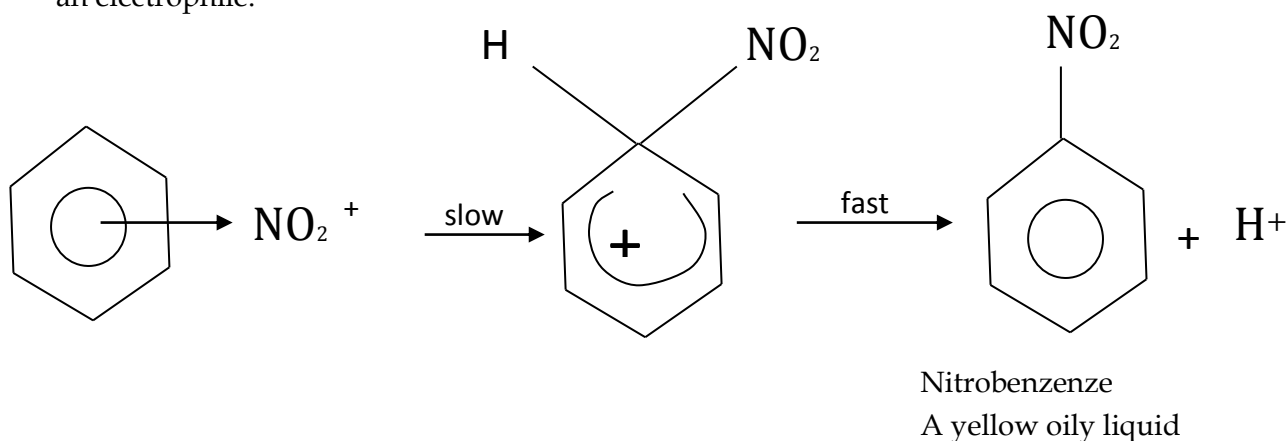
Nitration

This is the addition of a nitronium/nitryl ion NO_2^+ to the benzene ring. This ion is produced by reacting concentrated sulphuric acid and concentrated nitric acid. Sulphuric acid

being a stronger proton donor than nitric acid donates a proton to nitric acid to produce an unstable compound H_2NO_3 which breaks down to give water and the nitronium ion.



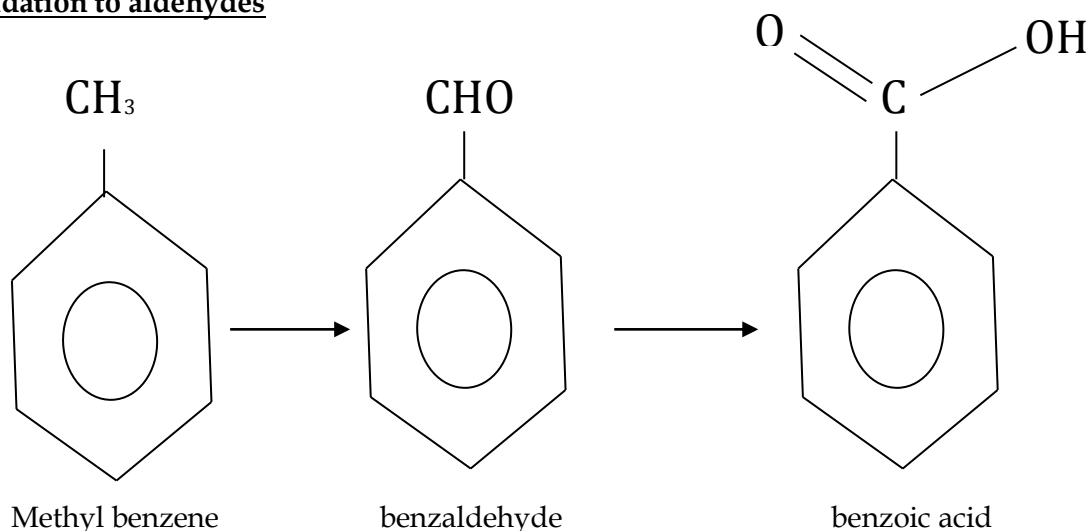
The mechanism of reaction of the NO_2^+ ion with benzene is shown. Notice that the NO_2^+ is an electrophile.



Oxidation of the side chain

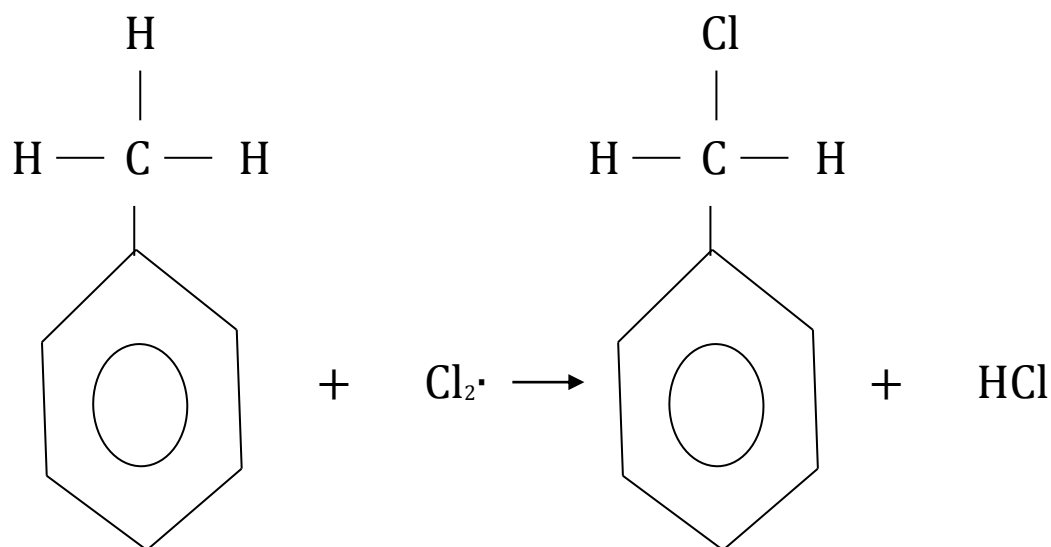
The side chains are much more susceptible to oxidation than the benzene ring itself. The use of strong oxidising agents like acidified manganate (vii) and dichromate (vi) ions enables oxidation of aliphatic side chains to aldehydes and finally to carboxylic acids.

Oxidation to aldehydes



In the above reaction the CH_3 group is oxidised to a carboxylic acid. But as you know about the unreactivity of alkanes, oxidising agents have no effect on alkanes. However, when alkanes are linked to the benzene ring they are reactive.

Chlorine reacts with methylbenzene in two ways. In the presence of light which produces chlorine free radicals, the hydrogen atoms of the methyl group are substituted in a series of reactions.



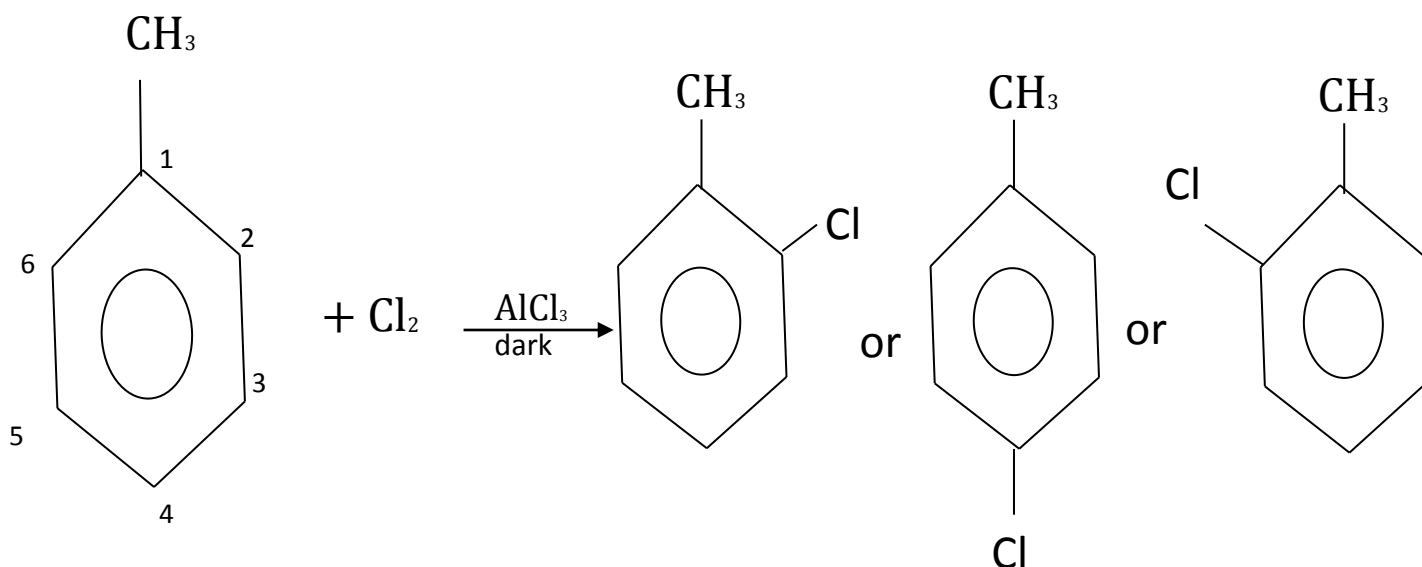
By- product is HCl which appears as steamy fumes.

However, in the presence of a halogen carrier AlCl_3 substitution occurs on the ring itself resulting in chlorobenzene. Do you remember how the substitution occurs? You can refer back to substitution by halogens.

The substitution reaction with methyl-benzene in which AlCl_3 is used proceeds faster than with benzene alone. This is because the saturated CH_3 increases the electron density of the ring by pumping electrons into it.

We can conclude from the reactions above that reaction conditions determine the course of a reaction. By altering the reaction conditions, substitution can occur either on the benzene ring or on the side chain.

The presence of a substituent on the ring can determine the position of the incoming group. For example in methylbenzene the incoming chlorine atom can occupy the 2, 4 and 6 positions. The CH_3 group is said to be 2, 4 and 6 directing.



More of the 2-isomer forms than the 4-isomer since there are two ring positions that give the 2-isomer and only one position gives the 4-isomer.

Unsaturated substituents e.g. NO_2 and CO_2H are ring deactivators. They direct incoming electrophiles to ring position 3.

Summary

1. Alkanes are generally unreactive but can undergo combustion and free radical substitution.
2. The functional group in alkenes is the double bond. Alkenes undergo addition reactions with hydrogen, steam, halogens and hydrogen halides. Alkenes form diols with mild oxidising agents. However, with strong oxidizing agents like hot concentrated, MnO_4^- there is rupture of the double bond. This reaction is used to determine the position of a double bond in an alkene.
3. Polymerisation is the joining of small usually unsaturated molecules (monomers) to produce long chains. In addition polymerisation monomers are added to each other in the presence of a catalyst. In condensation polymerisation a water molecule is usually ejected from between monomers
4. Crude oil is the source of hydrocarbons which are separated by fractional distillation. Cracking is the breaking down of long alkanes to smaller more useful alkanes and alkenes
5. Alkanes burn in excess oxygen to produce carbon dioxide, water and energy. In a limited supply of oxygen carbon monoxide and carbon are also produced.
6. Benzene undergoes electrophilic substitution reactions on the ring. Substituents on the ring determine the position of the incoming group. Alkanes react when attached to the benzene ring.

Questions

- Describe the reaction mechanism for the formation of the following from ethane:
 - Chloroethane
 - 1, 2-dichloro-ethane
 - 1, 2- dibromo-ethane
 - ethane-1, 2- diol
 - Ethanol
- Give the possible products when the following alkanes undergo craking:
(a) C_5H_{12} (b) C_8H_{18} (c) $C_{10}H_{22}$
- Describe the environmental hazards of CO_2 , CO and NO. Explain using equations how NO is formed and how its emission is reduced.
- Describe and explain stating the conditions, how the following are produced.
 - Chlorobenzene
 - Nitrobenzene
 - Dichloro-methyl benzene
 - Benzoic acid

REFERENCES

- Hill G. and Holman J
Chemistry in Context
Thomas Nelson and Sons Ltd
Surrey UK
3rd Edition
- Rister T and Renshaw J
Understanding Chemistry
Stanley Thornes Ltd
Cheltenham UK
1994 Edition.
- Murray J
Organic Chemistry
Cornell University
Brooks/ Cole Publisisng company California USA
- Cambridge A Level Chemistry Syllabus.
- Zimsec A Level Chemistry Syllabus.

CHAPTER 4

HALOGEN DERIVATIVES

At the end of this chapter you should be able to:

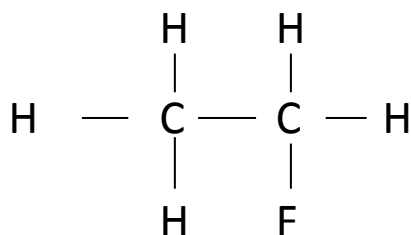
- (a) Recall the chemistry of halogenoalkanes as exemplified by:
 - (i) nucleophilic substitution reactions of bromoethane ; hydrolysis ; formation of nitriles and formation of primary amines by reaction with ammonia
 - (ii) the elimination of hydrogen bromide from 2- bromopropane.
- (b) describe the mechanism of nucleophilic substitution in halogenoalkanes.
- (c) interpret the different reactivities of halogenoalkanes and chlorobenzene with particular reference to hydrolysis and the relative strengths of the C-hal bonds.
- (d) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative inertness e.g anaesthetics, flame retardants.

Introduction

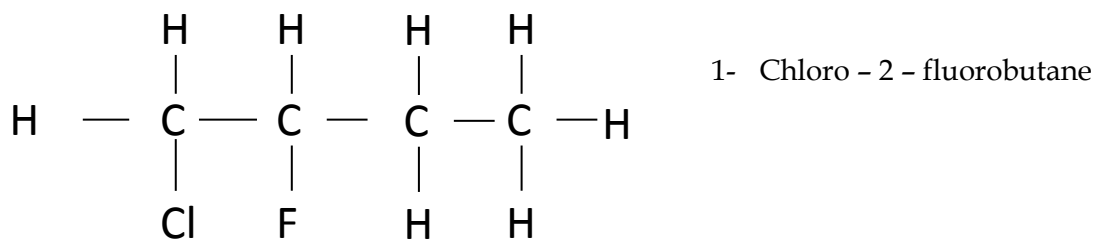
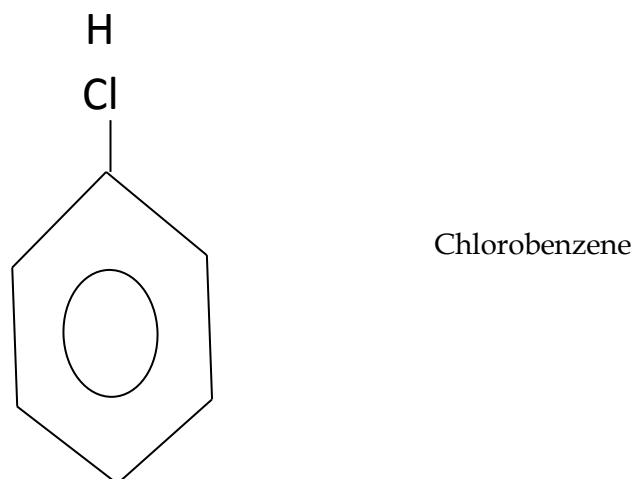
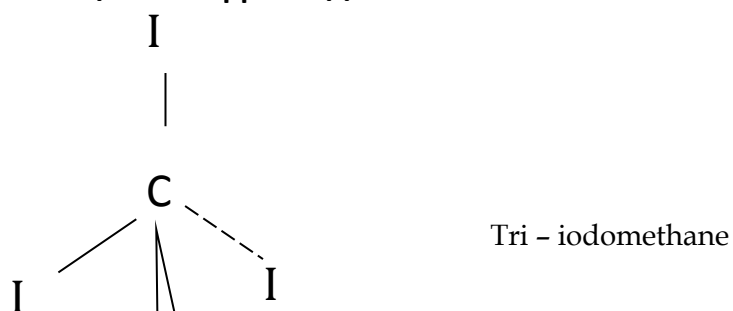
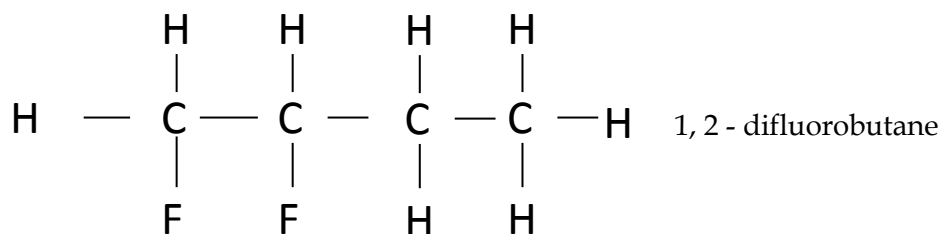
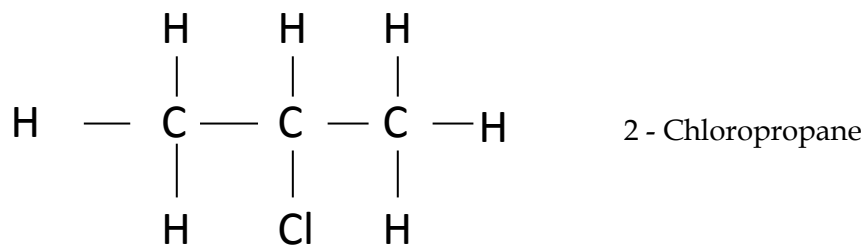
Halogenoalkanes are an important group of organic compounds. They are widely used in the dry- cleaning industry, as electrical insulators, as plastics, non-stick frying pan surfaces and in refrigeration. These are a few examples. We will discuss more examples in the chapter. Useful as these compounds are some of them have lately been found to interfere with the ozone layer which protects us from harmful ultra-violet rays. Before considering the reactions of the derivatives, let us remind ourselves about how they are named systematically.

Naming organoalkanes.

As we learnt earlier, the following are used as prefixes: fluoro- chloro- bromo - and iodo - . . . In some compounds numbers are used to indicate the position of the carbon atom to which they are attached on the chain . The number of halogen atoms in the chain is indicated by the prefixes di -, tri-, and so on . Let us name a few of these compounds.



Fluoroethane



Reactions of organoalkanes.

As you will recall bonds are made and broken during chemical reactions. The strengths of these bonds will give us some idea of how a compound will react.

Bond (C- X)	Energy kJ mol ⁻¹
C - F	467
C - Cl	346
C - Br	290
C - I	228

In some substitution reactions, a hydrogen atom is replaced by a halogen atom and so it is necessary that we compare the above energies with that of C- H which is 413kJmol^{-1} . As you may expect the trend shows a decrease down the halogen group. Can you explain this trend? (Hint: refer to atomic size and nuclear attraction). Which bonds will be easier to break and which will be more difficult to break? Perhaps you might want to consider another related property of halogen atoms, their electronegativities. See the data below.

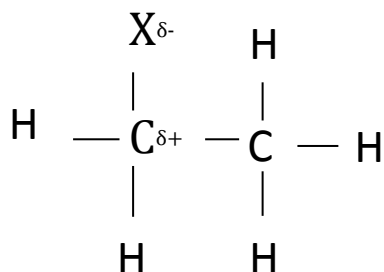
Halogen	Electronegativity
F	4,0
Cl	3.0
Br	2.8
I	2.5

It is also necessary for us to compare the above values with those of carbon (2,5) and hydrogen (2,1) These elements are involved in bonding in haloalkanes. Differences in electronegativities also give rise to uneven sharing of covalent bond electrons. The more electronegative atom tends to have a larger share of bond electrons. This causes the bond to be polar. Thus in the bond, the halogen (X) being more electronegative than carbon will acquire a slight negative charge while the carbon acquires a slight positive charge. This carbon atom which now becomes electron deficient can be attacked by nucleophiles (remember these carry either a negative charge or a lone pair of electrons. With the information above we can now examine reactions of haloalkanes.

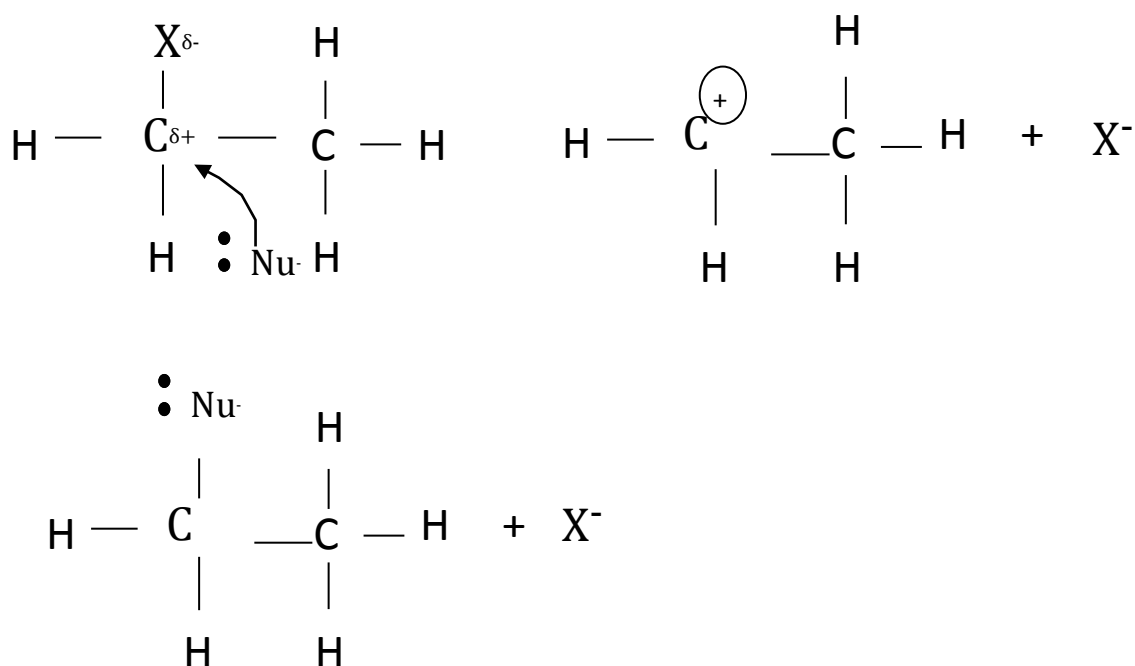
Reactions of halogenoalkanes.

Nucleophilic substitution.

First we will discuss a general reaction between a nucleophile ($:Nu^-$) and a halogenoalkane shown.

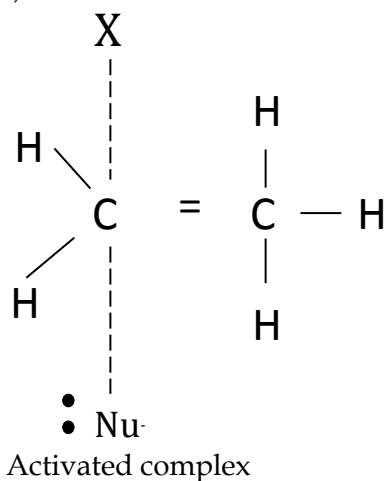


The reaction starts with the nucleophile attack on the carbocation (C^+). This weakens the $C-X$ bond resulting in its fission with the halogen carrying away the bond electrons



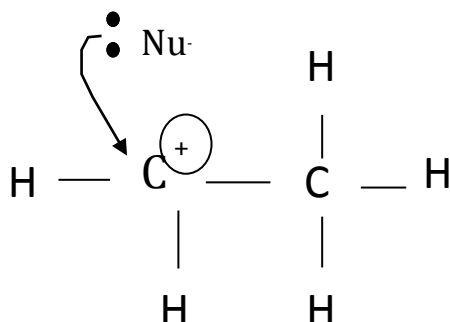
Thus the halogen has been replaced by the ($:Nu^-$) in the haloalkane molecule. This is a substitution reaction.

Another possibility in the course of the reaction is the halogen that can attack the carbocation centre at the same time as the hydrogen leaves (also called the leaving group). This results in the formation of a temporary compound which is unstable (the activated complex) as shown



The activated complex then breaks down to give the compound. The ion is released. Let us now consider the two possible reactions in detail.

First possibility is that the reaction can go through a carbocation followed by a nucleophilic attack as shown.



Experiments have revealed that the formation of the carbocation is a slow reaction while the nucleophilic attack is fast. In chemical reactions, the overall rate of a multi step reaction is determined by the slow stage called the rate determining step. The reaction rate can also be determined by the concentration of reactants, given by rate = k "reactant concentration". In this example the rate depends on the concentration of the haloalkane only, rate = $k \times [\text{haloalkane}]$ where k is the reaction constant. A reaction rate that depends on the concentration of one reactant is called a first order reaction. Thus the above reaction is a nucleophilic substitution reaction of the first order, represented by S_N1 where S stands for substitution, N for nucleophilic and 1 for first order.

Let us now examine the other possibility in which the reaction goes via an activated complex.

The activated complex is formed by the simultaneous nucleophilic attack on the carbocation and the exit of the leaving group. Hence the reaction rate depends on the concentration of two molecules, the haloalkane and the nucleophile that is rate = $k [\text{haloalkane}] \times [\text{nucleophile}]$. A reaction whose rate depends on the concentration of two reactants is said to be second order (2). Thus the above reaction is a nucleophilic substitution reaction which is second order S_N2 where S stands for substitution, N for nucleophilic and 2 for second order.

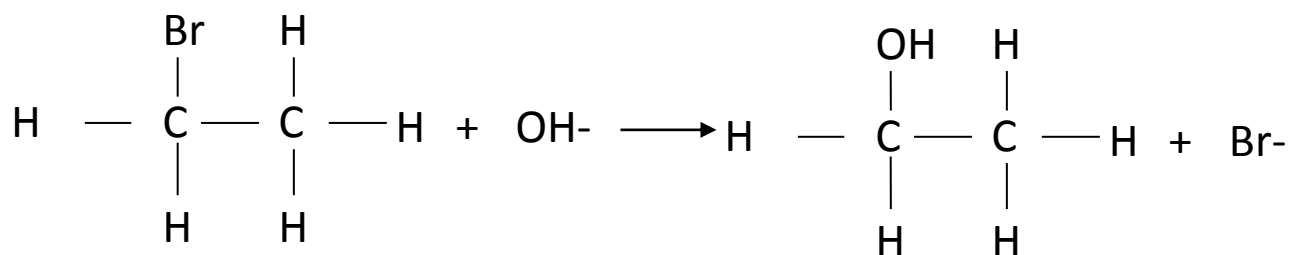
In our discussion of S_N1 and S_N2 reactions above we considered the concentration of reactants as a factor that determines the rate of a reaction. However, there are other factors. Let us consider two of these. First, let us discuss the effect of the C - X bond strength (refer to the table of C - X bond energies). You will notice that the C - X bond energy weakens down the halogen group. This means that it is energetically easier for the C - X bond to break as we go down the group. So the carbocation will be easier to form for C - I than for C - F. Therefore the substitution reaction will be faster with an iodoalkane than with a fluoroalkane.

Secondly, let us consider the effect of increasing the CH_3 groups on the carbocation. Methyl groups as you saw earlier, tend to push electrons towards the carbocation (called positive inductive effect) making the ion more stable. Thus the nucleophile will have enough time to attack the carbocation. Therefore we will expect the carbocation in tertiary haloalkanes (bonded to three CH_3 groups) to be more stable than secondary haloalkanes (bonded to two CH_3 groups). Thus tertiary haloalkanes will proceed by S_N reactions, while primary haloalkanes reactions proceed almost exclusively by the S_N1 mechanism.

Reactions involving specific nucleophiles,

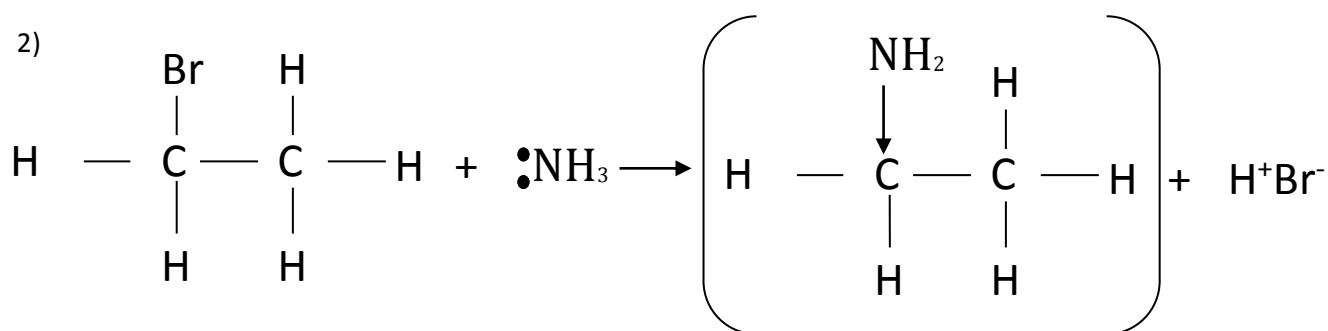
As we have discussed earlier a nucleophile can be represented by: Nu^- . We will now consider halogen substitution mechanisms by the following nucleophiles : $:OH^-$, $:NH_3$, O^-CH_3 , $:N \equiv N$, $CH_3CO_2^-$; on the haloalkane

Reaction with nucleophile $:OH^-$

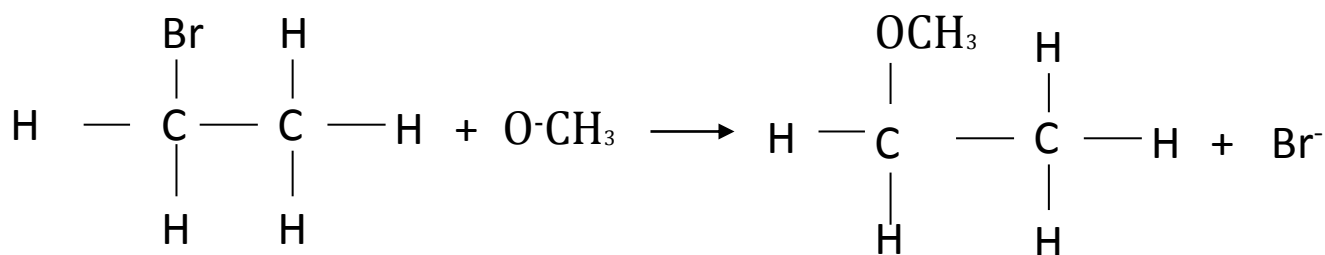


Reaction with nucleophile (diag)

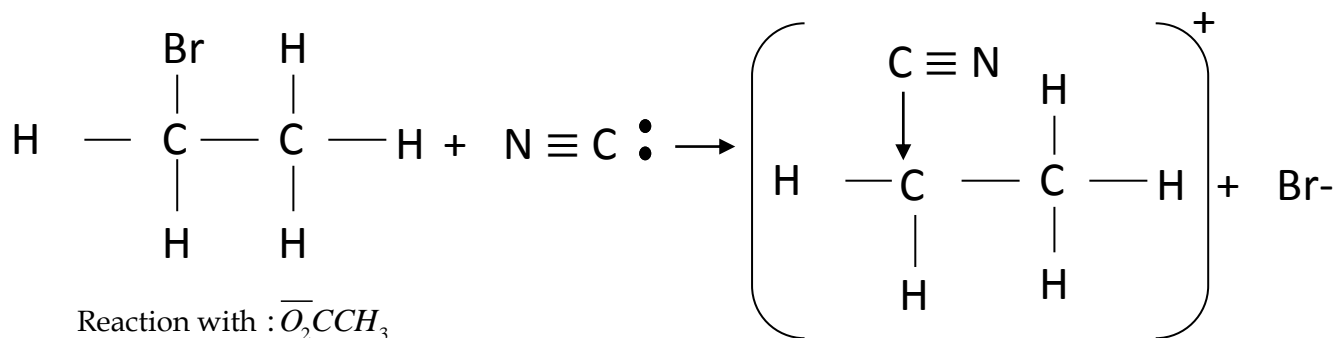
Reaction with nucleophile $:NH_3$



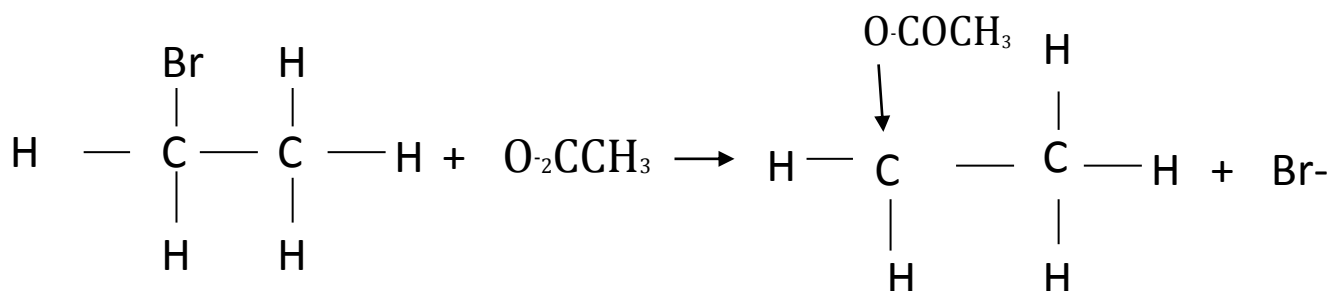
Reaction with O^-CH_3



Reaction with $N \equiv C$:

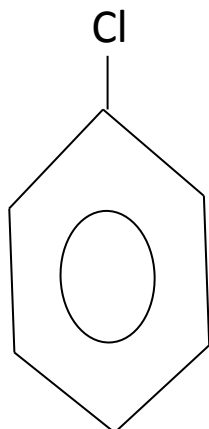


Reaction with $:\overline{\text{O}}_2\text{CCH}_3$

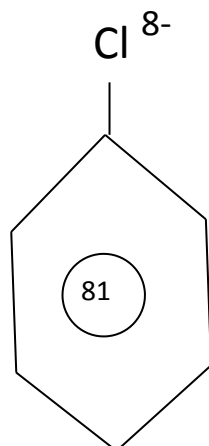


Reactions of halogenoarenes

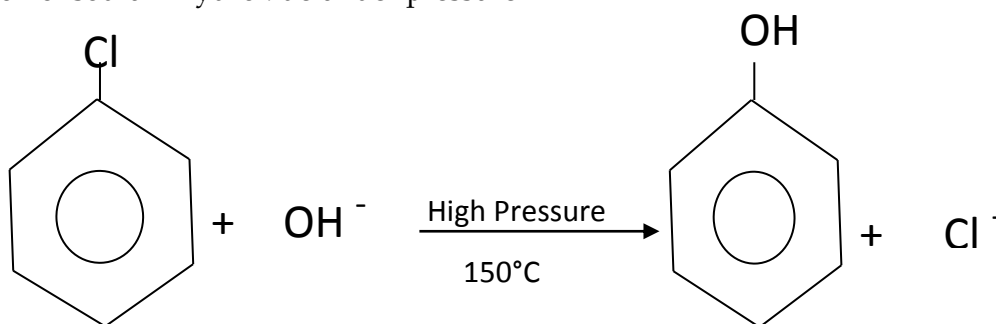
Consider a mono substituted haloarene like chlorobenzene



Chlorine has a strong affinity for electrons (see electronegativities) . Therefore we would expect it to draw away electrons from the electron rich benzene ring. This will make it possible for nucleophiles to attack the ring.



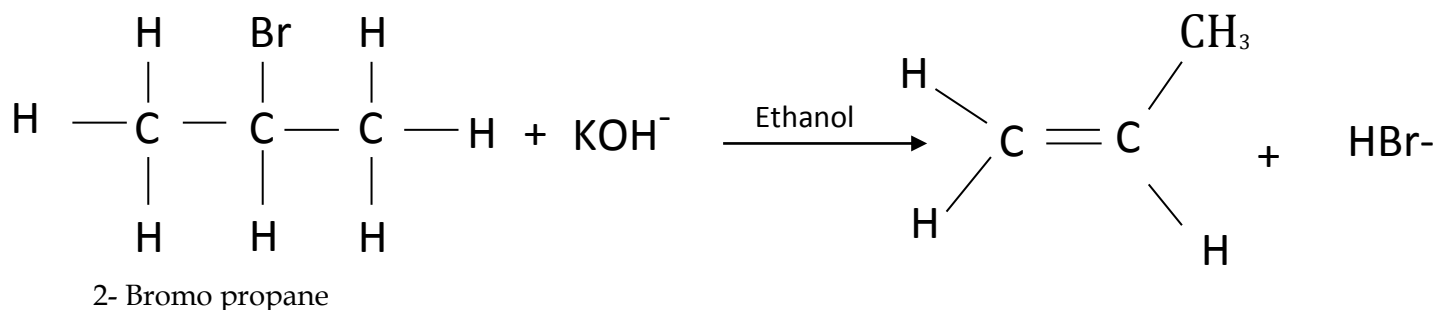
For example chlorobenzene can be hydrolysed by substitution to phenol when boiled with a solution of sodium hydroxide under pressure



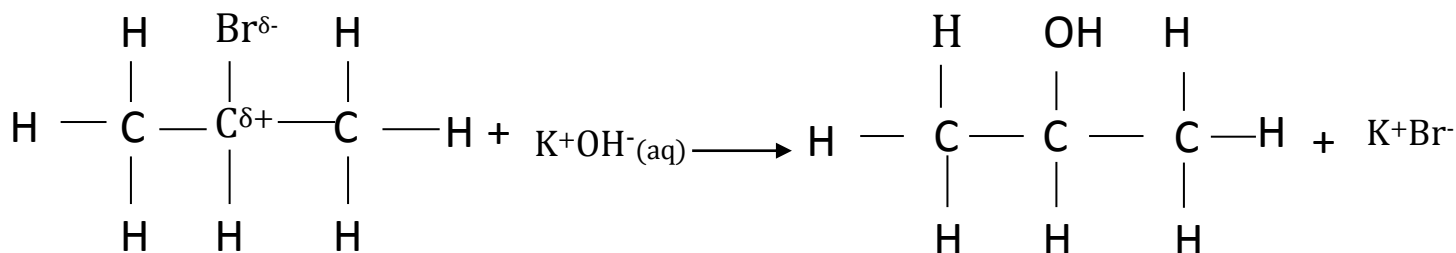
The substitution of chlorine by the :OH^- requires more drastic conditions than in chloroalkanes. This is because the C - X bond is shorter and stronger in chlorobenzene than in a chloroalkane. This makes the C - X bond in a chlorobenzene harder to break hence more severe conditions like heat and high pressure are required. Corresponding haloalkanes are hydrolysed more readily under room conditions.

Elimination reactions

Do you still remember what is meant by an elimination reaction? We will examine one of these reactions involving a haloalkane. You will find that in such reactions a small molecule is lost from a larger molecule resulting in the formation of a double bond. For example when 2 - bromopropane reacts with a mixture of hot KOH and ethanol, HBr is eliminated as the small molecule. The reaction mechanism is as shown.

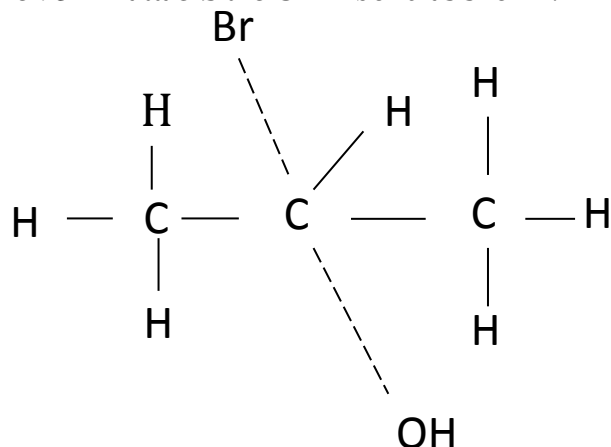


Notice that 2 - bromo-propane has lost the HBr molecule forming a double bond. However, if cold aqueous KOH is used, a substitution reaction occurs.



Elimination reactions can also be classified as first and second order. Elimination reaction involving 2 - bromopropane can proceed in two ways depending on conditions. The rate of

the reaction proceeding via carbocation is first order as it depends on the concentration of 2-bromopropane only. The reaction is designated E_1 , meaning it is a first order elimination reaction. However the reaction can also proceed via an activated complex in which the Br^- leaves as the $:\text{OH}^-$ attacks the C - H bond as shown.



The rate depends on the concentration of 2-bromo-propane and the $:\text{OH}^-$ nucleophile. Rate = k [2-bromopropane] $[\text{OH}^-]$ The order is 2 and is designated E_2 .

Uses of halogenoalkanes

Haloalkanes are unreactive compounds due to strong C - X bonds as seen from the bond energy table given earlier. The C - F bond energy is particularly high (467 kJmol^{-1}). Fluoro-chlorocarbons are unreactive and non-flammable. Generally their beneficial properties that make them useful are that they;

- are very stable and non-flammable.
- are not poisonous.
- have low boiling points.

The table shows some of the commonly used halocarbons.

Name of halocarbon	Molecular	Use(s)
Dibromo-dichloro methane	CCl_2Br_2	Fire extinguishers
Dichlorodifluoromethane	CCl_2F_2	Refrigerant, aerosol propellant
I - bromo - I - chloroethane	CHBrClCH_3	
2, 2, 2 - trifluoro ethane	$\text{CH}_3 - \text{CF}_3$	Anaesthetic
Chlorofluoro methane	CH_2ClF	solvent dry cleaning agent, degreaser

Disadvantage of using chlorofluoro-carbons.

Though these compounds are useful they are not readily decomposed when they escape into the atmosphere. This is because they are inert. However they have been found to break up into very reactive free radicals when subjected to atmospheric ultraviolet rays. These free radicals attack ozone (O₃) which forms a protective layer against harmful powerful ultraviolet radiation. 'Holes' have been found particularly at the earth poles where the ozone layer has been completely depleted by these free radicals. This exposes the earth's surface to harmful radiation. In some countries, the use of CFCs as refrigerants is prohibited.

Summary

1. In halogenoalkanes, the C - X is polar in which the carbon atom acquires a slight positive charge while the halogen (X) has a slight negative charge $C^{\delta+}-X^{\delta-}$.
2. Halogenoalkanes undergo substitution reactions in which the halogen is replaced by an incoming nucleophile.
3. Substitution reactions that proceed via the carbocation are first order and designated S_N1.
4. Substitution reactions that go via activated complex are second order and are S_N2 reactions.
5. Substitution reactions involving haloarenes need more drastic conditions to occur due to the strengths of the haloarene C-X bond.
6. Haloalkanes also undergo elimination reactions in which a haloacid (HX) is eliminated as a small molecule and a double bond formed, depending on conditions. Elimination reactions can be either E₁ or E₂.
7. Haloalkanes are inert due to the large C-X bond energy. They are used as anaesthetics, flame retardants in fire extinguishers, cleaning agents, as aerosol propellants and as refrigerants.
8. Haloalkanes deplete the ozone layer because they break up to produce highly reactive free radicals which attack the ozone molecules.

Study Questions

1. Name the following halogenoalkanes and give the displayed formula of each;
 - (a) C₃H₇Br
 - (b) C₃H₆BrCl
 - (c) C₃H₅Br₂Cl
 - (d) C₄H₇Br₂Cl
 - (e) CCl₃F
 - (f) CCl₂F - CClF₂

2. (a) Predict the products of the reaction between $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and NH_3 .
 (b) Explain in detail how these products are formed.
3. Four drops of 1 - chlorobutane are added to a test-tube standing in a water bath at 60°C . When a few drops of silver nitrate solution are added to the test tube, a cloudiness appears after 15 minutes
- (a) Given that silver ions Ag^+ form precipitates with halide ions X^- , explain the appearance of the cloudiness,
 (b) If the same procedure is carried out with 1 - bromobutane a precipitate forms after six minutes. Explain the difference in the time for the appearance of cloudiness and the appearance of a precipitate in the two halogenoalkanes. (Hint: bond energies $\text{C} - \text{Cl}$, 346; $\text{C} - \text{I}$ 284 kJmol^{-1} .)
4. In chlorofluoro carbons (CFCs) some of the hydrogen atoms have been replaced by chlorine and fluorine atoms. The formula of one CFC which boils at 17°C is $\text{CHClF} - \text{CHF}_2$ (X)
- (a) Suggest what this CFC is used for.
 (b) What environmental hazard is it likely to cause? Explain chemically how this hazard arises.
 (c) Explain why the boiling points of the following CFCs are likely to differ from that of X.
- | | |
|------------------|-------------------------------|
| CHClF_2 | $\text{CHClF} - \text{CCl}_3$ |
| CFC Y | CFC Z |
- (d) A CFC contains the following elements in percentages by mass
 C 17,8%
 H 1,5 %
 Cl 52,6%
 F 28.1%
 Given that M_r for the CFC is 138, find:
 (a) The empirical formula of the CFC.
 (b) The molecular formula of the CFC .

References

1. Hill G. and Holman J
Chemistry in Context
Thomas Nelson and Sons Ltd
Surrey: United Kingdom
3rd Edition
2. Lister T and Renshaw J
Understanding Chemistry
Stanely Thornes (Publishers) Ltd
Cheltenham, England
1994 Edition
3. Mc Murray J
Organic Chemistry
Cornell University, USA
ISBN 0 - 534- 01204-3
4. Cambridge 'A' Level Chemistry Syllabus
5. Zimsec 'A' Level Chemistry Syllabus
6. Cambridge 'A' Level Chemistry past paper.

CHAPTER 5

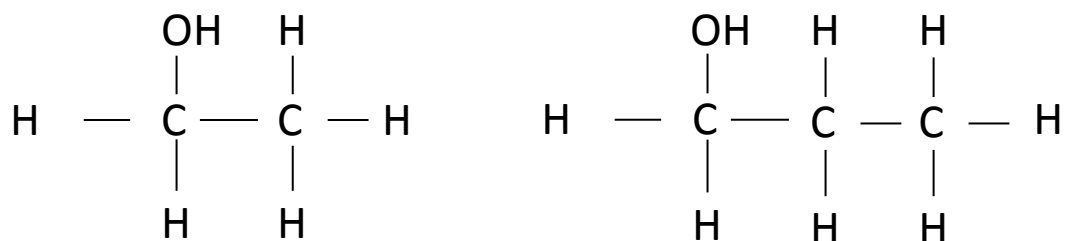
HYDROXY COMPOUNDS

By the end of this chapter you should be able to:

- a) recall the chemistry of alcohol exemplified by ethanol;
 - (i) combustion.
 - (ii) substitution to give halogenoalkanes.
 - (iii) reaction with sodium.
 - (iv) oxidation to carbonyl compounds and carboxylic acids.
 - (v) dehydration to alkenes.
 - (vi) ester formation.
- b) classify hydroxyl compounds into primary, secondary and tertiary alcohols.
- c) Suggest characteristic distinguishing reactions e.g mild oxidation.
- d) deduce the presence e.g $CH_3CH(OH)$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodonethane.
- e) Recall the chemistry of phenol as exemplified by the following reactions:
 - (i) with bases.
 - (ii) with sodium.
 - (iii) nitration and bromination of the aromatic ring.
- f) Explain the relative acidities of water, phenol and ethanol.

Introduction

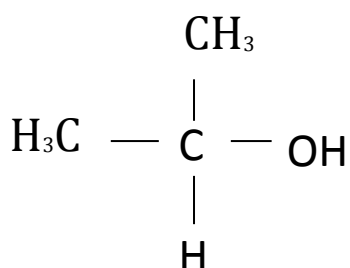
Alcohol, ethanol in particular has been used by humans for ages as an intoxicant. The first documents on the use of phenol was as a disinfectant by sailors. Structurally, both alcohols and phenols have $-OH$ as the functional group. In alcohols the $-OH$ group is bonded to a carbon chain while in phenols the $-OH$ is bonded to the benzene ring directly. Before we study alcohols and phenols in detail let us start by naming them.



Ethanol

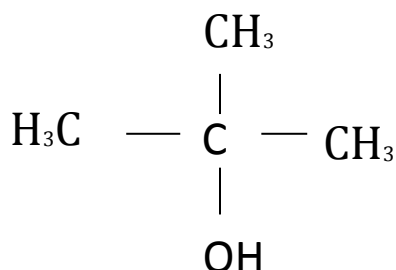
Propan-1-ol

In secondary alcohols designated 2^o, two CH_3 groups are bonded to the carbon atom carrying the $-\text{OH}$ group example



In tertiary alcohols designated 3^o, three CH_3 groups are bonded to the carbon atom carrying the $-\text{OH}$ group.

Example



2-Methylpropan-2-ol

Combustion of alcohols

Here we will confine ourselves to ethanol because of its use as a fuel in everyday life. You should be familiar with its use in blend petrol and as methylated spirit in burners. In excess oxygen, ethanol undergoes complete combustion to water and carbon dioxide.

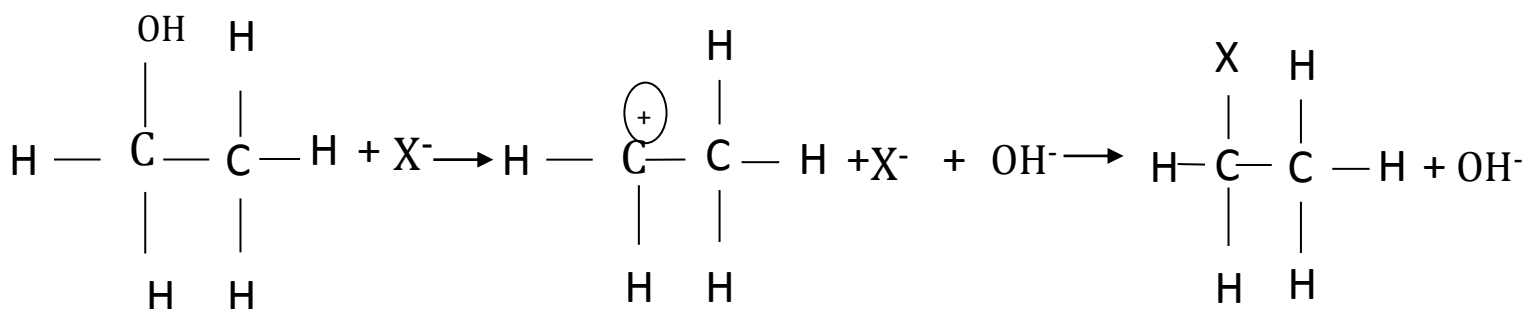


Reactions with halogen acids (HX)

Alcohols react with hydrogen halides to give halogenoalkanes. The acids are produced in the same reaction vessel by action of concentrated sulphuric acid on a sodium or potassium halide. The rate of reaction has been found to follow the order $HI > HBr > HCl$. Can you explain this trend in reaction rate? Chlorides or bromides of sodium or potassium are reacted to generate HCl or HBr . Iodides are not used as the concentrated H_2SO_4 readily oxidises the HI to iodine.

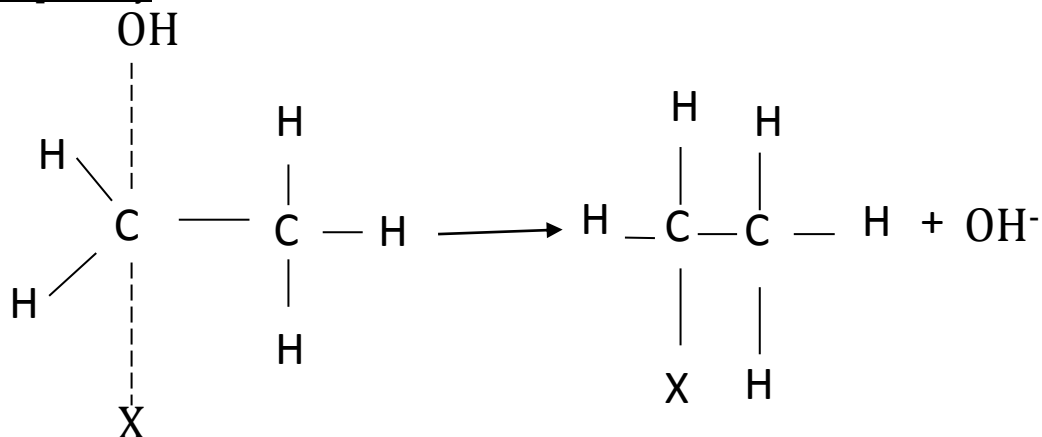
In these reactions, the $-OH$ is substituted by X^- and this can happen through two reaction pathways.

First pathway



As we saw earlier the reaction rate depends on the halogenoalkane, the concentration of the alcohol and whether or not the reaction proceeds via the carbocation. From what you have learnt what is the order of the reaction? The carbocation formation is the slow stage and therefore the rate determining. Notice that this reaction is S_N1 .

Second pathway



The reaction rate depends on the concentration of the X^- and on the concentration of the alcohol. Thus the reaction is second order.

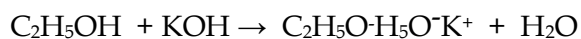
$$\text{Rate} = k[\text{alcohol}][\text{Halide}]$$

Notice that the reaction is S_N2

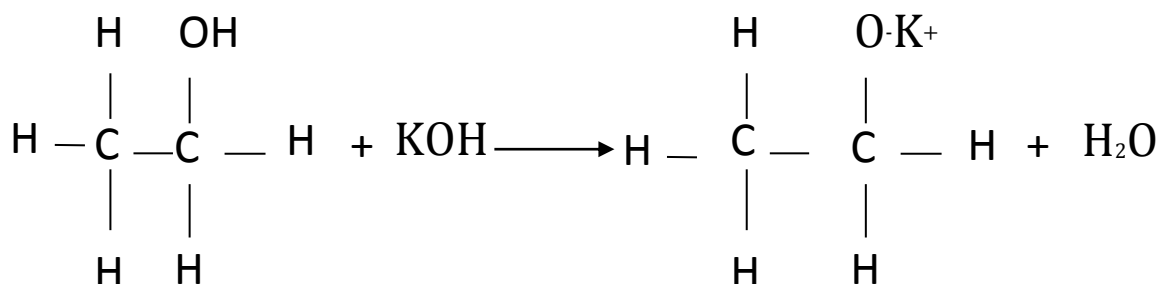
Reaction of alcohols (ethanol)

With sodium metal

Alcohols can behave as both acids and bases. This means they can accept and donate protons

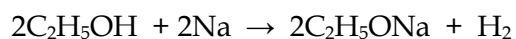


As an acid ethoxide ion $\text{C}_2\text{H}_5\text{O}^-$ is formed.



As a base.

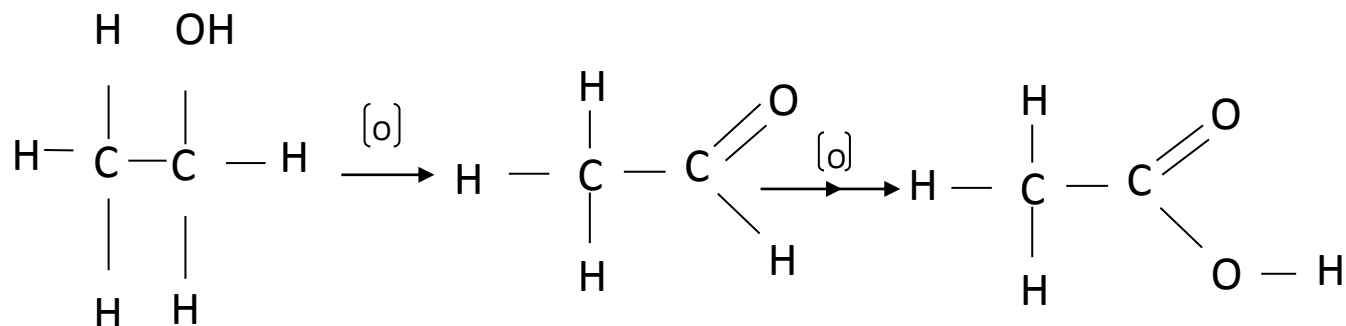
The reaction of ethanol with sodium metal shows the acidic property.



As you can see from the equation, hydrogen gas is evolved. This shows the acidic nature of ethanol. The reaction is also used to test for the presence of the $-\text{OH}^-$ group in an organic compound

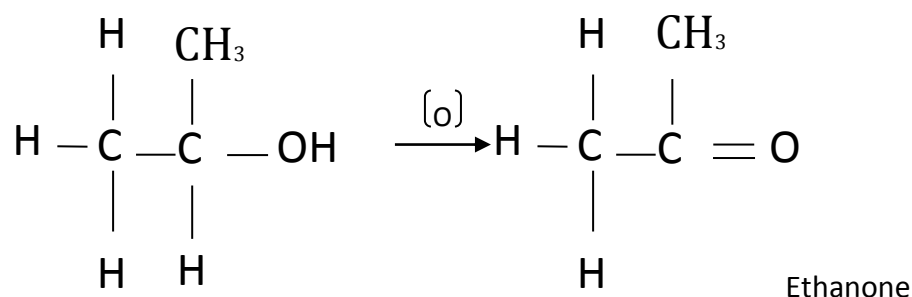
Oxidation of alcohol

Alcohols can be converted to aldehydes by the removal of hydrogen using mild oxidising agents like dichromate (VI) or manganate (VII) ions in acid solutions. Further oxidation of aldehydes yields carboxylic acids.



Secondary alcohols yield ketones on oxidation by removal of hydrogen. No further oxidation of ketones occurs.

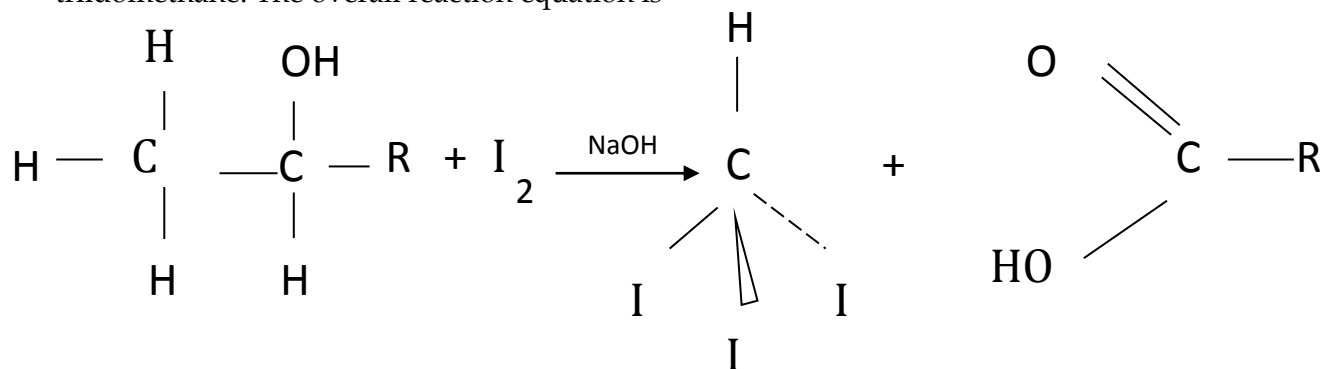
Example



We can use the above oxidation reactions of alcohols to distinguish between primary, secondary and tertiary alcohols. As we have seen, primary alcohols produce aldehydes on mild oxidation. Strong oxidation converts primary alcohols to carboxylic acids. Secondary alcohols give ketones on mild oxidation. However, ketones do not undergo further oxidation, tertiary alcohols resist oxidation altogether.

Alcohols can also be distinguished by the triiodomethane (iodoform) test. This test works with alcohols containing the $\text{CH}_3\text{CH}(\text{OH})$ - group so the test will work with ethanol and propan-2-ol. However, the test will not work with methanol or propan-1-ol. Can you see why the test will not work with methanol or propan-1-ol?

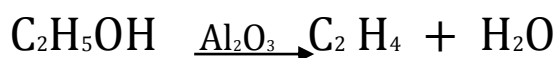
The iodoform test involves warming the alcohol with a sodium hydroxide solution containing iodine. Alcohols with the group $\text{CH}_3\text{CH}(\text{OH})$ will form a yellow precipitate of triiodomethane. The overall reaction equation is



Where R is an alkyl group or hydrogen

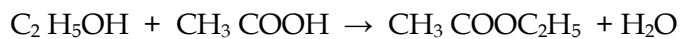
Dehydration of alcohols

As we saw earlier, alcohols can be dehydrated in the presence of heated aluminium oxide to produce alkenes. Let us look at the mechanism involved using ethanol as an example.

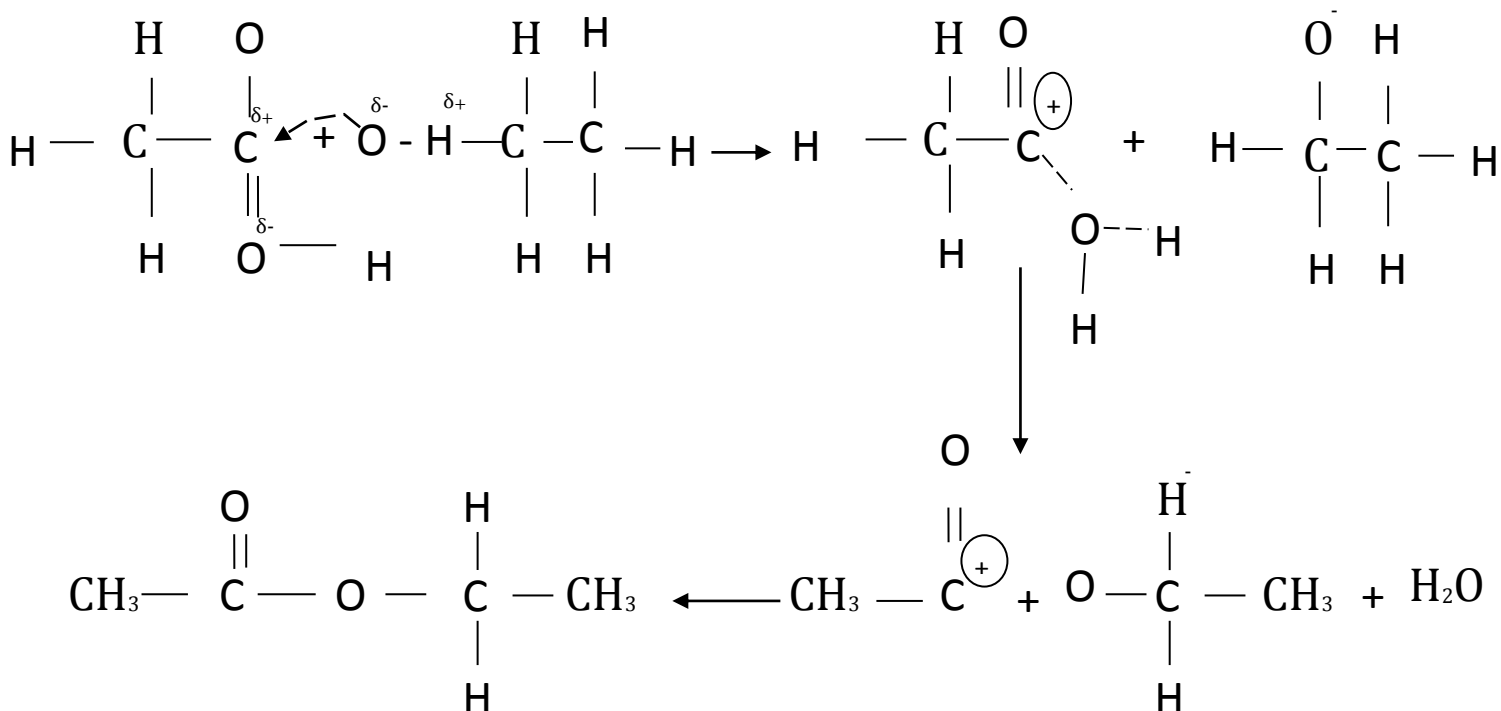


Esterification

Carboxylic acids react with alcohols in the presence of an acid catalyst to produce esters. Let us examine the reaction pathway in a reaction between ethanol and ethanoic acid. The overall reaction equation is shown.



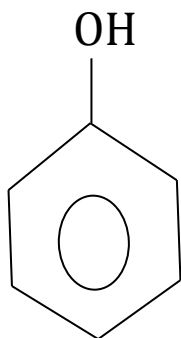
Reaction pathway



The reaction is thought to start with the protonation of the carboxylic acid followed by the elimination of a water molecule. The reaction shown above is slow and reversible.

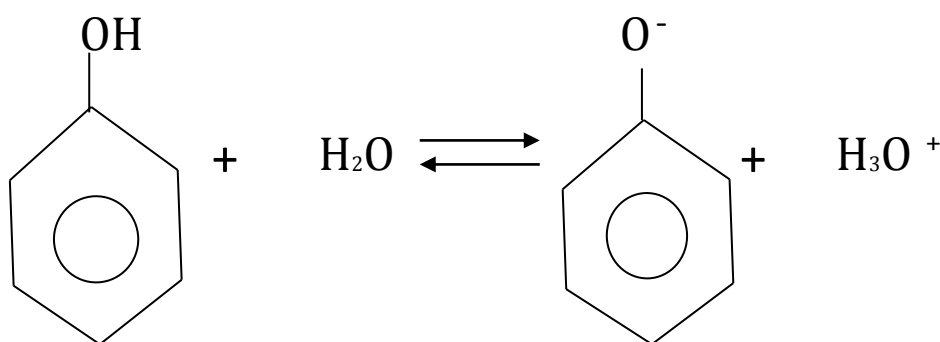
Chemistry of phenol

In this topic we will explore the reactions of phenol with bases and sodium, nitration and bromination in the ring. We will also compare the acidity of water, phenol and ethanol. Remember in a phenol molecule the OH group is attached directly to the benzene ring and this is in contrast to alcohol in which the OH group is bonded to an alkyl group.

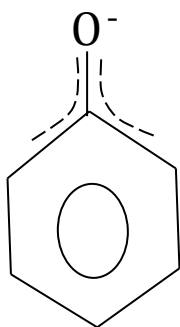


The antiseptic properties of phenol and its derivatives have been known since historical times. Phenol in tar was used to prevent infection after surgery. Today we use it in soaps and disinfectant agents as carbolic acid. Reaction of phenol with bases.

In an aqueous solution phenol behaves as an acid.

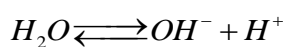
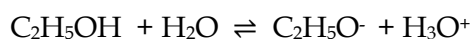


The phenoxide ion is stabilised by the delocalisation of the charge on the oxygen in the benzene ring.



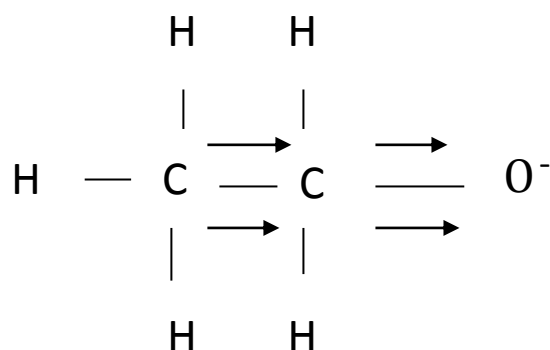
Acidity of phenol, ethanol and water.

We have seen above that phenol is acidic in an aqueous solution. How does the acidity of phenol compare with that of ethanol and water. Let us see how ethanol behaves in an aqueous solution and compare with water.



You will notice from the equation that water and ethanol also behave as weak acids. However, the charge on the oxygen of the ethoxide ion is not delocalised in the alkyl group.

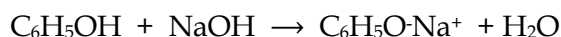
Moreover, the CH_3 group has a tendency to press electrons towards the ethoxide oxygen (positive inductive effect).



This reduces the acidic nature of the ethoxide but increases its basicity. Thus phenol will behave as a stronger acid than ethanol. The same reason above makes ethanol less acidic than water.

Reaction of Phenol with Bases.

We have just seen that phenol behaves as an acid. How then does it react with bases? Let us examine its reaction with a base like NaOH.



Reaction of Phenol with Sodium

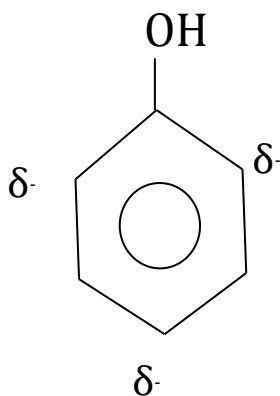
Phenol will react with sodium readily producing hydrogen.

Although sodium also reacts with ethanol releasing hydrogen, the reaction is less vigorous than when sodium reacts with water and phenol. We should expect this from the comparative acidities of water, phenol and ethanol. So in terms of acidity we have phenol > water > ethanol.

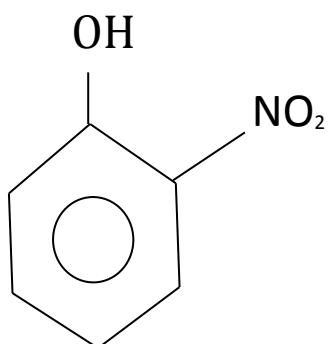
Nitration of Phenol

Phenol reacts with dilute nitric acid readily to produce a nitrophenol. Compare this reaction with nitration of benzene alone which required heating with a mixture of concentrated nitric acid and sulphuric acid.

We have discussed the delocalisation of the charge on oxygen of the phenol in the ring. This makes the ring a strong nucleophile at the ring carbons 2, 4 and 6. Thus the nitronium/nitryl group, NO_2^+ from nitric acid bonds at the position 2, 4, and 6. Notice that all these are electrophilic substitution reactions.



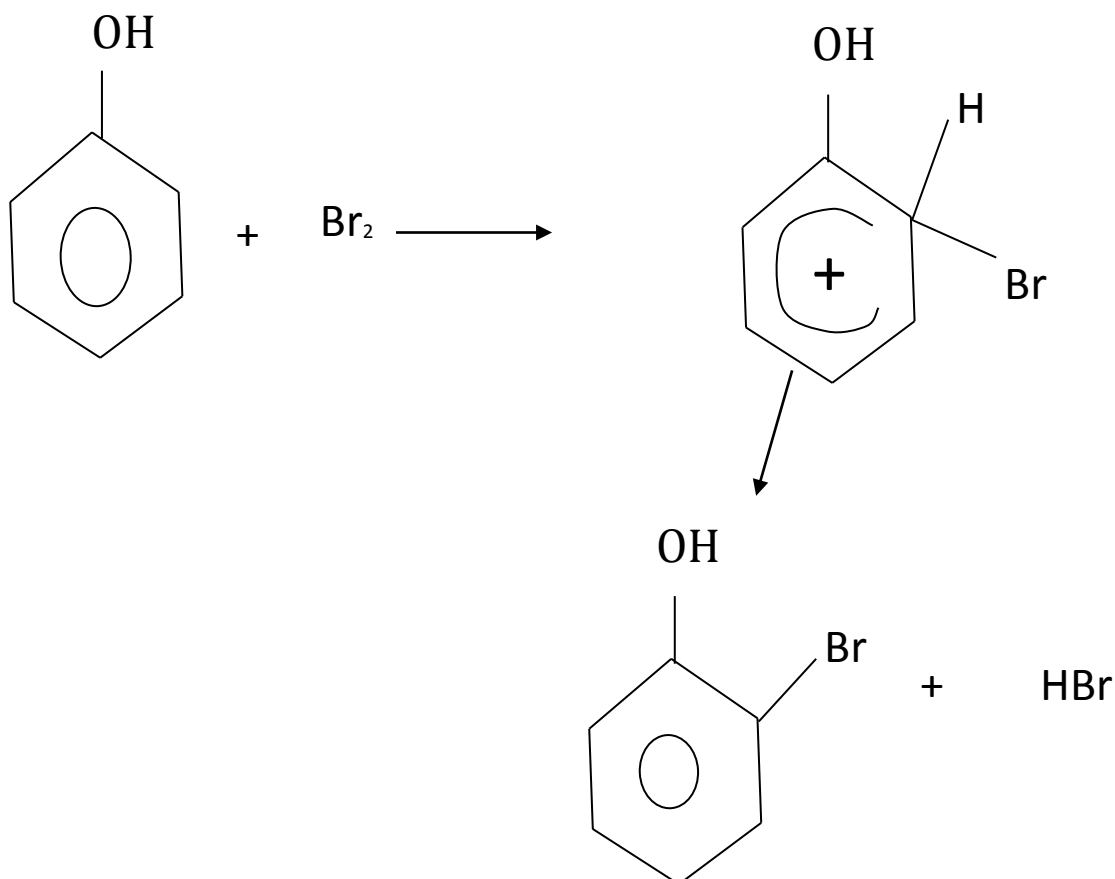
Looking at the nitro group we find that it tends to draw electrons away from the ring



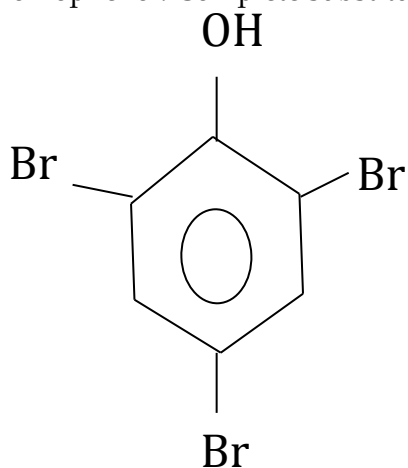
Thus further nitration of the ring will be more difficult and hence formation of 2,4,6 nitrophenol will require drastic conditions like heating with concentrated nitric and sulphuric acids.

Bromination of phenol

Aqueous bromine will react readily with phenol at room temperature to produce 2,4,6 tribromo-phenol. Hence there is no need for a catalyst. Compare this reaction with that of bromine and benzene.



Further bromination occurring at the 4 and 6 carbons by the same mechanism gives 4-bromophenol and 6-bromophenol. Complete substitution yields 2,4,6-tribromophenol.



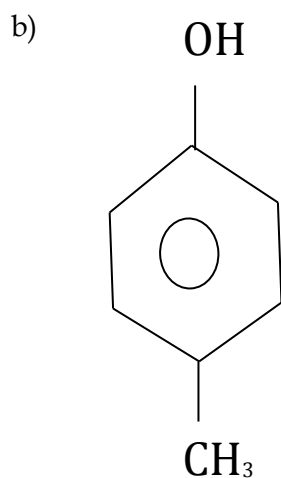
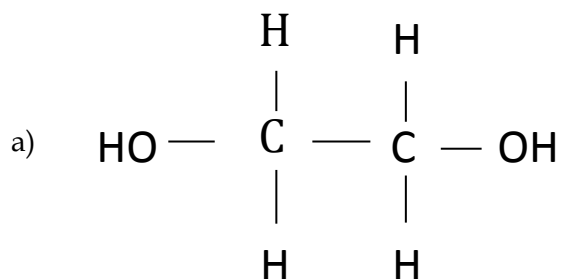
Summary

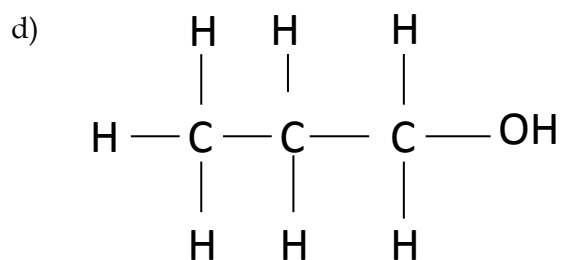
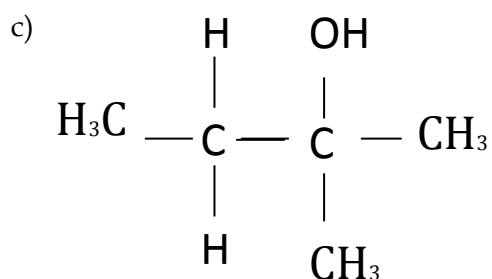
1. In alcohols the -OH group is bonded to an alkyl group.
2. In primary alcohols the -OH is bonded to a carbon atom attached to one CH_3 group.
3. In secondary alcohol the -OH is bonded to a carbon atom attached to two CH_3 groups.
4. In tertiary alcohols the -OH is bonded to a carbon atom attached to three CH_3 groups.

5. Alcohols undergo nucleophilic substitution of the $-OH$ with a halogen when reacted with a halogen acid.
6. Ethanol reacts with sodium to produce sodium ethanoate and hydrogen.
7. Mild oxidation of primary alcohol produces aldehyde and carboxylic acid whereas oxidation of secondary alcohols gives ketones only. Mild oxidation has no effect on tertiary alcohols.
8. Complete combustion of ethanol produces water, carbon dioxide and energy.
9. Alcohols undergo dehydration to alkenes.
10. Alcohols react with carboxylic acids to give esters.
11. The presence of the $CH_3CH(OH)-$ group in an alcohol is shown by heating the alcohol with alkaline aqueous iodine to form a precipitate of tri-iodomethane.
12. The phenoxide ion is stabilised by delocalisation of charge in the benzene ring.
13. The relative acidity is phenol $>$ water $>$ ethanol.
14. Phenol reacts with bases to give phenoxides and water. They react with sodium to give a phenoxide and hydrogen gas.
15. Nitration and bromination of phenol occurs on the ring by nucleophilic substitution to give nitro and bromo-phenols.

Examination Type Questions

1a) Name the following;





2. Give the displayed formulae of;

a) 2-chloropropan-1-ol.

b) 2-bromo-2methylbutan-1-ol.

c) 2,4-dinitrophenol.

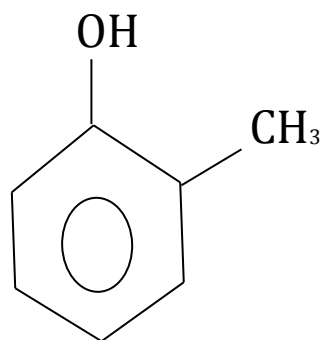
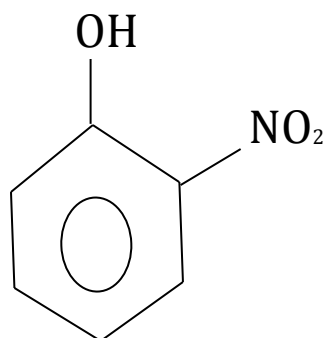
3. Explain how the reactions of the following alcohols differ on;

a) mild oxidation.

b) reacting with sodium metal .

(i) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{CH}_3)$ (ii) $\text{C}_2\text{H}_5\text{OH}$ (iii) $\text{C}_6\text{H}_5\text{OH}$

4) Given that $-\text{NO}_2$ has a negative inductive effect and $-\text{CH}_3$ a positive a inductive effect, compare the acidity of the following;

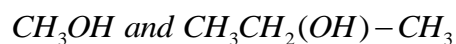


Explain your answer

5. Show the reaction mechanisms for converting,

- a) Ethanol to ethene.
- b) Ethane to dibromoethane.
- c) Phenol to 4-bromophenol.
- d) Phenol to sodium phenoxide.

6. Explain how you would distinguish between the compounds.



REFERENCES

1. Hill G. and Holman J.
Chemistry in Context
Thomas Nelson and Sons Ltd
Survey: United Kingdom
3rd Edition
2. Lister T and Renshaw J
Understanding Chemistry
Stanley Thornes (Publishers) Ltd
Cheltenham: England
1994 Edition
3. Mc Murray J.
Cornell University USA
ISBN 0-534-01204-3
4. Cambridge 'A' Level Chemistry syllabus
5. Zimsec 'A' Level Chemistry Syllabus

CHAPTER 6

CARBONYL COMPOUNDS

At the end of this chapter you should be able to:

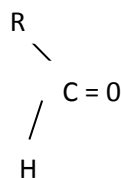
- describe the formation of aldehydes and ketones from primary and secondary alcohols using $Cr_2O_7^{2-} / H^+$.
- describe the reduction of aldehydes and ketones using $NaBH_4$.
- describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.
- describe the use of 2, 4-dinitrophenyl-hydrazine (2,4- DNPH) to detect the presence of carbonyl compound.
- deduce the nature (aldehydes or ketones) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollen's reagents; ease of oxidation).
- describe the reaction of CH_3CO- compounds with alkaline aqueous iodine to give tri-iodomethane.

Introduction

Carbonyl compounds are characterised by the functional group $C = O$. They form part of some biological molecules and used in medicines such as painkillers. In this chapter we will discuss two types of carbonyl compounds, aldehydes and ketones. In the general formula of aldehydes, the carbon in $C = O$ is bonded to a hydrogen atom and alkyl group.

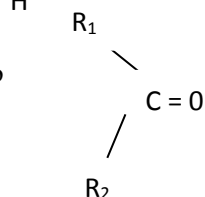
The general displayed formula is

(Where R is the alkyl or aryl group)



In Ketones on the other hand the group

(Where R_1 R_2 are alkyl or aryl groups)

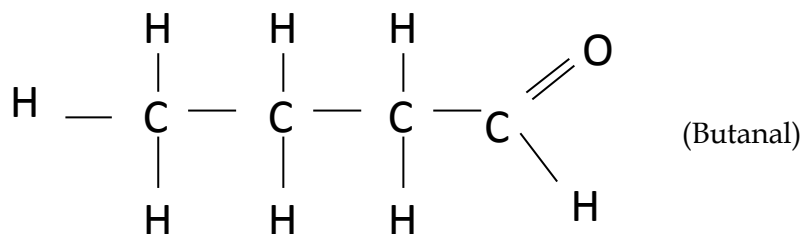
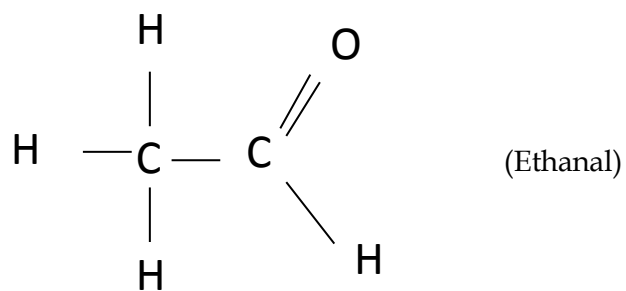


is bonded to two alkyl group.

Naming aldehydes and Ketones

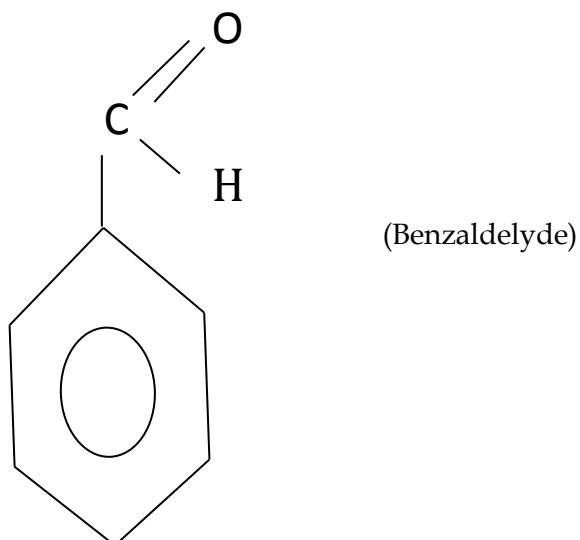
In aldehydes -al is suffixed to the stem of the main group, the carbon of the functional group being counted as part of the stem.

Example: (where R is an alkyl group)

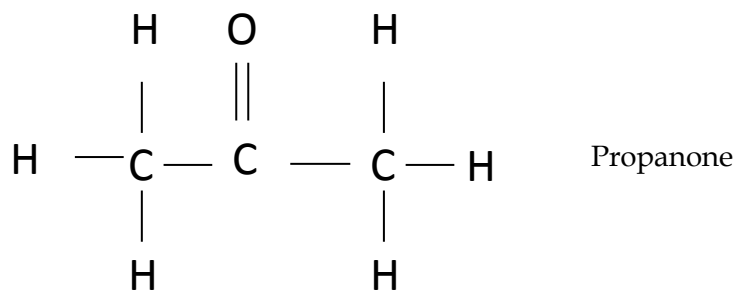


Notice that the group (OH) is at the end of the molecule

Example: (where R is an aryl group)

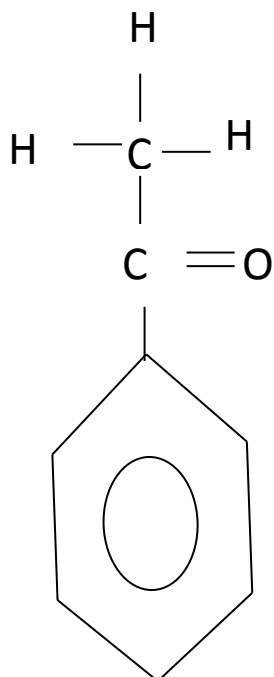


Example (when R and R¹ are alkyl groups)



Notice that the functional group appears inside the molecule

Example (where R is alkyl and R¹ aryl)

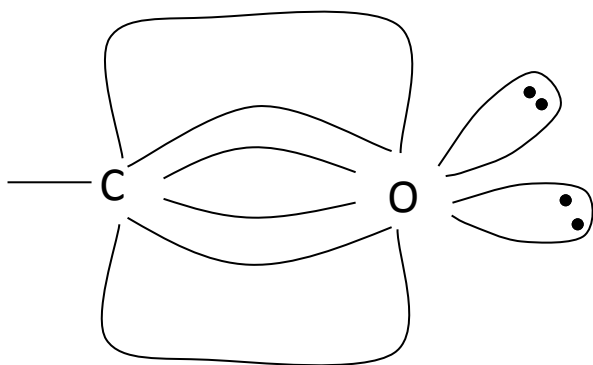


Phenylethanone

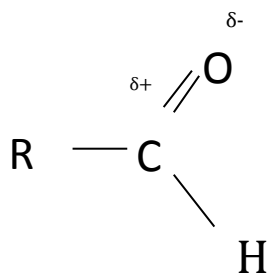
Structure of the carbonyl functional group:

It is important that we start by discussing the electronic structure of the double bond because this has a bearing on how the double reacts.

As you saw with alkenes, the bonds are formed from sp^2 hybridised orbitals from the carbon atom. The unhybridised 2p orbital forms the π bond.

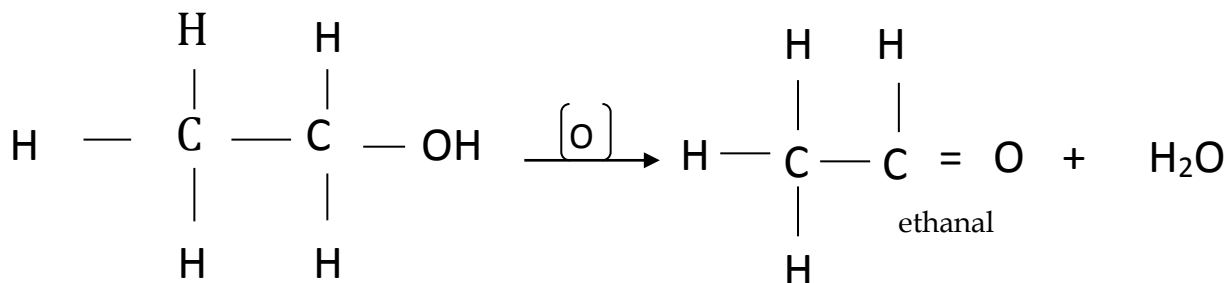


Due to the greater electronegativity of oxygen over that of carbon the bond electrons are drawn towards the oxygen making it slightly negative. The carbon then becomes electron deficient becoming slightly positive.

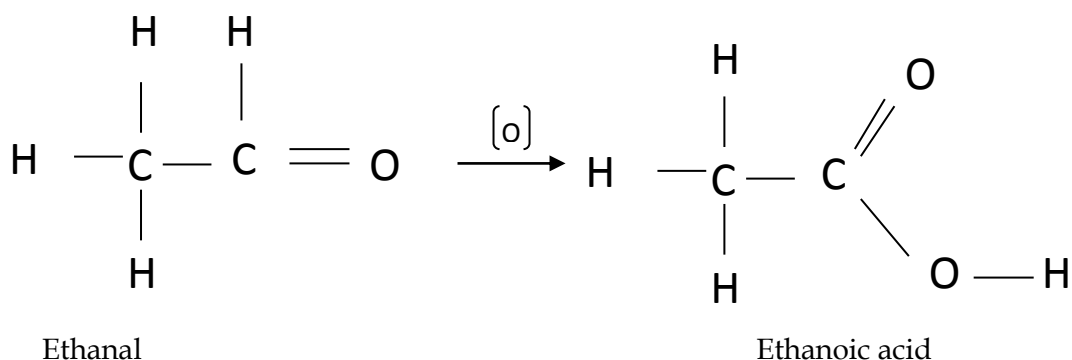


Formation of aldehydes and ketones from primary and secondary alcohols respectively was covered in the previous chapter. Do you still remember the reaction conditions? Here we will only explore the reaction mechanisms.

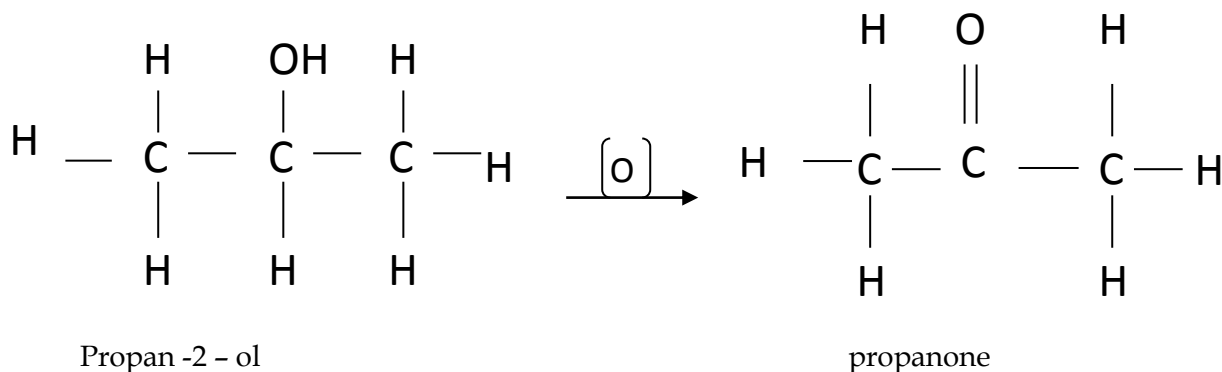
Aldehyde ()



As you can see from the equation that the reaction is an elimination reaction. The reaction is thought to start with the attack of the $\text{Cr}_2\text{O}_7^{2-}$ on the $-\text{OH}$ groups of the alcohol. A hydrogen atom is removed by the $\text{Cr}_2\text{O}_7^{2-}$. This is followed by the removal of the second hydrogen resulting in the $\text{C}=\text{O}$ double bond formation. Notice that in this case oxidation involves removal of hydrogen. Further oxidation converts the aldehyde to a carboxylic acid.



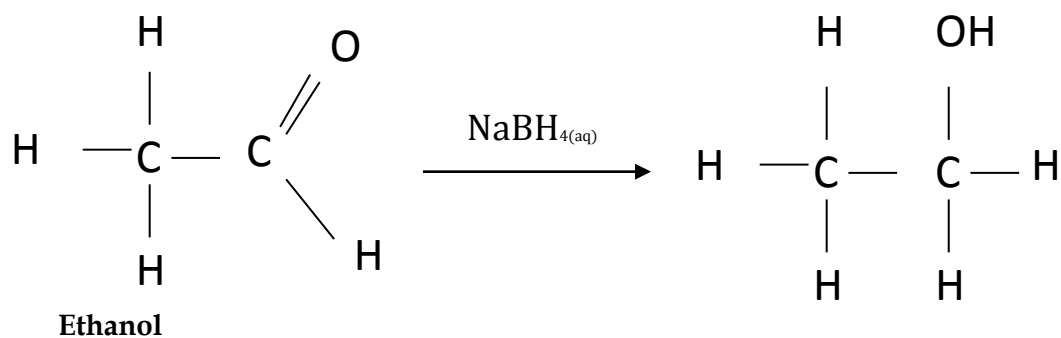
Ketone formation



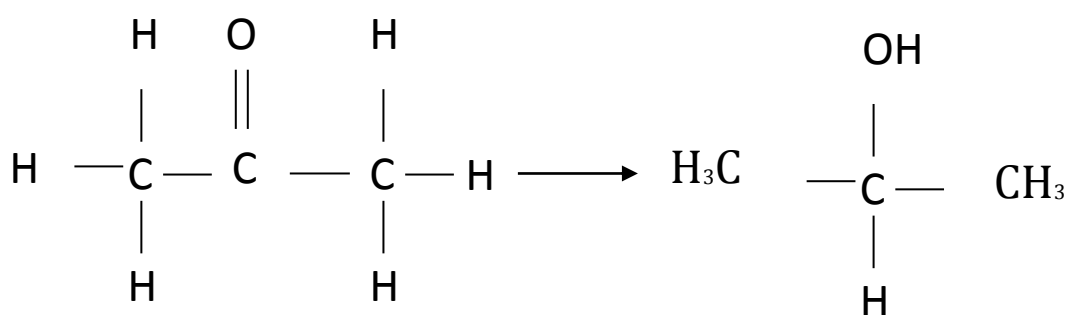
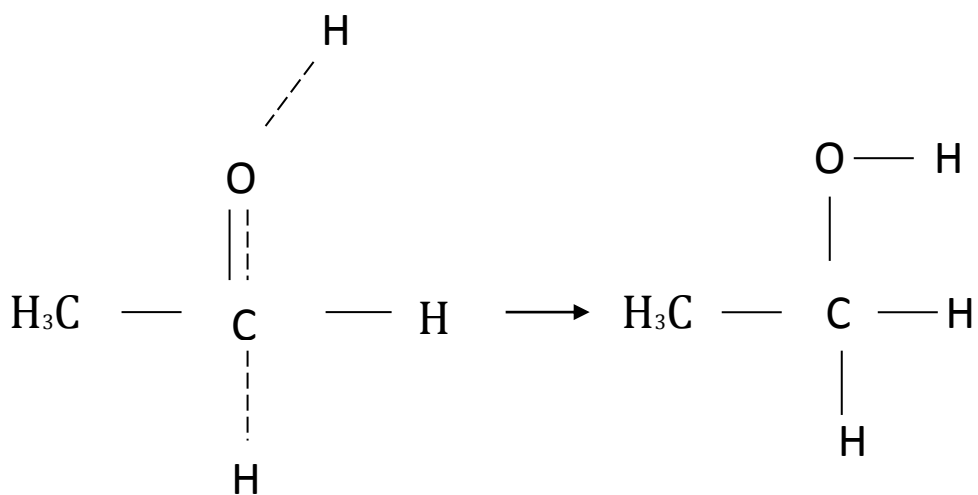
Formation of an aldehyde, is an elimination reaction.

Reduction of aldehydes and Ketones.

In these reactions reduction involves the addition of hydrogen from sodium tetrahydrido borate (iii) (NaBH_4)

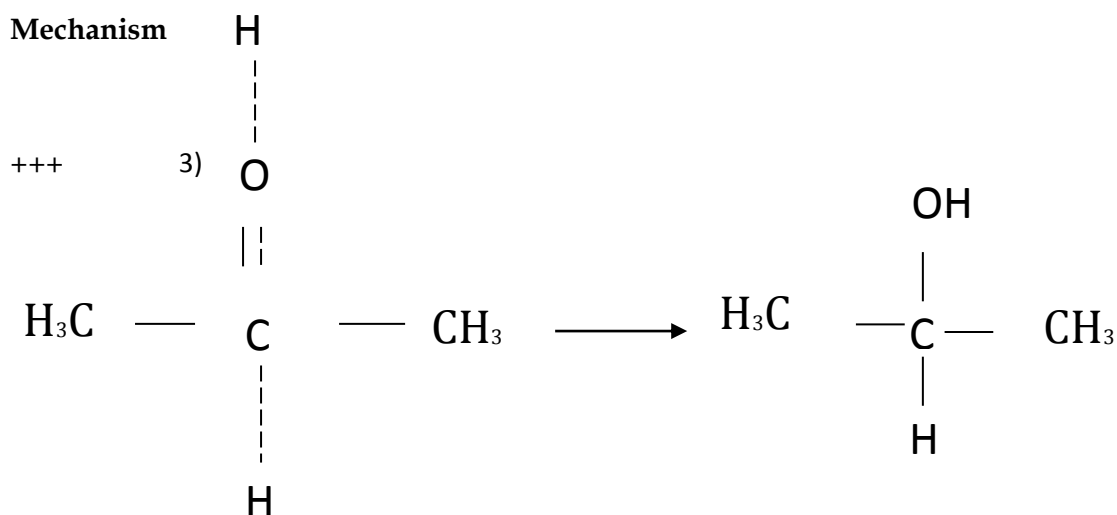


Mechanism



Propanone

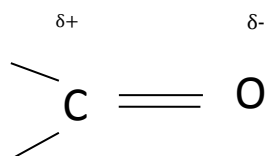
propan - 2 - ol



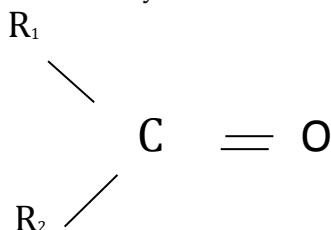
Notice that both reactions involve a OH^- nucleophile and an H^+ electrophile. In the above reactions one would expect reduction of the aldehyde to proceed faster than that of propan-2-ol. Can you suggest why this is likely? (Hint: effect of the CH_3 inductive effect).

Nucleophilic additions

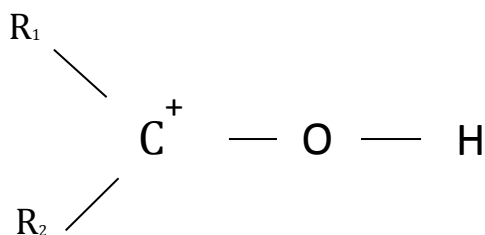
Before we go into a discussion of these reactions we will revisit the $\text{C}=\text{O}$ double bond. As indicated earlier, the double bond is polar, that is the carbon is slightly positive while the oxygen is slightly negative.



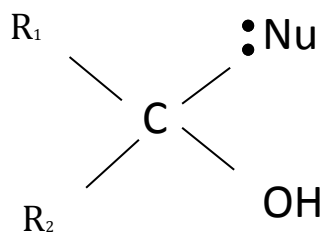
Do you still remember the reason for this polarity? (Hint: Electronegativity of oxygen). We can represent carbonyl bond in an aldehyde as follows.



Under reaction conditions a carbocation is formed from the protonation of O

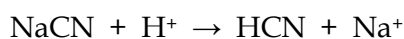


The carbocation is attacked by a nucleophile ($:Nu$) followed by protonation of oxygen.



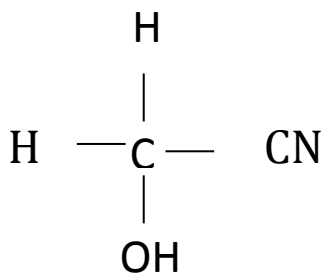
The mechanism of reaction of an aldehyde with hydrogen cyanide (HCN) from the reactions above should be pretty clear. In this reaction hydrogen cyanide is generated from a mixture of sodium cyanide and acid.

Mechanism:



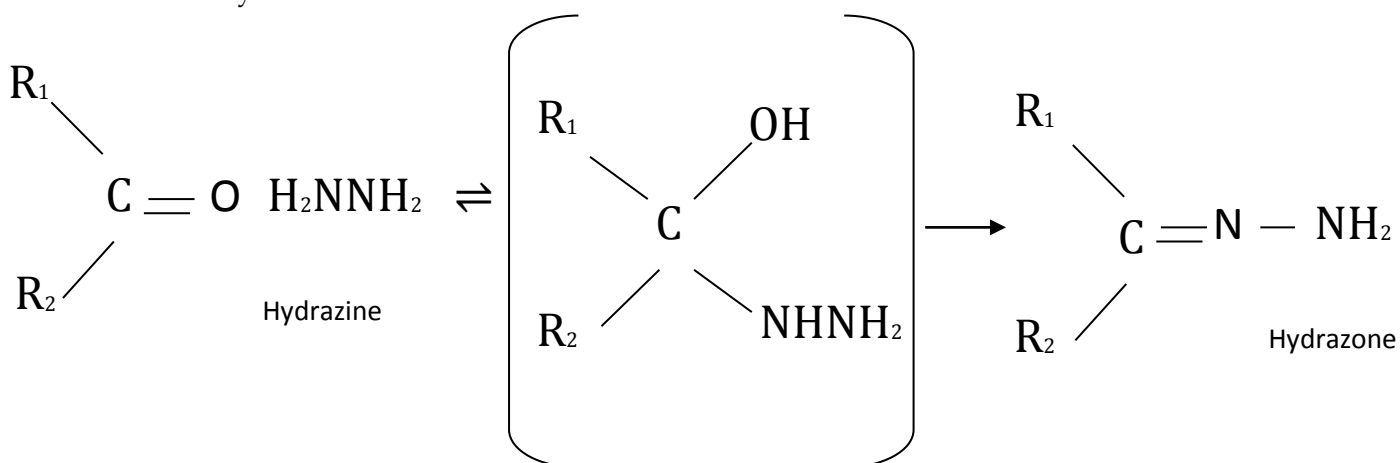
Reaction with Ketones.

Mechanism



2 - Hydroxynitrile

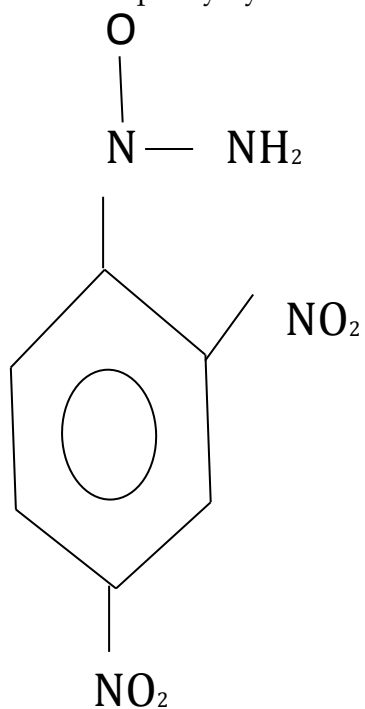
Reaction of a carbonyl with hydrazine N_2H_4 . The hydrazine molecule is the nucleophile with an aldehyde.



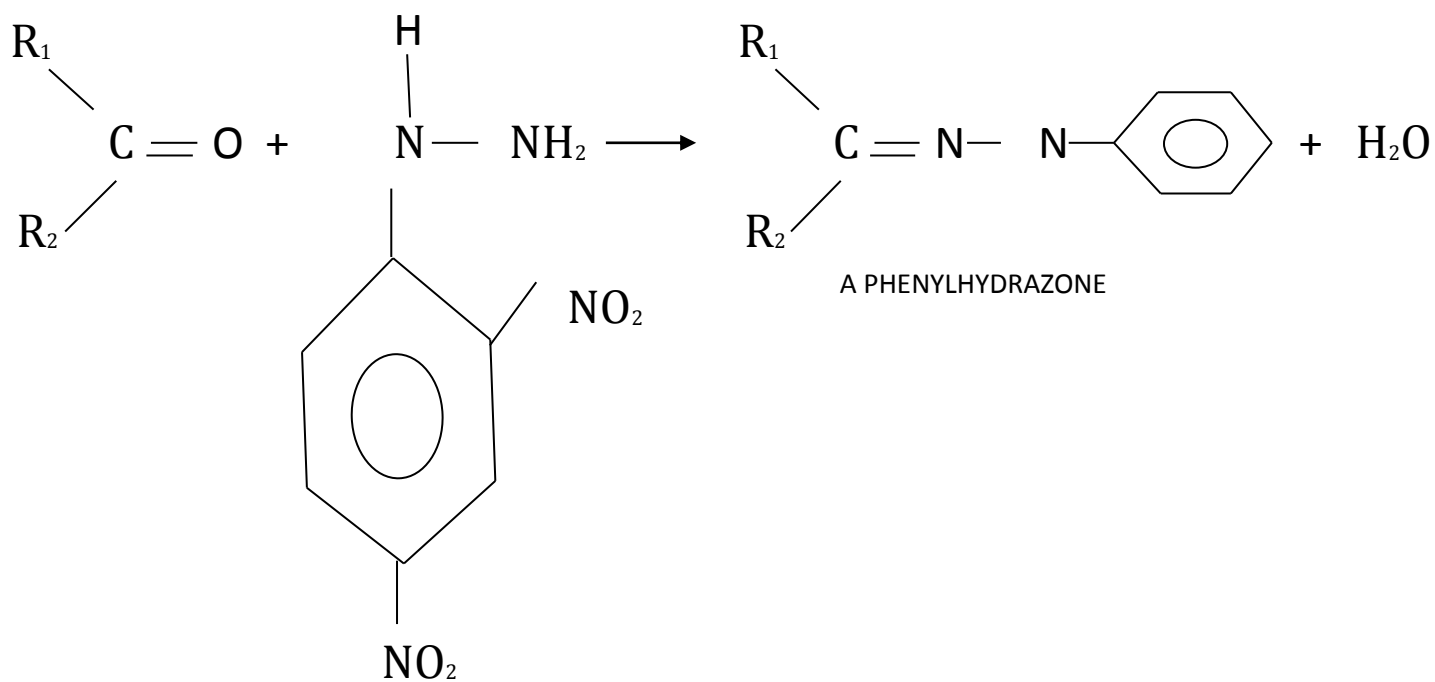
This is an addition - elimination reaction because there is addition of the = NNH₂ and elimination of H₂O.

Reaction with 2,4-dinitrophenyl-hydrazine

The 2,4-dinitrophenylhydrazine is the nucleophile



Reaction with carbonyl compounds

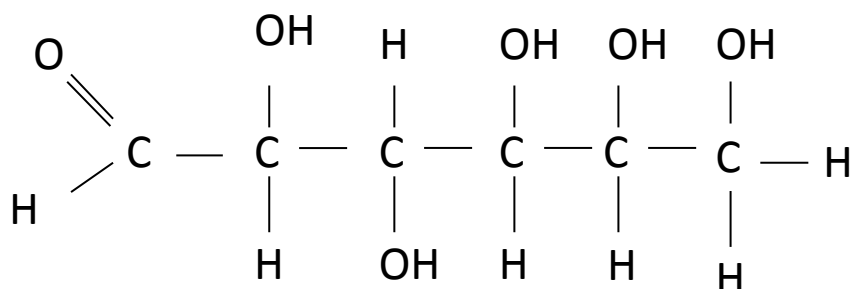


2,4-dinitrophenylhydrazine

The nucleophile 2, 4 - dinitrophenylhydrazine is used to detect the presence of carbonyl compounds . with which it forms orange crystals of 2,4 - dinitrophenylhydrazone.

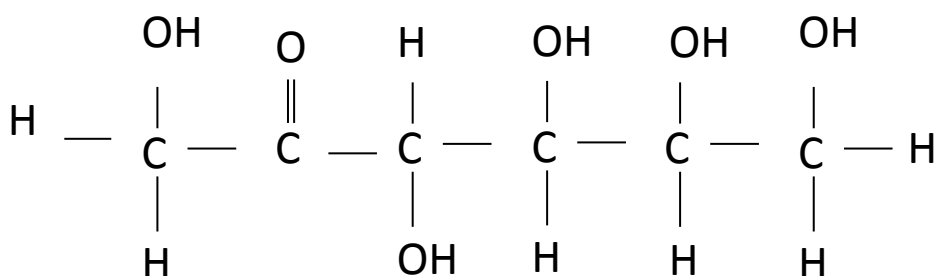
Testing for aldehydes and Ketones: Fehlings' solution.

You should be familiar with Benedict's or Fehlings' solutions as standard tests for reducing sugars. This is basically a test for the presence of the aldehyde group in these sugars. In this reaction as you know the copper (II) is reduced to copper (I) oxide, a brick red precipitate.



Glucose

Sucrose on the other hand does not react with Fehlings' solution and therefore does not contain the aldehyde group. Fructose is a Ketone but because it is partially converted to glucose on heating does give a positive test with Fehling's solution.



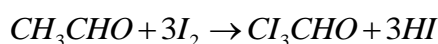
Fructose

The presence of an aldehyde group can also be tested using Tollen's reagent. Basically, the reagent is a mild oxidizing agent which converts an aldehyde to a carboxylic acid. The reagent consists of a mixture of silver oxide and ammonia, and on heating the mixture with an aldehyde in a test tube, silver is deposited on the walls of the test tube.

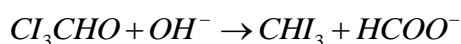
This shiny deposit is called a silver mirror. Ketones on the other hand are not affected by mild oxidizing agents. However, if they are heated with strong oxidising agent the C - C bond next to the C - O group breaks to form smaller carboxylic acids.

The tri-iodomethane test

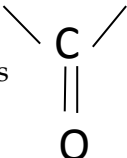
When tri-iodomethane is formed in a reaction between an organic compound and alkaline aqueous iodine, it shows that the organic compound contains the group $\text{CH}_3\text{CO}-$ group.



The carbon-carbon bond breaks in the presence of an alkaline to form triiodomethane

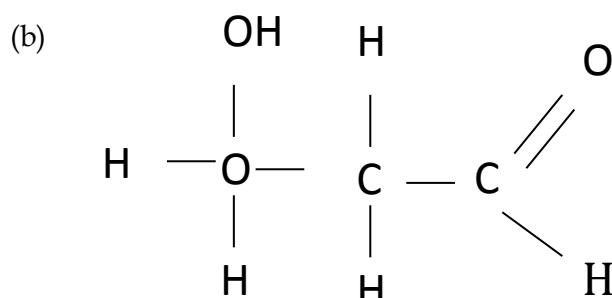
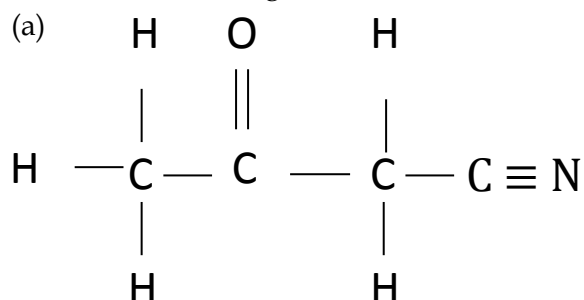


Summary

- The aldehyde functional group is -CHO and that of ketones is 
- Aldehydes are formed from primary alcohols by mild oxidation.
- Ketones are produced by mild oxidation of secondary alcohols.
- Aldehydes can be reduced to primary alcohols by reduction with sodium Tetrahydrido borate (iii) ($NaBH_4$).
- $NaBH_4$ is used to reduce ketones to secondary alcohols.
- Aldehydes and ketones undergo nucleophilic addition reactions with hydrogen cyanide, hydrazine and 2,4-dinitrophenyl hydrazine DNP is also used to test for the presence of the carbonyl group.
- Fehlings' solution and Tollens' reagent are used to test for aldehydes in order to distinguish between reducing sugars (aldoses) and non-reducing (ketoses)

Examination Type Questions

1. Name the following



2. Give the displayed formulae for the following :
- Butan-1-ol
 - Pentan-2-one
 - Methanol
3. Show the reaction mechanisms and products of the following reactions.
- $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} + \text{acidified } \text{Cr}_2\text{O}_7^{2-}$
 - $\text{CH}_3 - \text{CH}_2 - \text{C} + \text{HCN}$
 - $\text{CH}_3 - \text{CH}_2 - \text{C}$
 - $\text{CH}_3 - \text{CH}_2 - \text{C}$
 - $\text{CH}_3 - \text{C} - \text{CH}_3 + \text{HBr}$
4. From the following compounds, identify those that will give a pale yellow precipitate when warmed with alkaline aqueous iodine:
- CH_3COCH_3
 $\text{CH}_3\text{CH}_2\text{CHO}$
 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
 $\text{CH}_3\text{CH}_2\text{OH}$
 $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

For the compounds which give a precipitate, write the structural formulae of the organic products.

REFERENCES

- Hill G and Holman J
 Chemistry in Context
 Thomas Nelson and Sons Ltd
 Surrey. United Kingdom
 3rd Edition
- Lister T and Renshaw J.
 Understanding Chemistry
 Stanely Thomas (Publishers) Ltd
 Cheltenham: England
 1994 Edition
- Mc Murray J
 Organic Chemistry
 Cornell
 ISBN 0 - 53 - 012 04 - 8
- Cambridge 'A' Level Chemistry Syllabus
- Zimsec 'A' Level Chemistry Syllabus

CHAPTER 7

Organo- Nitrogen Compounds

At the end of this chapter you should be able to:

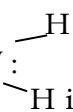
- a) describe the formation of ethylamine (by nitrile reduction) and phenylamine (by reduction of nitrobenzene).
- b) explain the basicity of amines.
- c) explain the relative basicities of ammonia, ethylamine and phenylamine in terms of their structure.
- d) describe the reaction of phenylamine with:
 - i) aqueous bromine.
 - ii) nitrous acid to give the diazonium salt and phenol.
- e) describe the coupling of benzenediazonium chloride and phenol and the use of similar reactions in the formation of dyestuff.
- f) describe the formation of amides from the reaction between RNH_2 and $RCOCl$.
- g) describe the acid/base properties of amino acids and the formation of zwitterions.
- h) describe the amide hydrolysis on treatment with aqueous alkali or acid.
- i) describe the formation of peptide bonds between amino acids and hence explain protein formation.
- f) describe the hydrolysis of proteins.
- k) describe the formation of polyamides.

Introduction

Nitrogen is found in a wide range of organic compounds found in nature. Proteins which are found in plant and animal materials contain nitrogen. Some by products of metabolism in living organisms also contain nitrogen. Some of these nitrogen compounds find use as medicines (drugs) and polymers. These compounds are thus manufactured on a large scale. Research is very active in this area and led to the discovery of new drugs and polymers.

In this chapter, however, we will focus on the chemistry of selected groups of compounds. These groups will include amines, amides, nitriles, amino acids and proteins.

Amines

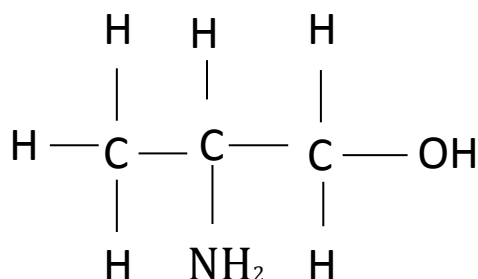
The functional group is N :  in which the nitrogen is bonded to an alkyl group or phenyl group. You will notice that the nitrogen carries a lone pair of electrons.

Naming Amines

Amines are derived from the ammonia molecule (NH_3) in which the hydrogen atoms are replaced by other groups (alkyl) or aryl) The amines are named after these groups, alkylamines or aryl amines. You will notice that the suffix amine is used in conjunction with the carbon chain or ring.

Carbon chain/group	Formula	Amine	Formula
<i>Methyl</i>	CH_3	<i>methylamine</i>	CH_3-NH_2
<i>Ethyl</i>	C_2H_5	<i>ethylamine</i>	$C_2H_5NH_2$
<i>Phenyl</i>	C_6H_5	<i>phenylamine</i>	$C_6H_5NH_2$

Notice that the amine group appears at the end of the molecule. However, if the NH_2 group appears within the main molecule the name of the molecule is prefixed with amino- for example the molecule is 2-aminopropan-1-ol. The locant 2 giving the position of the carbon atom to which the NH_2 group is attached in the alcohol molecule.



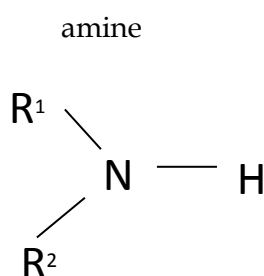
Classification of amines

Amines are classified as primary (1°), secondary (2°) and tertiary (3°). Which other group of compounds were classified similarly? As indicated earlier the hydrogen atoms in ammonia are replaced by alkyl or aryl groups one at a time. In a primary amine, one hydrogen is replaced by one alkyl group R.

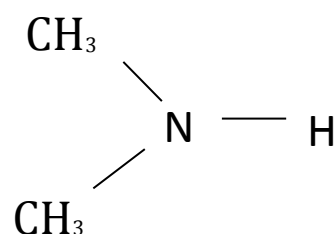


In a secondary amine two hydrogens are replaced example

No. of H
Replaced
2



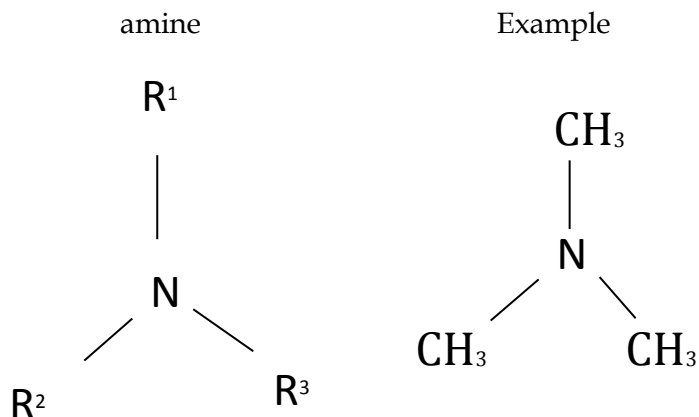
Example



In a tertiary amine all three hydrogens are replaced

Examples

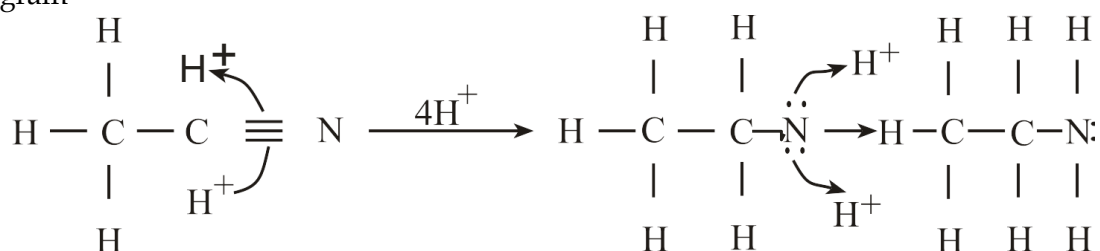
No. of H
3°



Formation of an amine (Ethylamine)

Amines can be prepared by reacting a nitrile (R-CN) with a strong reducing agent for example $LiAlH_4$ (lithium tetrahydridoaluminate). Hydrogen alone or produced in the reaction mixture can be used as a reducing agent in the presence of a catalyst. The reaction involving the formation of ethylamine is

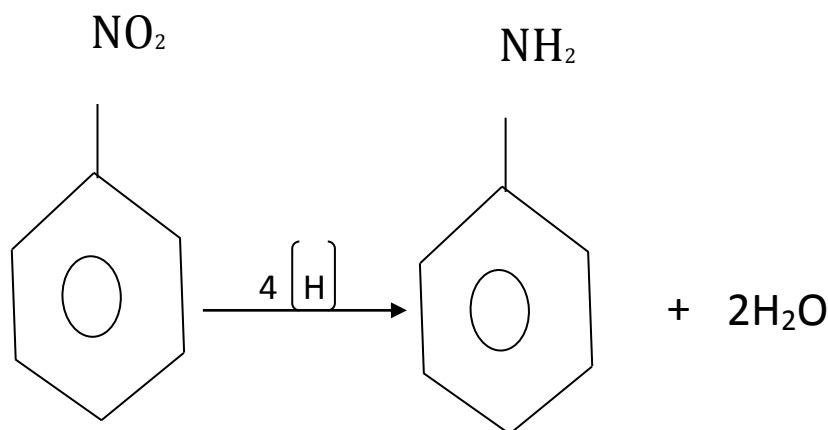
diagram



We can see from the equation that the reaction involves protonation due to the two π bonds. Notice that a carbon atom has been added to the chain

Formation of phenylamine

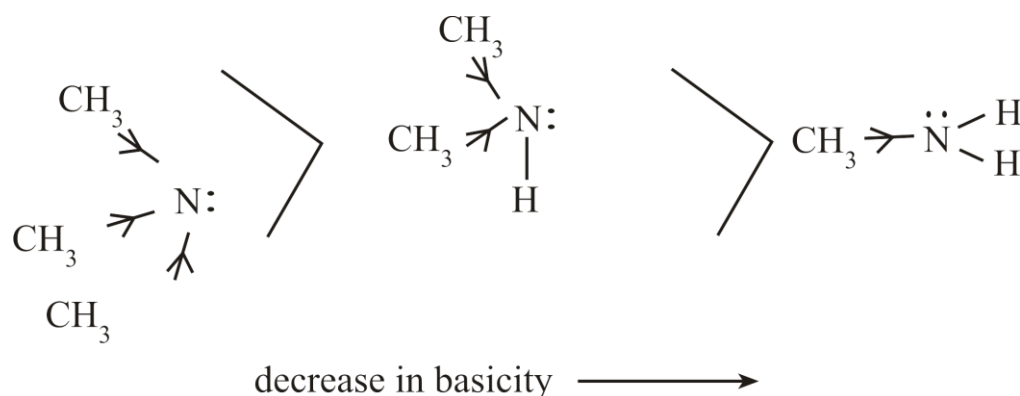
In this reaction nitrobenzene is reduced. This reaction is similar to that of the production of a primary amine. The reducing agent is the same lithium tetrahydridoaluminate (iii) or hydrogenation in the presence of a catalyst.



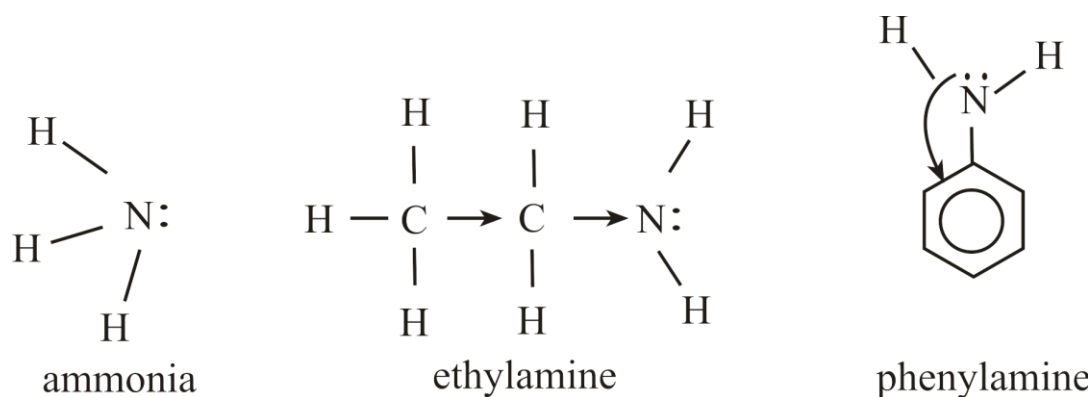
As you can see from the equation, the reaction involves removal of oxygen.

Basicity of Amines

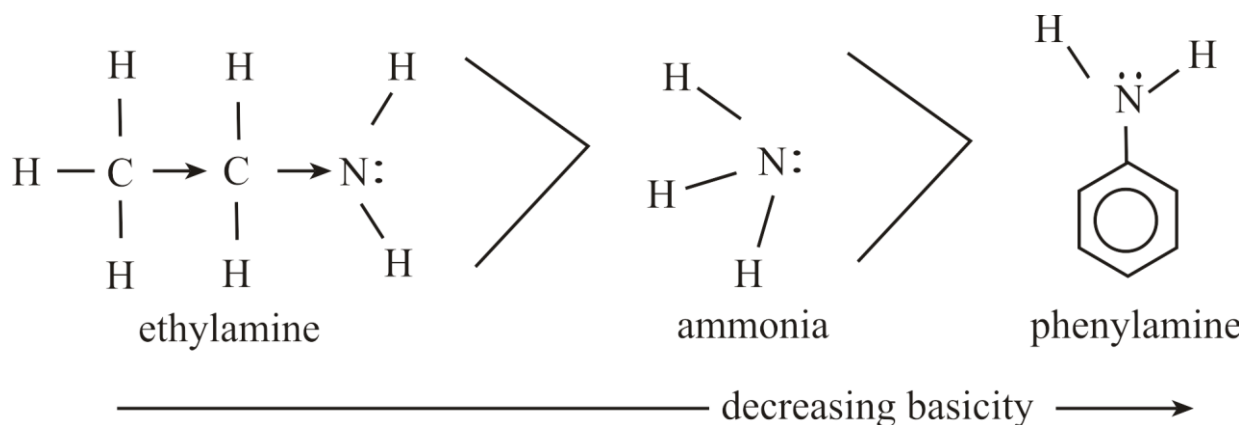
As already indicated the nitrogen in the amine carries a lone pair of electrons which can form a dative bond with a proton. The readiness with which this lone pair forms a dative bond is a measure of the basicity of the amine. The more readily the lone pair is donated, the more basic the amine. However, electron releasing groups like CH_3 will enable the amine group to donate electrons more readily, that is, making it more basic. We would then expect an amine with two CH_3 groups to be more basic than that with one CH_3 . Similarly the amine with three CH_3 groups will be the most basic. The basicity can be arranged as:



Relative basicity of ammonia, ethylamine and phenylamine. The molecules are:

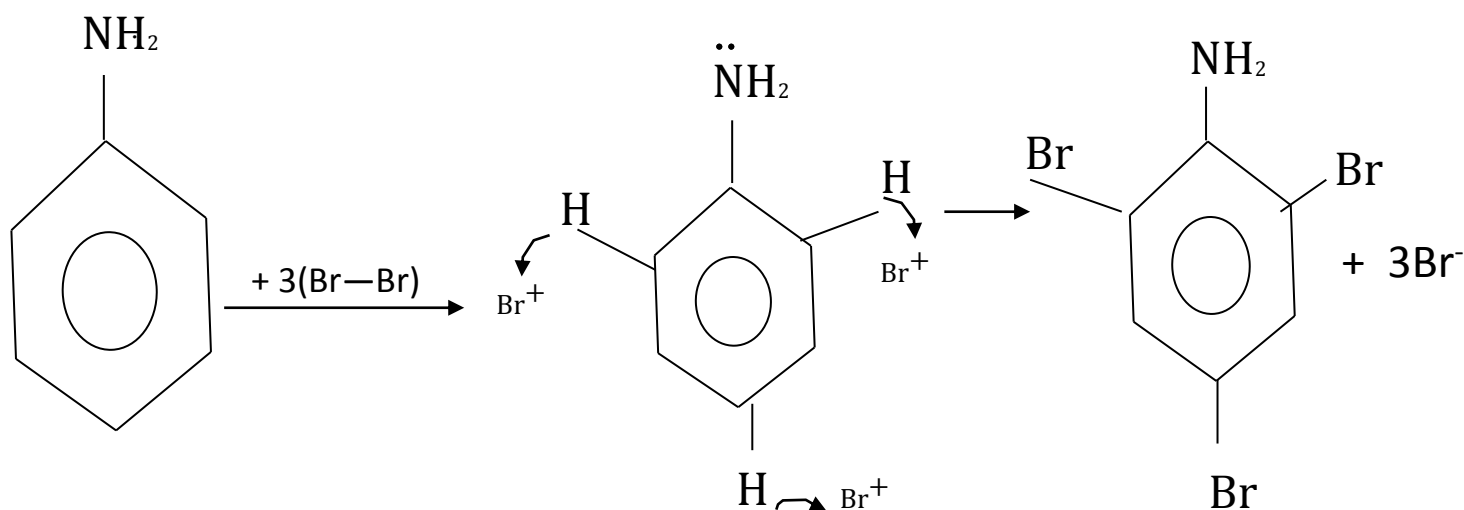


As you notice from the molecular structures, ethylamine carries an electron releasing group CH_3 which will make the amine group more basic. However, the phenylamine molecule carries a benzene ring with its delocalized π electrons. The lone pair of electrons on the amine nitrogen will merge with the π electrons of the ring and be delocalized as well. The delocalized pair will be enhanced by the near flat pyramidal structure of the phenylamine. The lone pair of the nitrogen will then be less available for dative bond formation with an incoming electrophile. The order of basicity is therefore as follows:



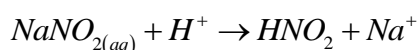
Reactions of phenylamine

The reaction of arylamines with bromine can be illustrated with the reaction of bromine with phenylamine. We have already seen that the lone pair on the nitrogen is delocalized in the benzene ring making the ring electron rich. This makes the ring more prone to attack by electrophile than the benzene molecule. Thus, aqueous bromine will react with phenylamine readily without the need for a catalyst.

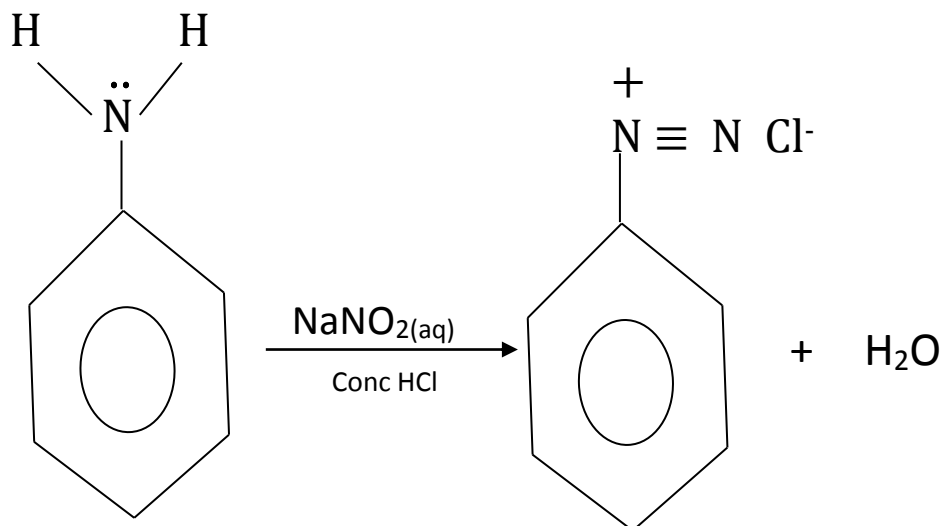


Reaction of Phenylamine with Nitrous acid.

The nitrous acid is generated from acidifying sodium nitrite.

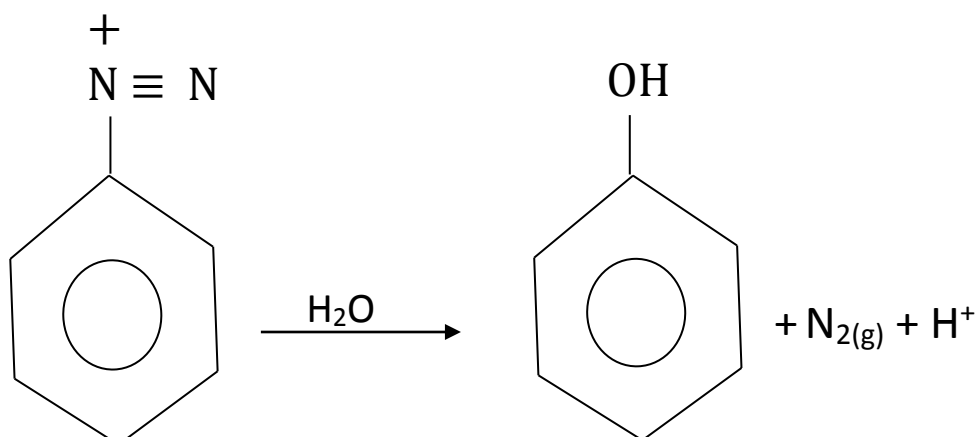


A cold solution of sodium nitrite is added to a mixture of phenylamine and concentrated hydrochloric acid. The equation of the reaction is:



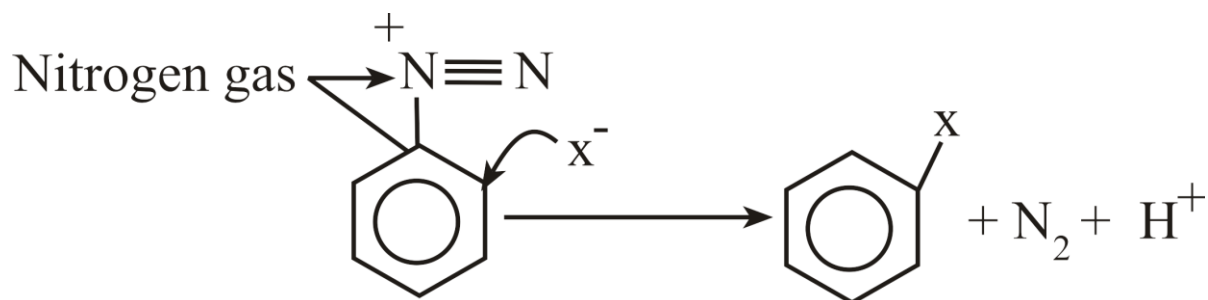
The compound formed is a phenyldiazonium chloride. The phenyldiazonium ion is unstable at room temperature so the reaction mixture must be kept as a solution below 5°C. At a higher temperature and in the solid state the diazonium ion decomposes explosively releasing nitrogen gas and phenol. However, in solution the positive charge on the nitrogen stabilizes the diazonium ion by spreading into the benzene ring.

Decomposition of the phenyldiazonium ion.



Diazonium-Phenol Coupling.

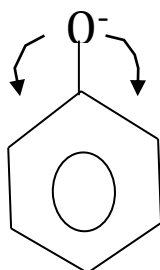
As we have already seen the positive charge on the ion $N^+ \equiv N$ spreads into the benzene ring making it positive. Hence the ring will be open to attack by nucleophiles resulting in a substitution reaction. For example, halide ions will attack the diazonium ion releasing nitrogen gas



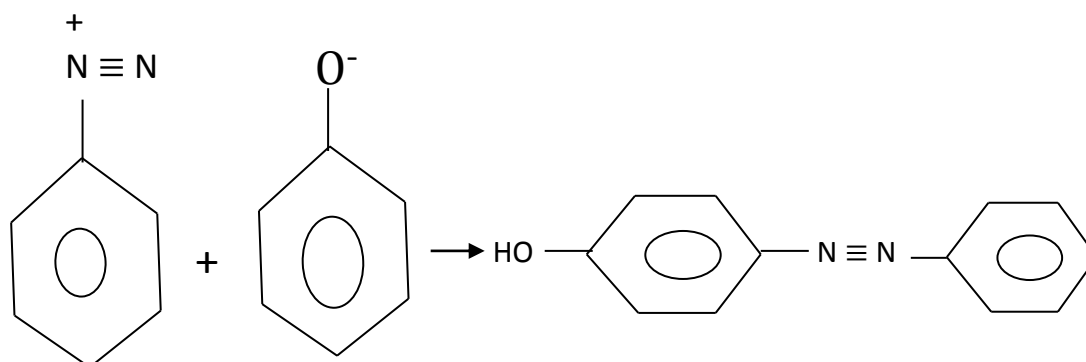
The reaction occurs readily on warming the reaction mixture.

A similar reaction will occur between the diazonium ion and any nucleophile. Let us consider the reaction of the ion with a phenol molecule. *O-H* As you know the hydroxyl group delocalizes its electrons into the ring making the ring more electron rich. One would then expect this phenoxide to react readily with a positive diazonium ion.

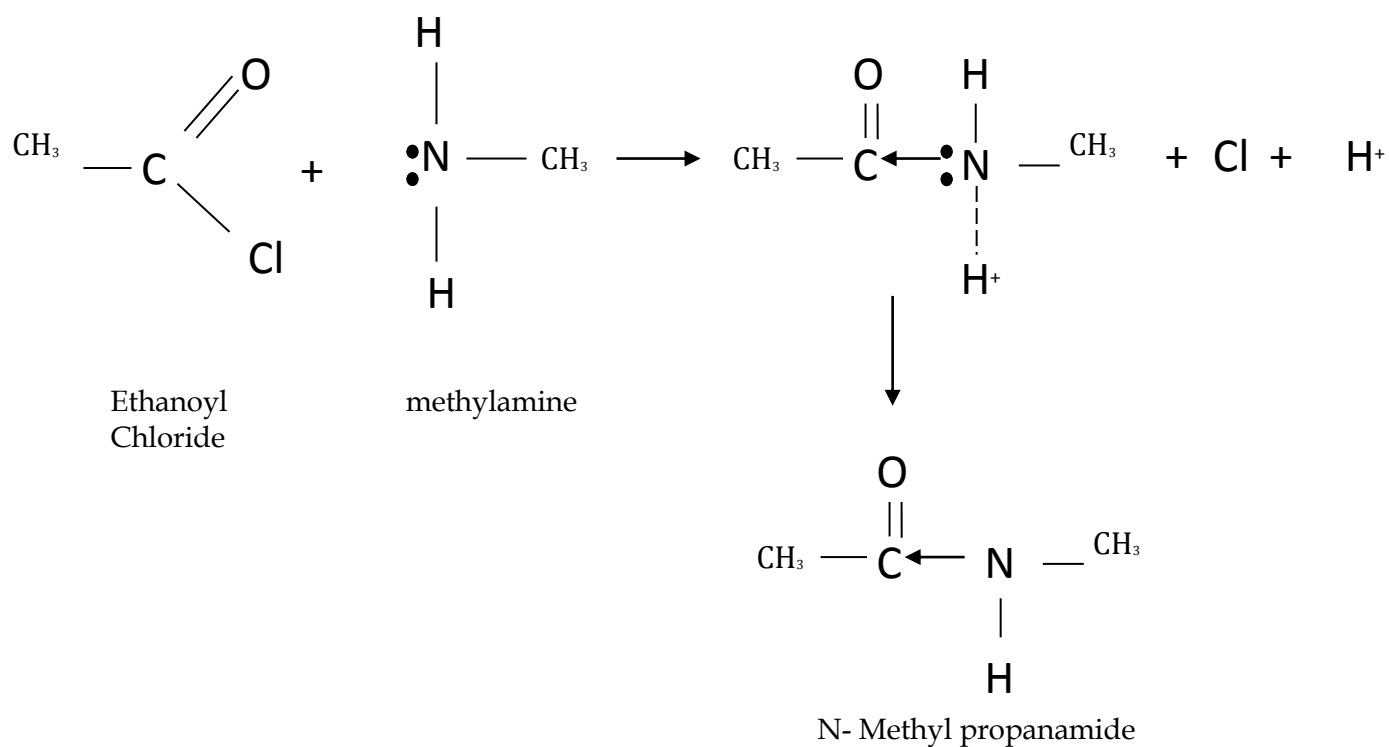
Phenoxide ion



Diazonium ion



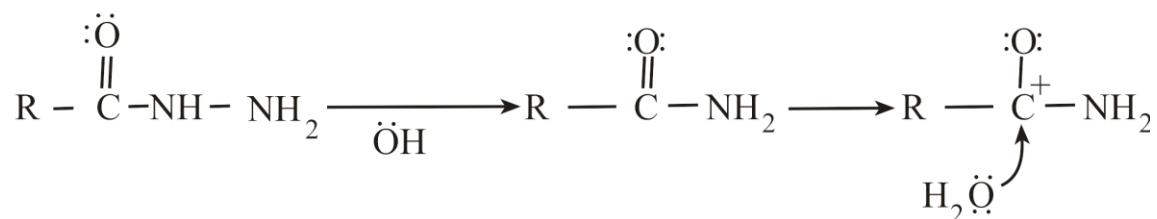
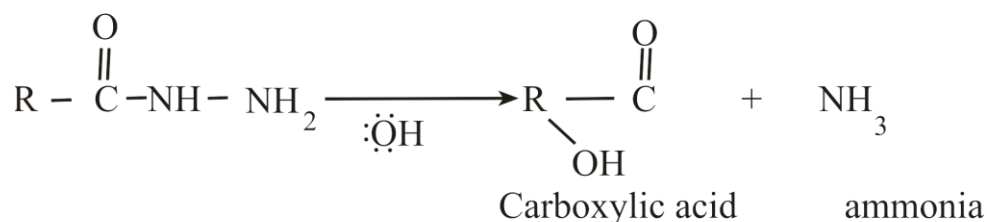
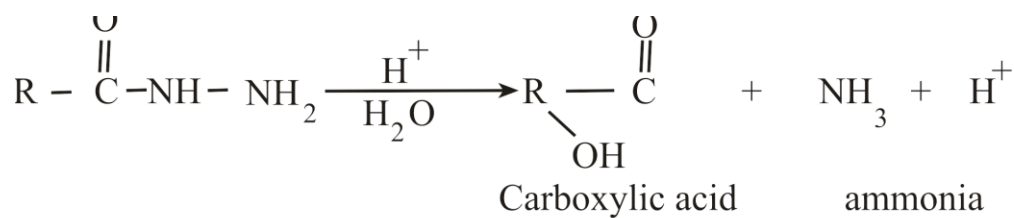
This reaction is also called a coupling reaction and occurs readily when a cold benzenediazonium chloride solution is mixed with another cold alkaline phenol solution. An orange precipitate of 4-hydroxy phenylazobenzene is formed. This reaction is used in the making of dyes of different colours. Phenyl diazonium ions are coupled to other benzene derivatives. The colours are produced by the electron transmission between the benzene molecules through the $-\text{N}=\text{N}-$ bonds



Hydrolysis of Amides

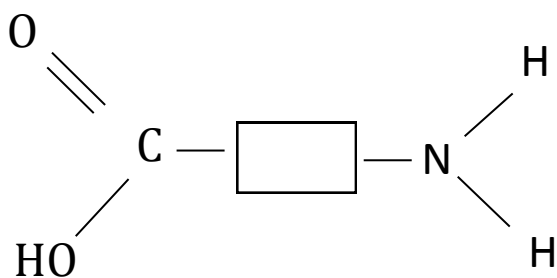
Hydrolysis of amides can occur either by reaction with acid or alkali solutions. The reaction goes via a carbocation. You will find that in both acid and alkali reactions a carboxylic acid and ammonia are produced.

The general reactions in acid and alkali solutions are:



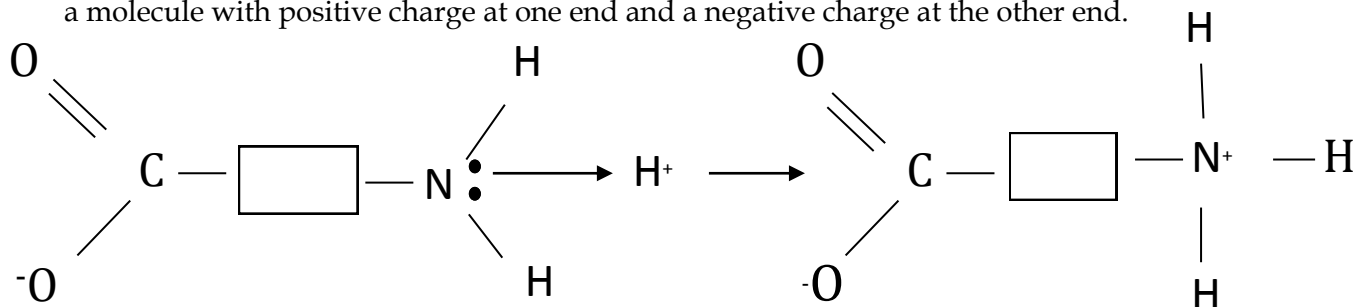
Amino Acids

In the introduction to this chapter it was indicated that proteins are found in living organisms. Proteins as you know are long molecules made up of amino acids. An amino acid molecule can be represented as:



Notice that the structure has an amine group at one end and a carboxylic acid at the other. Thus one molecule behaves as both an acid and a base.

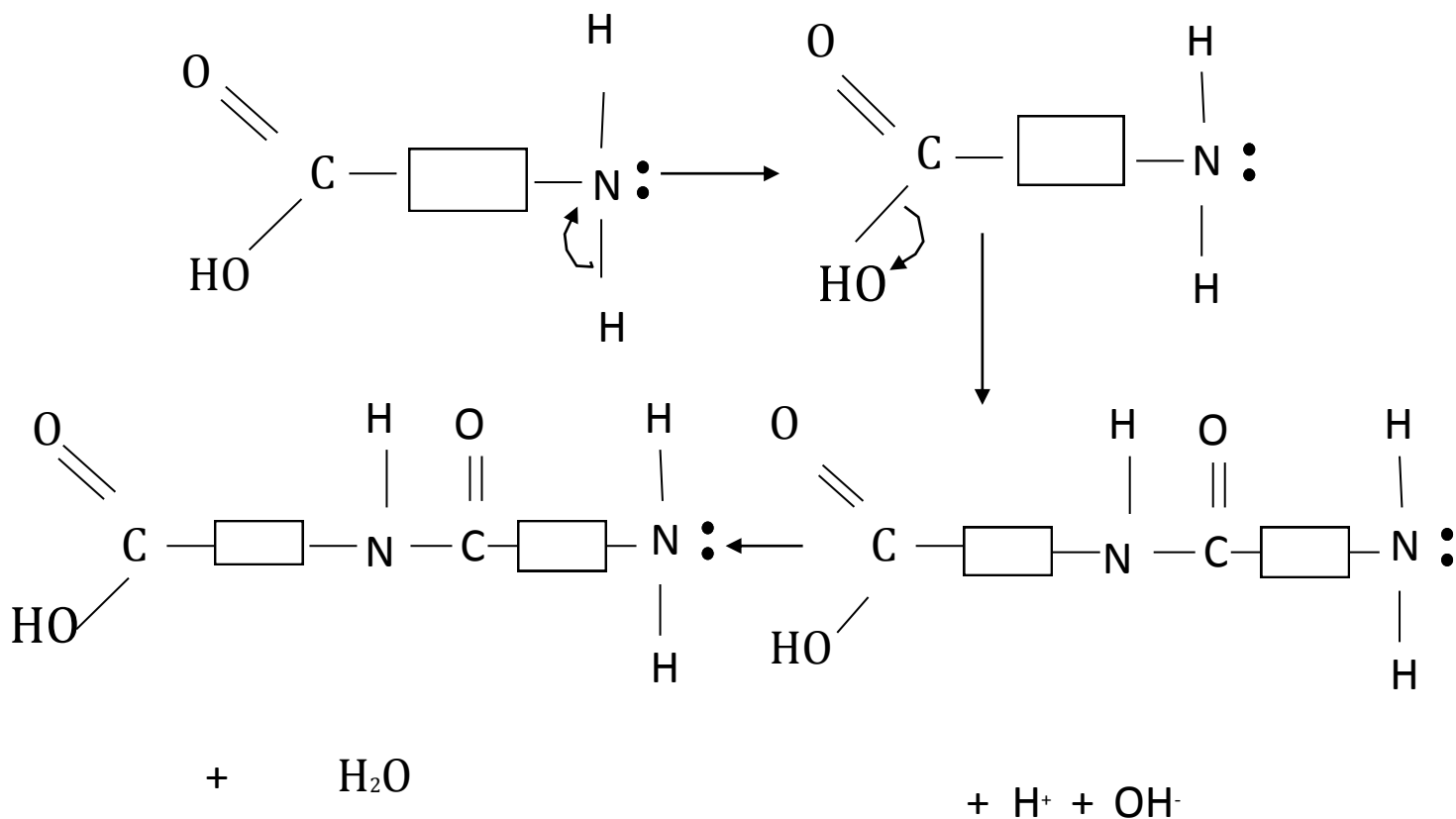
The basic group will accept a proton and the acid group will release a proton. This produces a molecule with positive charge at one end and a negative charge at the other.



A molecule which carries a positive charge and a negative charge is called a zwitterion.

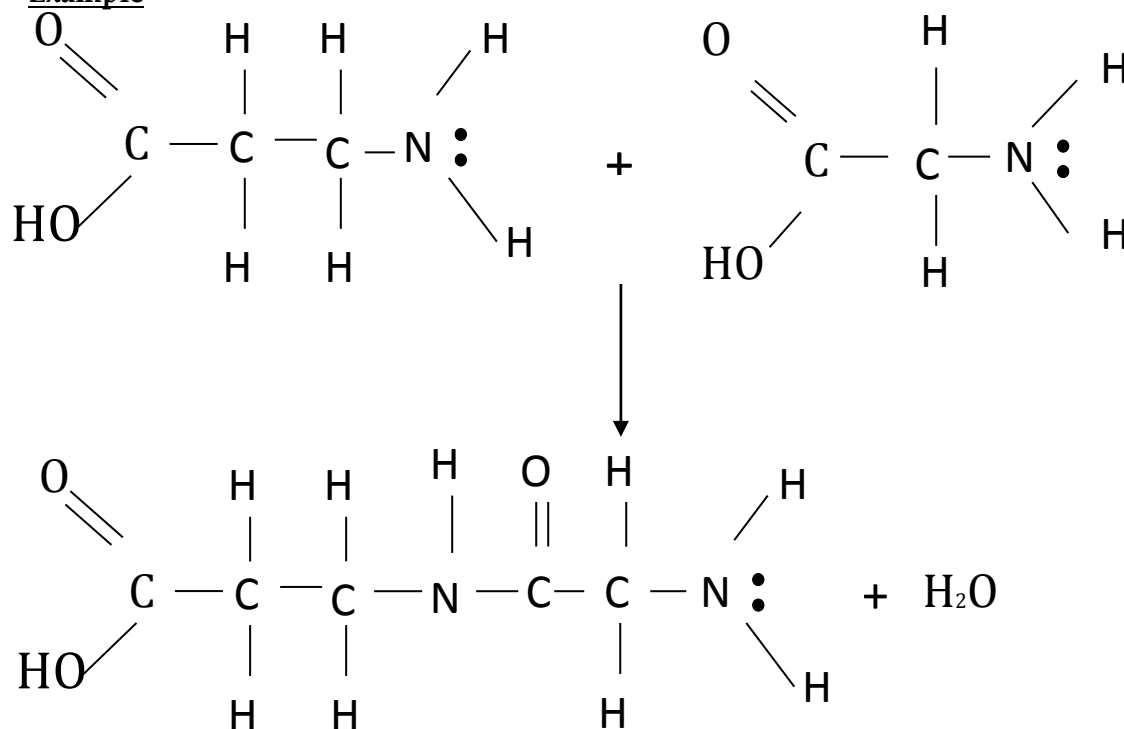
Formation of peptide bonds

Amino acid molecules combine among themselves to form larger molecules called peptides. The bond formed between the amino acids when they combined is called a peptide bond. We will use generalised amino acid molecules to show how a peptide is formed.



The group $-\text{NH}-\text{CO}-$ is called a peptide group

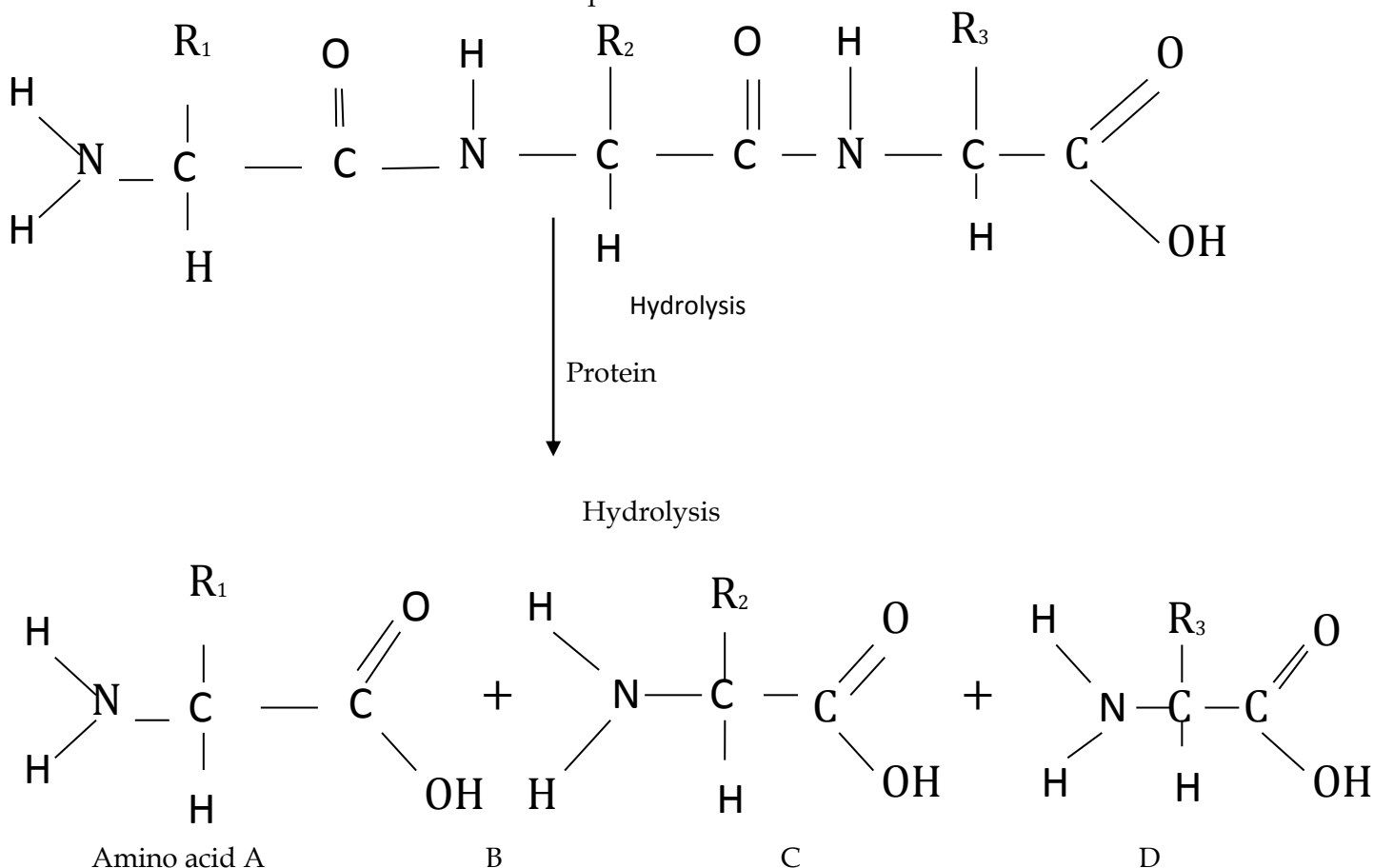
Example



Molecules containing more amino acids (up to 50) are called polypeptides. There are about twenty different amino acids in nature and you can imagine the number of possible combinations by the molecules to produce proteins. The sequence of the amino acids produces different proteins, with each protein molecule containing more than fifty acid units. In each protein the acid units are linked to form a helical structure which is held in place by hydrogen bonding.

Hydrolysis of Proteins

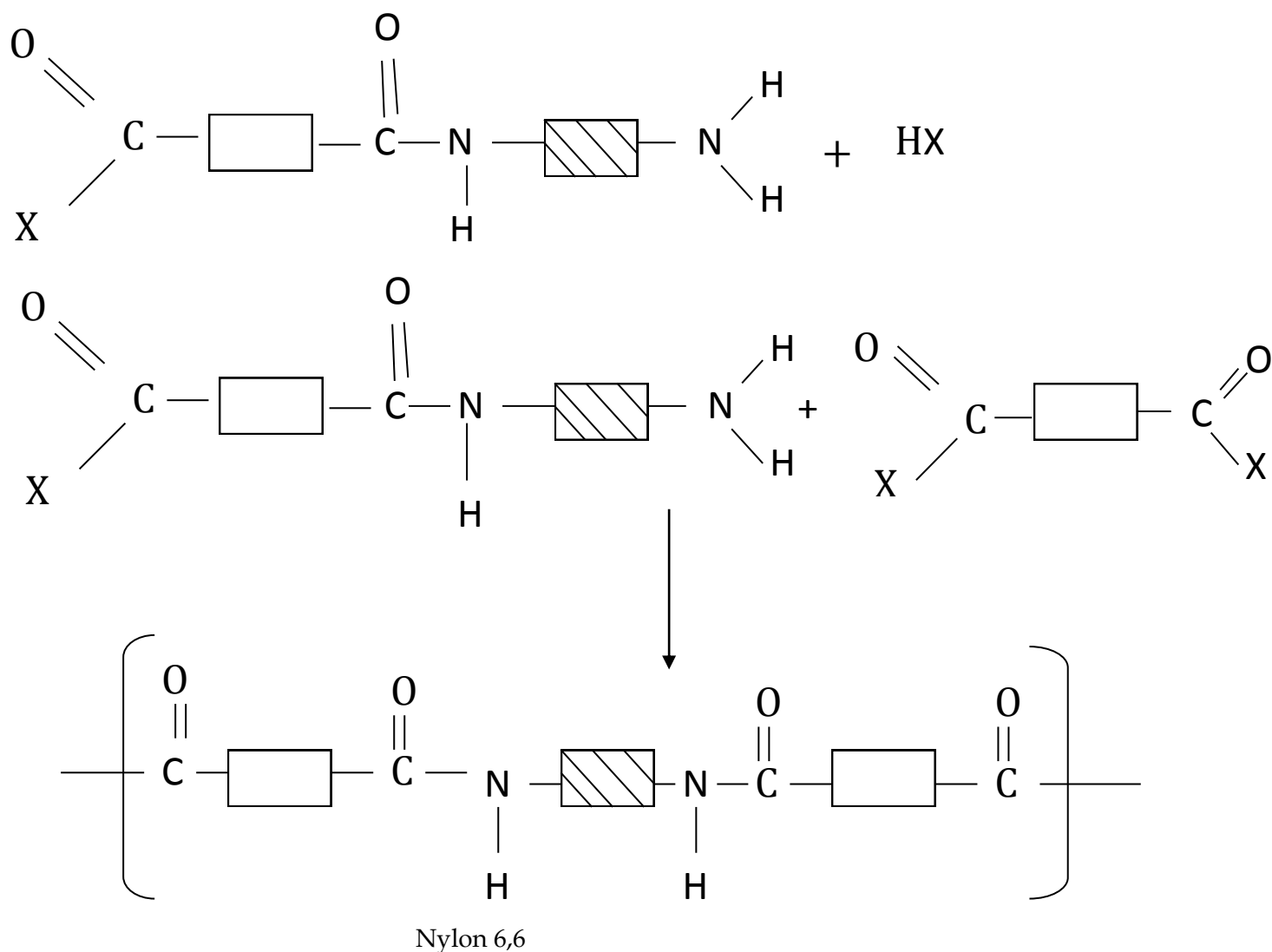
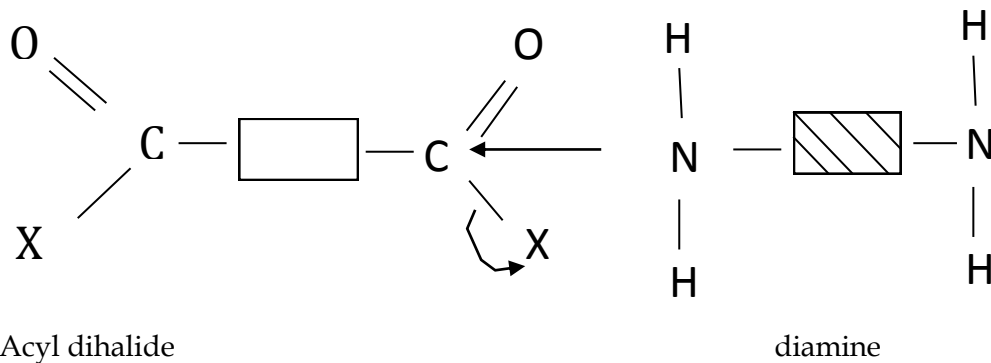
Hydrolysis occurs when a protein reacts with dilute hydrochloric acid. Peptide bonds are broken to release the amino acids in the protein molecules.



Notice that water molecules are added when the peptide bonds break

Polyamides

As the name suggests polyamides are long molecules made by linking amides together. Remember an amide has a general formula R-CONH₂ and is formed by linking an acyl halide with a primary amine. Do you still remember the reaction mechanism for the reaction? Several acyl dihalides and diamines can be linked to produce polyamides.



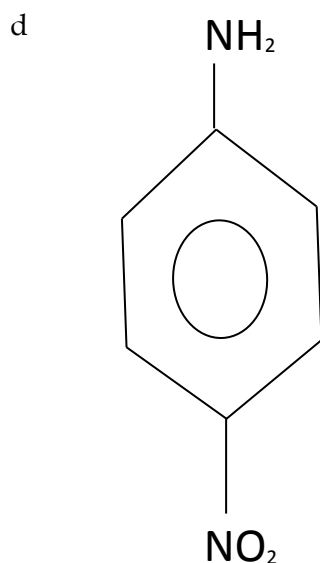
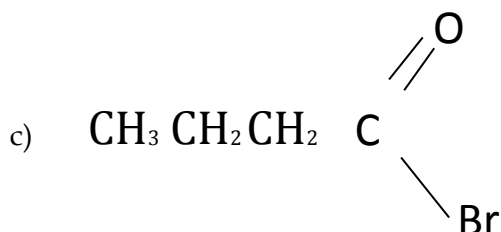
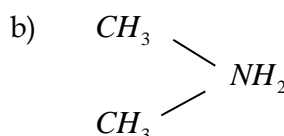
Summary

1. The functional group of amines is $-NH_2$ which can be linked to an alkyl group or an aryl group.
2. Amines are derived from ammonia (NH_3).
3. Amines can be primary, secondary or tertiary. $R-NH_2, (R)_2NH, (R)_3N$.
4. Amines can be formed from nitriles ($R-CN$) by reduction with $LiAlH_4$.
5. Phenylamine is formed from nitrobenzene by reduction with $LiAlH_4$.

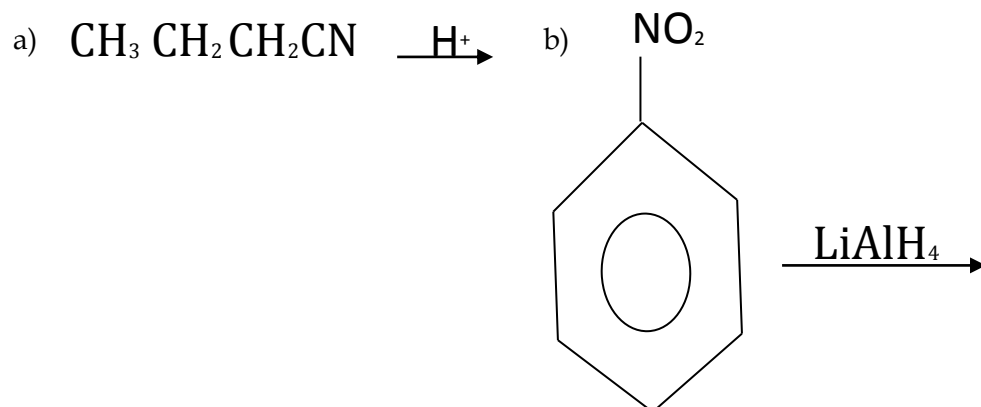
6. The basicity of amines decreases from tertiary amines through secondary amines to primary amines.
7. The basicity of ammonia, ethylamine and phenylamine decreases from ethylamine, through ammonia to phenylamine.
8. Phenylamine reacts readily with bromine to produce 2,4,6-tribromophenylamine.
9. Phenylamine reacts with cold nitrous acid to produce a phenyldiazonium salt.
10. Phenyldiazonium ions decompose to yield nitrogen gas and phenol.
11. The phenyldiazonium ion couples with phenol to produce an azo compound, hydroxyphenylazo-benzene, a dye.
12. Amides are formed by reaction of a primary amine and an acyl halide.
13. Amides are hydrolysed by aqueous acids and alkalis to yield carboxylic acids and ammonia.
14. An amino acid molecule behaves as both an acid and a base and it carries a negative charge and a positive charge (zwitterion).
15. Amino acids are linked by peptide bonds to form polypeptides.
16. There are 20 naturally occurring amino acids which link up to form proteins.
17. Polyamides can be formed from acyl dihalides and diamines. Nylon is formed this way.

Examination Type Questions

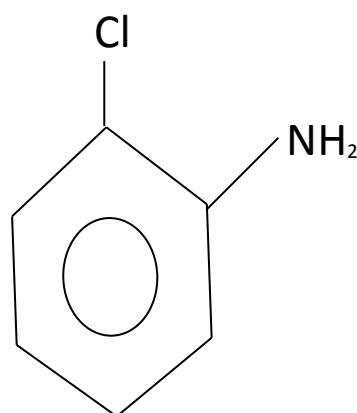
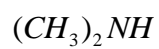
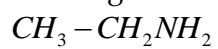
1. Name the following



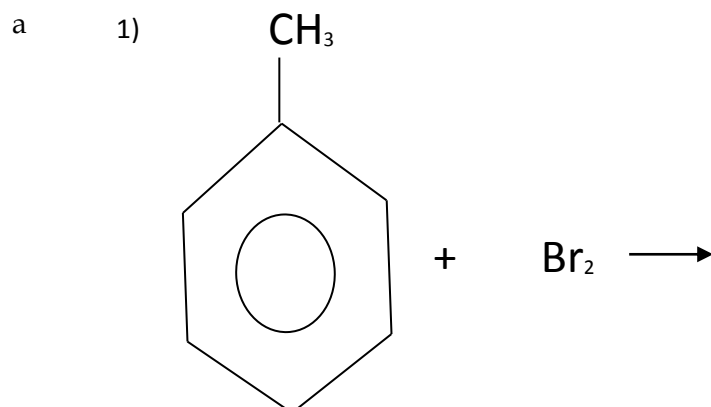
2. Complete the following equation.

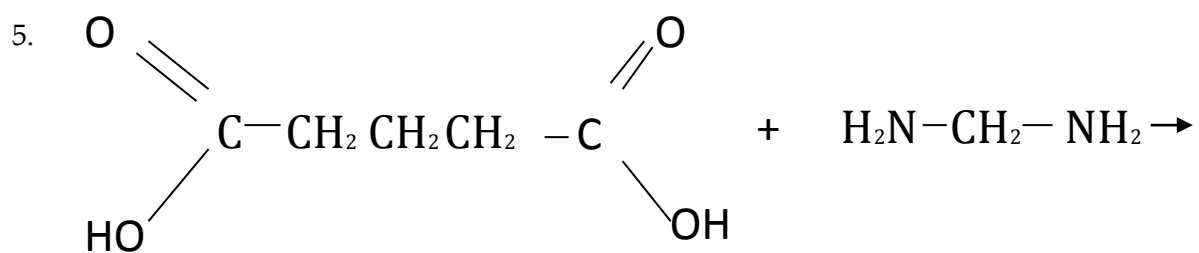
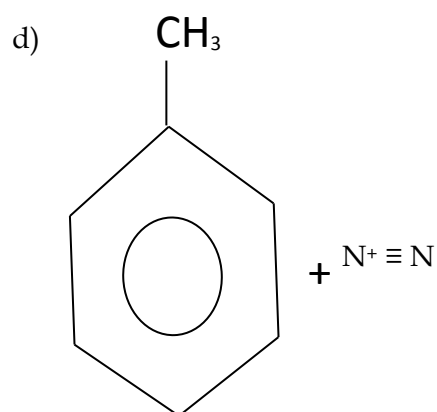
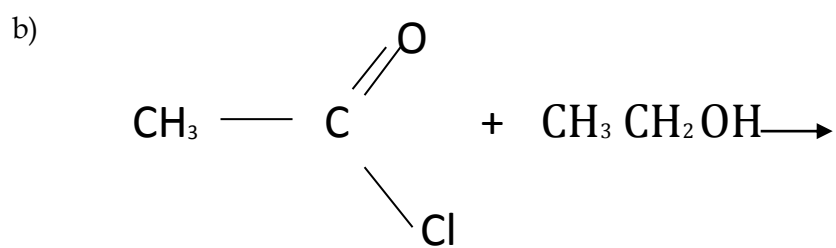


3. Arrange the following in order of decreasing basicity.



4. Complete the equations for the following reactions, showing the reaction mechanisms involved.





References

1. Mc Murray J
Organic Chemistry
Cornell University
Books/Cole Publishing Company
Monterey, California USA.
2. Hill G and Holman J
Chemistry in Context
Thomas Nelson and Sons Ltd
Surrey: UK.
3. Lister T and Renshaw J.
Understanding Chemistry
Stanley Thornes (Publishers) Ltd
Cheltenham England
4. Cambridge "A" Level Chemistry Syllabus
5. Zimsec "A" Level Chemistry Syllabus

CHAPTER 8

CARBOXYLIC ACIDS

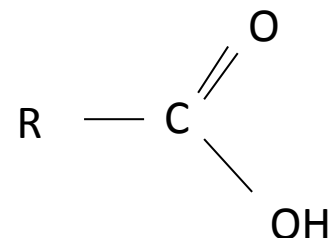
At the end of this chapter you should be able to:

- describe the formation of carboxylic acids from alcohols, aldehydes and nitriles.
- describe the reaction of carboxylic acids in the formation of salts.
- describe the formation of esters.
- describe the formation of acyl chlorides.
- explain the acidity of carboxylic acids and of chlorine substituted ethanoic acids in terms of their structure.
- describe the hydrolysis of acyl chlorides.
- describe reactions of acyl chlorides with alcohols, phenols and primary amines.
- explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.
- describe formation of esters from carboxylic acids and their acid and base hydrolysis.
- state the major commercial uses of esters.

Introduction

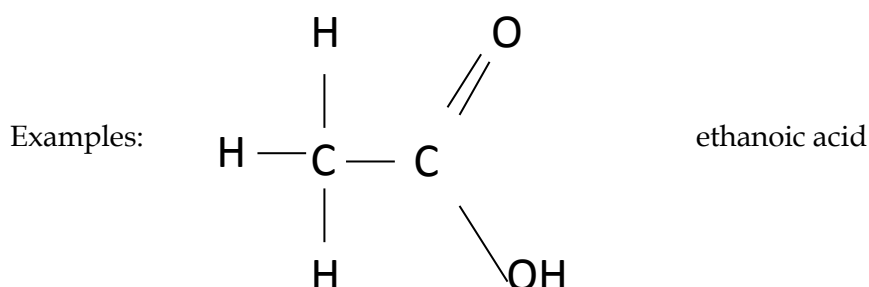
Carboxylic acids are widely distributed in nature, being found in insect stings, as metabolic by products in sweat, as fatty acids (stearic, oleic, palmitic) in plants and animals. The most commonly used carboxylic acid is ethanoic acid found in the kitchen as a pickle.

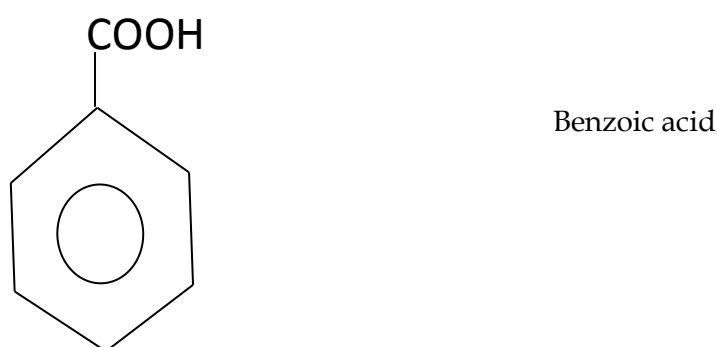
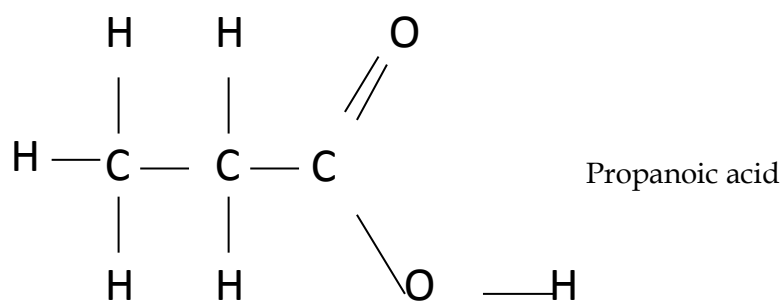
As you already know the functional group of carboxylic acids is
(Where R is alkyl, or aryl).



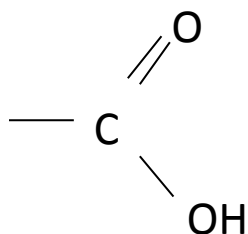
Naming carboxylic acids.

The suffix-*oic* is attached to the stem of the principal group. If the carboxylic acids are formed from alkanes the $-\text{CH}_3$ group is replaced by the *oic* group. In naming such carboxylic acids the *-e* of the alkane is replaced by *-oic*. The carbon on the carboxyl group is counted as part of the chain.

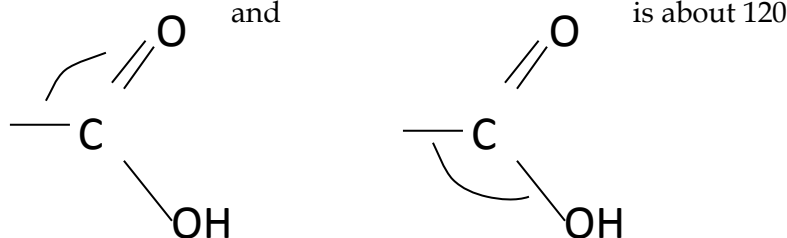




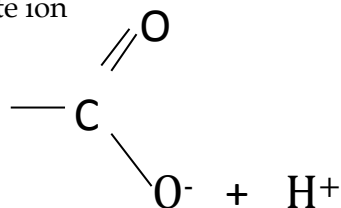
Structure of the functional group. You will notice that the structure



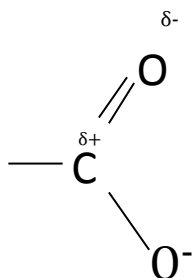
contains both a carbonyl group and a hydroxyl group. We would therefore expect carboxylic acids to exhibit some properties of both ketones and alcohols. As is the case in ketones, the carbon of the carbonyl group is sp^2 hybridised to form a planar structure in which the bond angles



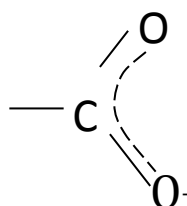
In solution the carboxylic acids form a stable carboxylate ion



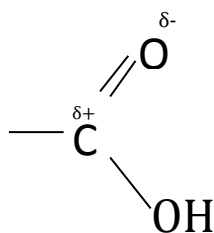
It is thought that the stability of the carboxylate is due to the delocalization of electrons between the two oxygens



The actual structure is a hybrid as shown below:



In this structure the charge is distributed equally between the oxygen atoms. Generally, like in the carbonyl group, the C=O in carboxylic acids is polarized for reasons indicated in the previous chapter.



This has significance in the reaction of carboxylic acids with nucleophiles.

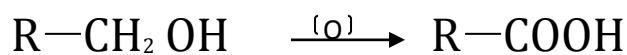
Formation of carboxylic acids

We will now review how carboxylic acids are formed from alcohols and aldehydes. We will also discuss how carboxylic acids are formed from nitriles.

Formation from a primary alcohol

As we saw in the previous chapter, the primary alcohol is first oxidized to an aldehyde but with prolonged heating with acidified $\text{Cr}_2\text{O}_7^{2-}$ the aldehyde is further oxidised to a carboxylic acid. This is carried out in a reflux condenser.

The overall equation is;

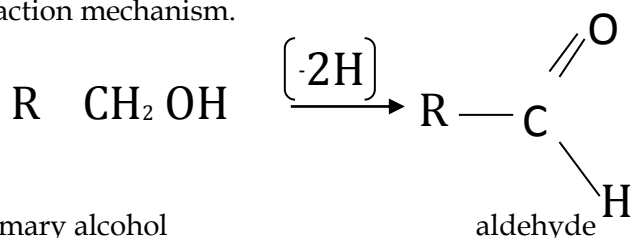


Primary alcohol

carboxylic acid

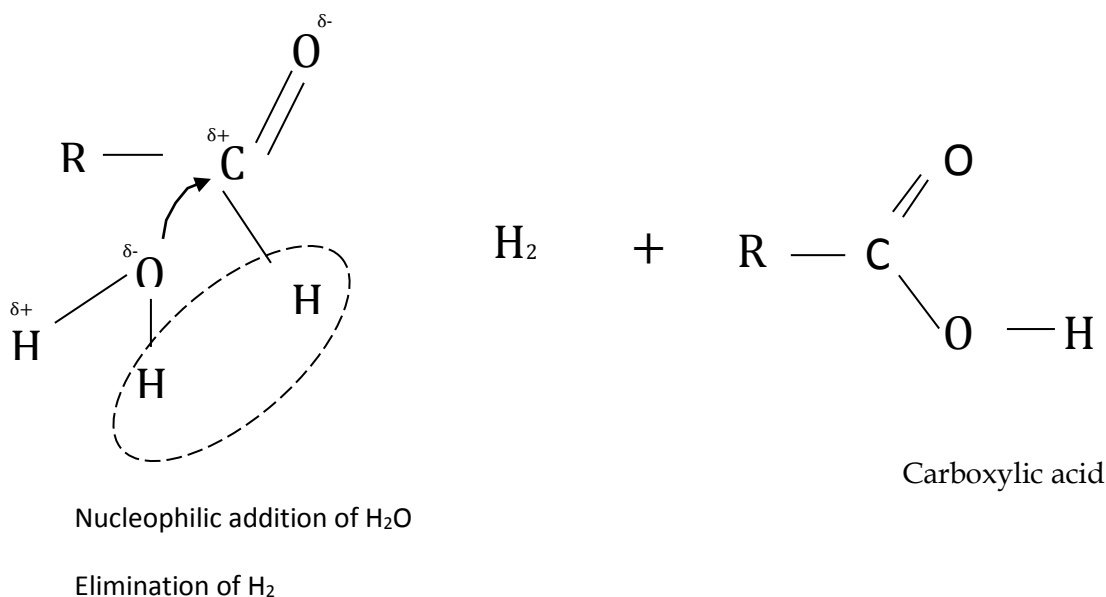
The reaction is thought to involve successive elimination of hydrogen atoms by the oxidising agent $\text{Cr}_2\text{O}_7^{2-}$.

Reaction mechanism.



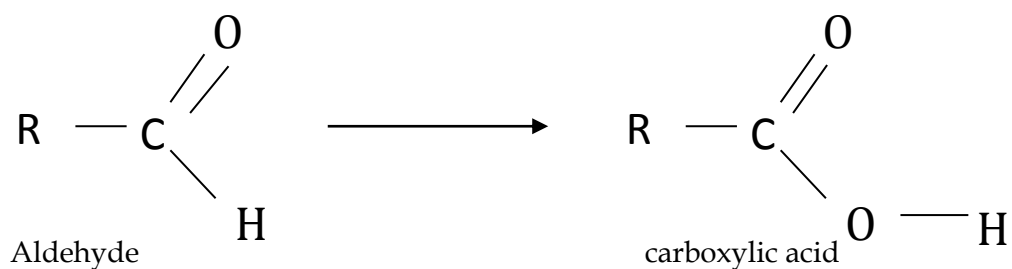
Elimination of hydrogen

The aldehyde undergoes nucleophilic addition of a water molecule after protonation.

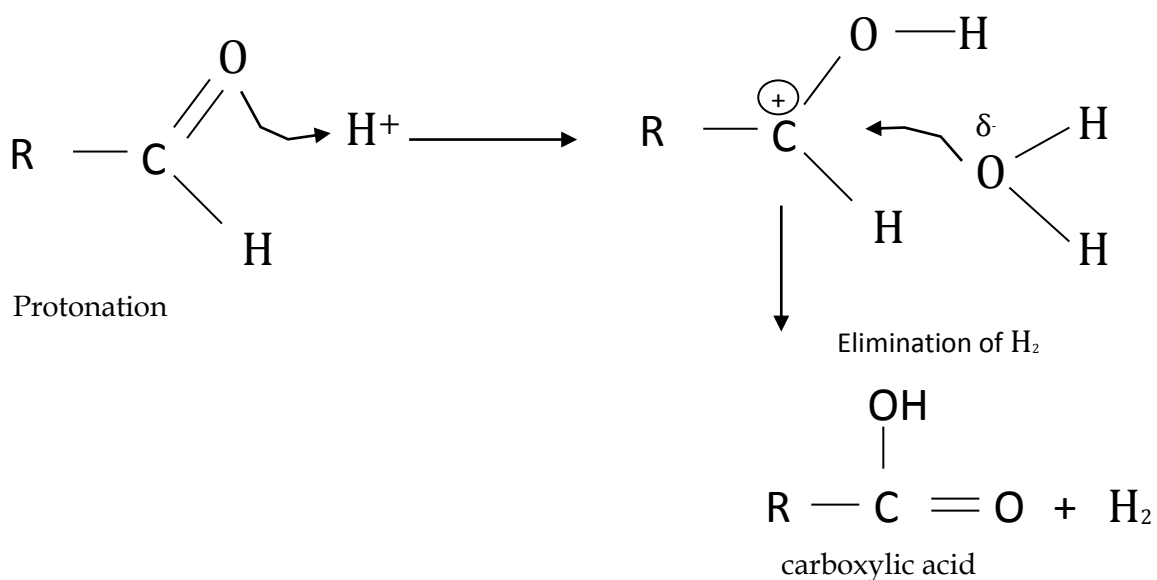


Formation from an aldehyde

The aldehyde is heated with acidified $\text{Cr}_2\text{O}_7^{2-}$ and the overall reaction is



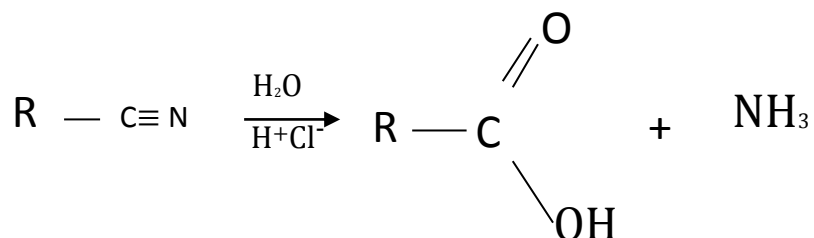
The reaction starts by protonation of an aldehyde followed by nucleophilic addition of H_2O



Formation from a nitrile

The preparation involves hydrolysis of a nitrile $\text{R} - \text{C} \equiv \text{N}$. The nitrile is heated with a strong aqueous acid. Strong acids are strong protonating agents.

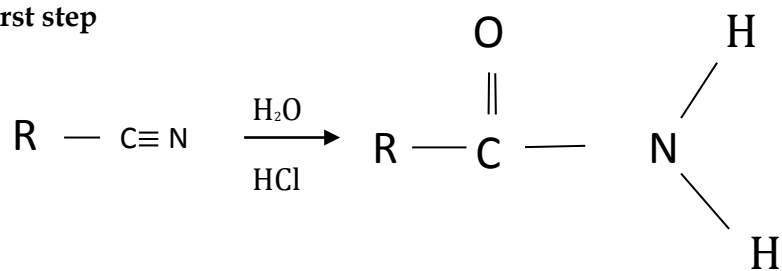
The overall reaction is



Ammonium ions are produced in the process.

The nitrile is first converted to an amide and the amide is converted to a carboxylic acid.

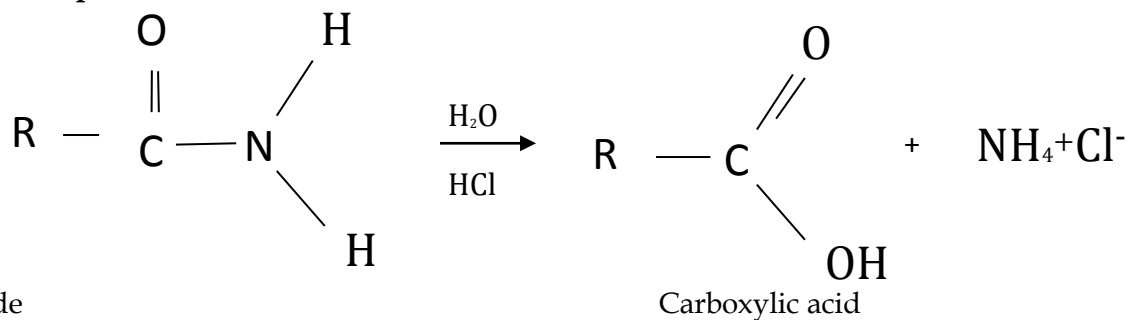
First step



Nitrile

amide

Second step

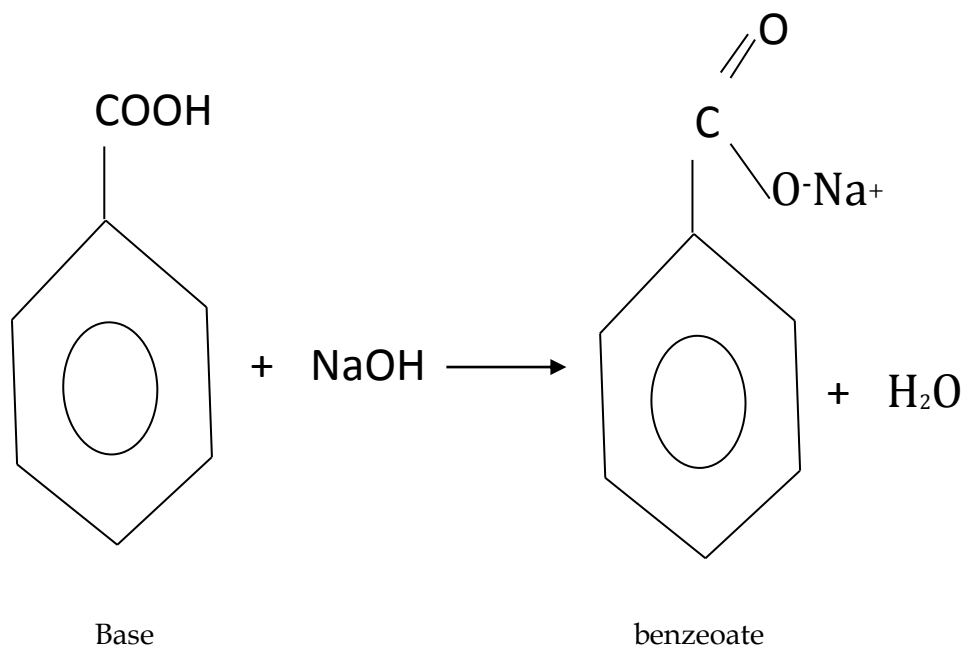


Amide

Carboxylic acid

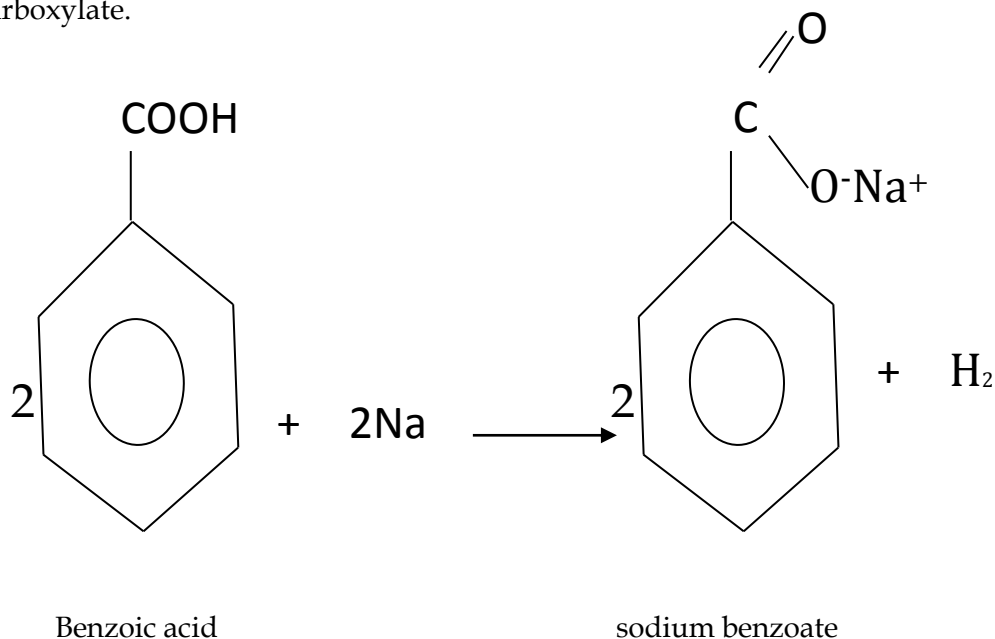
Reaction of carboxylic acids with bases

A typical acid/base reaction produces a salt and water only.



Reaction of carboxylic acid with metals

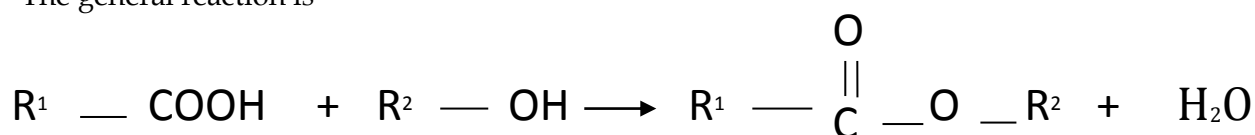
Reactive metals like sodium displace the hydrogen from the hydroxyl group forming a carboxylate.



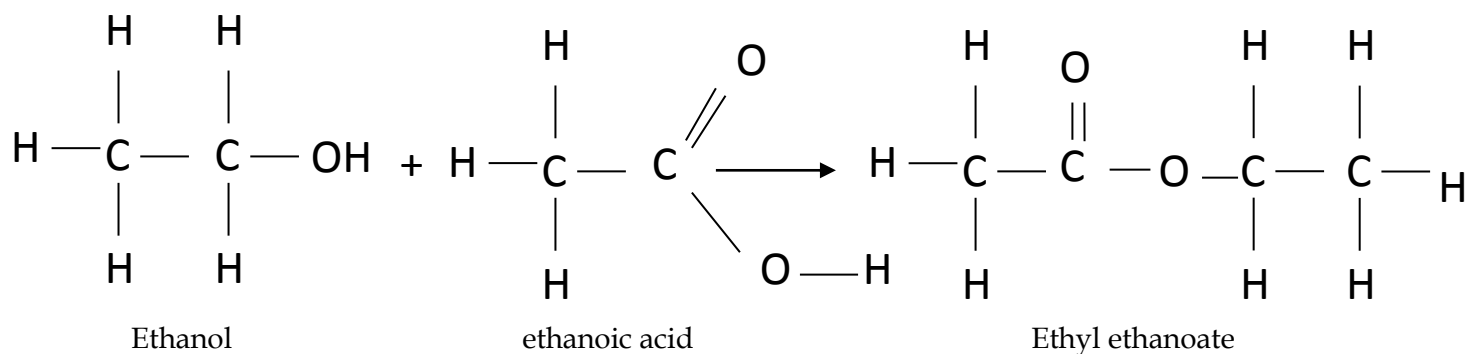
Formation of Esters

Carboxylic acids react with alcohols to form esters. The reaction is slow but faster in the presence of strong acid which acts as catalyst.

The general reaction is

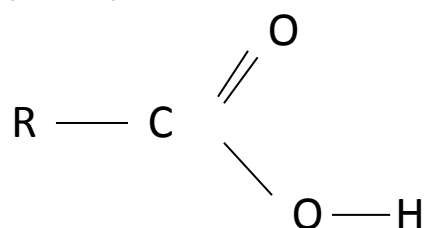


For example when ethanol is heated with acidified ethanoic acid, an ester, ethyl ethanoate is formed.

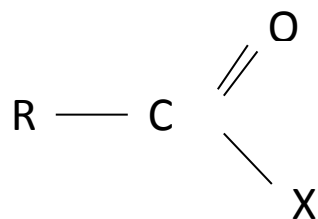


Formation of acyl chlorides

Carboxylic acids react with strong chlorinating agents like phosphorus pentachloride to yield acyl chlorides.



Carboxylic
Acid

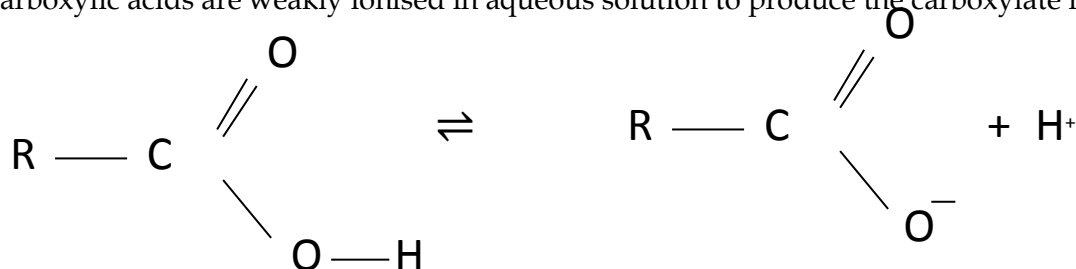


acyl chloride

Phosphorus pentachloride provides the chlorine which substitutes the OH group of the acid

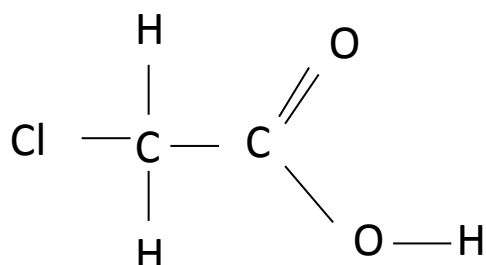
Acidity of carboxylic acids

Carboxylic acids are weakly ionised in aqueous solution to produce the carboxylate ion.



The equilibrium is well to the left. However, the acids do release carbon dioxide from carbonates. When R is an electron releasing group like CH₃, the acid strength is reduced. Hence methanoic acid is stronger than ethanoic acid. What happens to the strength of the acid when an electron withdrawing group is introduced into the acid molecule? Consider a chlorine substituted molecule like 2-chloro-ethanoic acid.

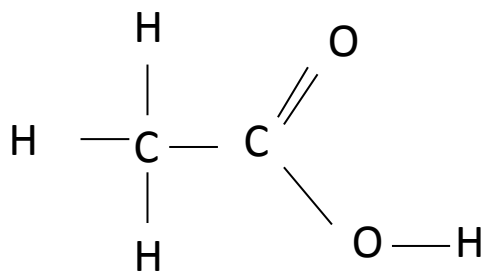
Remember chlorine is electron withdrawing (negative inductive effect) unlike the CH₃ group which is electron releasing (positive inductive effect) as we have seen above.



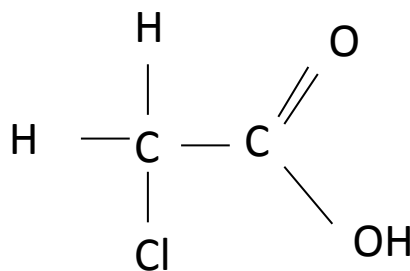
2-Chloro-ethanoic
acid

This electron withdrawing effect reduces the electron density in the carboxylate encouraging release of a proton. Thus 2-chloro-ethanoic acid is a stronger acid than ethanoic acid. It

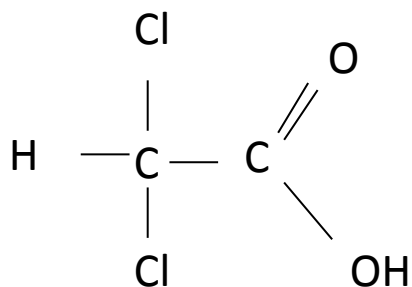
follows then that as we increase the electron withdrawing groups we also increase the acidity.



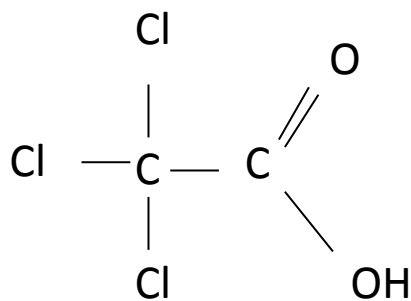
Ethanoic
Acid



2-chloro
ethanoic acid



2,2-dichloro
ethanoic acid

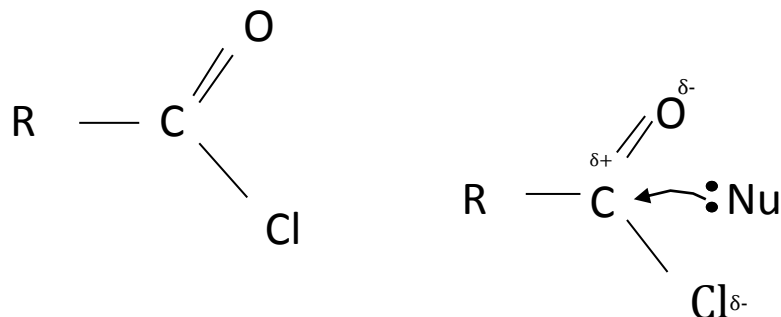


2,2,2-trichloro
ethanoic acid

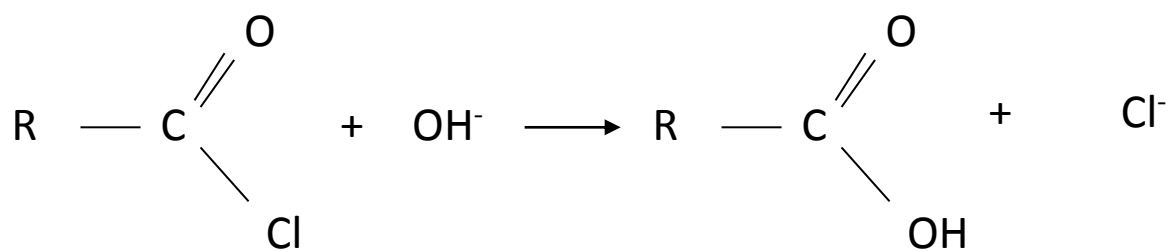
Hydrolysis of acyl chlorides

We start with the structure of the acyl chloride molecule:

As you know the C - Cl bond is polar and this will encourage nucleophilic attack.



In hydrolysis, the chlorine is substituted by the :O:H from a water molecule to form a carboxylic acid

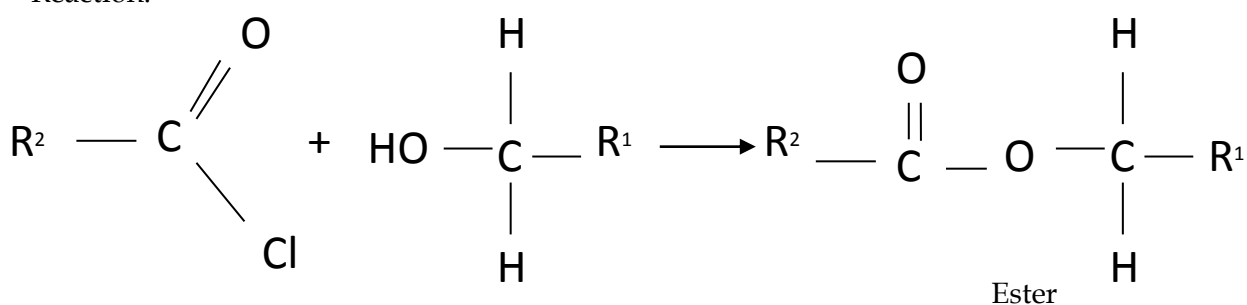


Carboxylic acid.

Reaction of acyl chloride with alcohols

The nucleophile is the alkoxide.

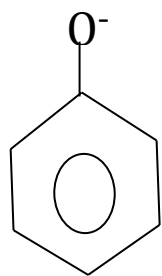
Reaction:



An ester is formed.

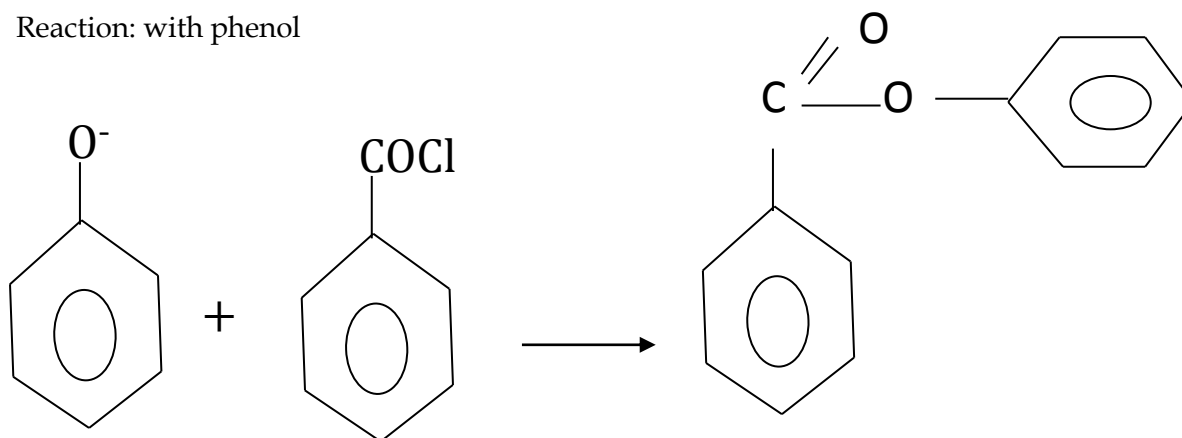
Reaction with phenol

The nucleophile is the phenoxide.



Phenoxide

Reaction: with phenol

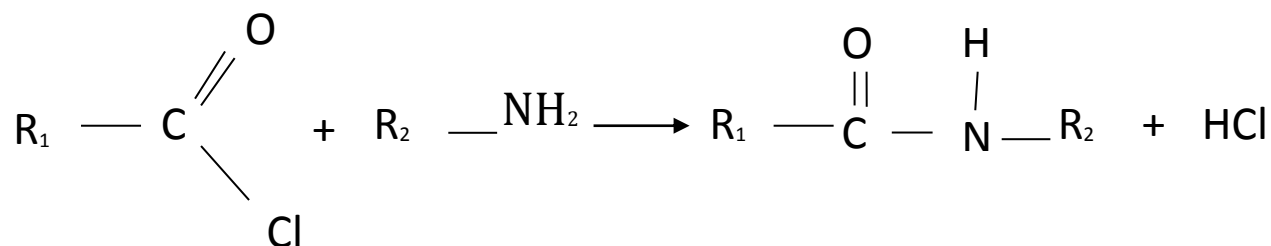


Phenyl ethanoate

Reaction with Primary amines

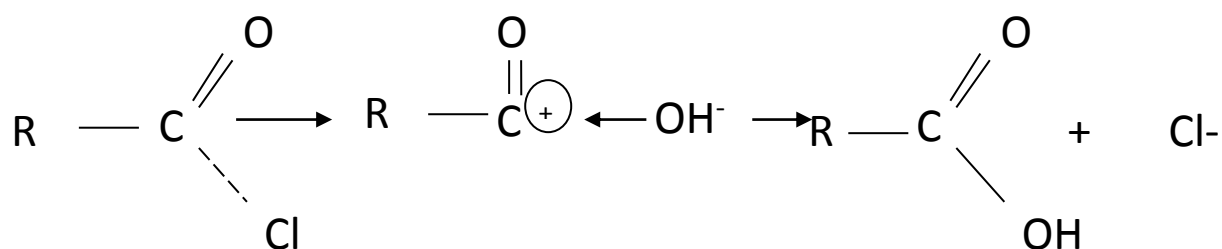
The reaction involves an nucleophilic addition in which the group -NH_2 is the nucleophile

Reaction:



Hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

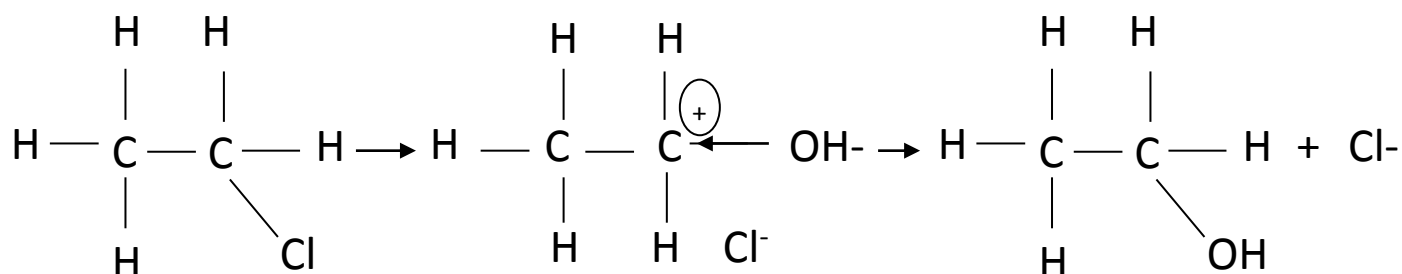
The reactions are shown where :O:H is the nucleophile.



Acyl chloride

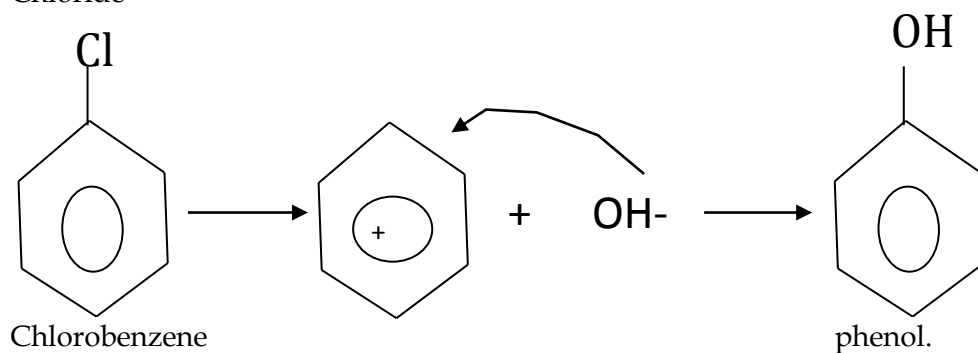
carbocation

carboxylic acid



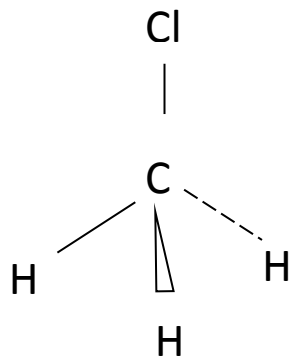
Alkyl
Chloride

alcohol

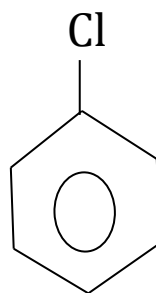


The ease of hydrolysis in the above reactions will depend on the density of the positive charge δ^+ on the carbocation. Electron withdrawing groups make the carbocation more positive and therefore more susceptible to nucleophilic attack. Where both electron releasing and electron withdrawing groups are bonded to the carbon atom, the electron withdrawing group has an overwhelming effect.

Comparing hydrolysis of alkyl chlorides and aryl chlorides:



Alkyl halide
Chloromethane



aryl halide
chlorobenzene

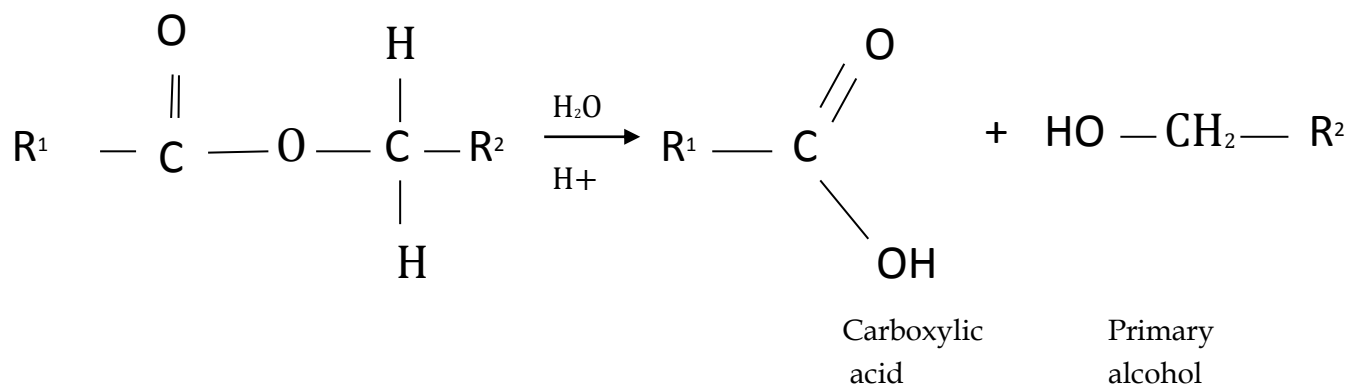
Due to the strong overlap of the chlorine electrons and the delocalized electrons in the benzene ring, the chlorine- benzene C - Cl ring bond is very strong. Also due to delocalized ring electrons, the positive charge $C^{\delta+}$ on the ring carbocation is not intense. Hence cleavage of the chlorine atom from the ring will be difficult. This will make the attack of the nucleophile $\bullet Nu$ on the ring equally difficult. You will find that hydrolysis requires drastic conditions. Thus hydrolysis of chlorobenzene occurs at high pressure and at a high temperature. On the other hand alkyl chloride hydrolyses at room temperature and pressure due to the weaker C - Cl bond.

In the hydrolysis of the acyl chloride though the positive inductive effect of the R will tend to reduce the C^+ of the carbon but it will not make nucleophilic attack by OH^- difficult due to the strong negative inductive effect of the $C = O$. Thus hydrolysis will occur at room temperature.

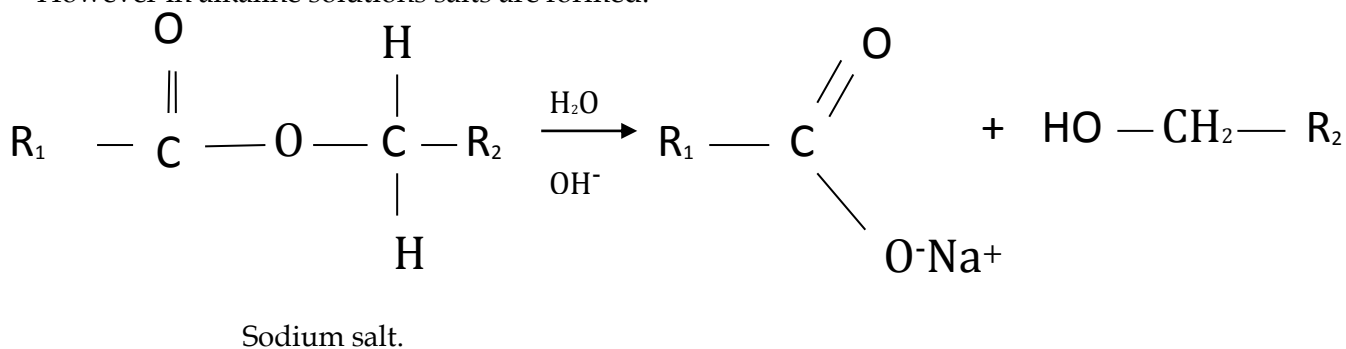
Hydrolysis of Esters

Acid hydrolysis

Esters are hydrolysed in acid aqueous solution to produce carboxylic acids and alcohols. Do you still remember how esters are formed? The acid hydrolysis is



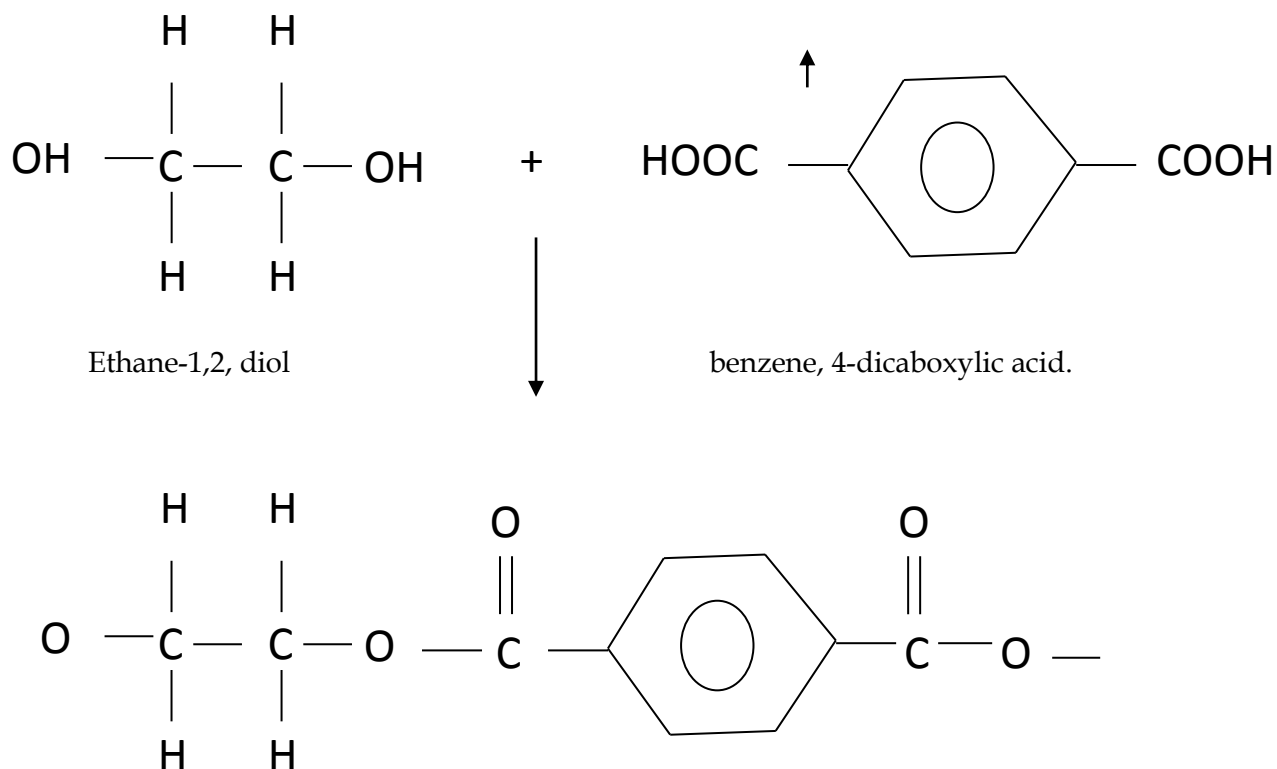
However in alkaline solutions salts are formed.



Ester polymers.

Polymers of esters are called polyesters.

Polyesters are formed by reacting a diol and a dicarboxylic acid. In the formation of the ester linkage, water is eliminated. This type of polymerization is called condensation polymerization.



Terylene

The polymer is melted and extruded through a fine nozzle to make the terylene fibre.

Uses of Esters.

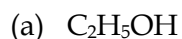
Esters as we have seen above are used to make polymers. Other uses include in the manufacture of perfumes, solvents, paints and medicines.

Summary

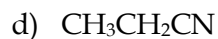
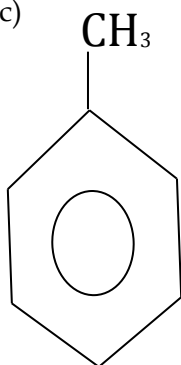
1. Carboxylic acids are formed from alcohols and aldehydes by oxidation.
2. Carboxylic acids are formed from nitriles by hydrolysis in a strong aqueous acidic solution.
3. Carboxylic acids react with bases and reactive metals to form salts.
4. Carboxylic acids react with alcohols in the presence of an acid catalyst to form esters.
5. Acyl chlorides are formed from carboxylic acids by reaction with strong chlorinating agents like PCl_5 .
6. Chlorinated carboxylic acids are more acidic than corresponding carboxylic acids due to the negative inductive effect of chlorine.
7. Acyl chloride are hydrolysed to yield carboxylic acids.
8. Acyl chlorides react with alcohols to produce esters.
9. Acyl chlorides react with phenols to produce phenyl esters.
10. Acyl chlorides react with primary amines to produce amides.
11. The ease of hydrolysis is more in alkyl chlorides and acyl chlorides than in aryl chlorides.
12. Esters react with acids to form carboxylic acids and alcohols.
13. Esters react with bases to form salts.
14. Polyesters are formed from a condensation reaction between a diol and a carboxylic acid.
15. Uses of esters include manufacture of polymers, perfumes, and as industrial solvents.

Examination Type Questions

1. Describe with reaction mechanisms how the following can be converted to carboxylic acids.



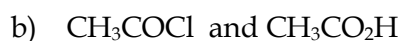
(c)



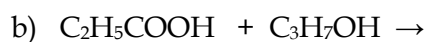
2. What are the products of the following reactions



3. How would you distinguish between the following pairs of compounds using laboratory tests?



4. Complete the following reactions



References

1. Hill G and Holman J
Chemistry in Context
Thomas Nelson and sons Ltd
Surrey: United Kingdom
3rd Edition
2. Lister T. and Renshaw J
Understanding Chemistry
Stanely Thornes (Publishers) Ltd
Cheltenham: England
1994 Edition.
3. MC Murray J.
Organic Chemistry
Cornell University USA
ISBN 0-534-01204-3
4. Cambridge A' Level Chemistry Syllabus
5. Zimsec "A" level Chemistry Syllabus

CHAPTER 9

POLYMERISATION

At the end of this chapter you should be able to:

- a) describe the characteristics of addition polymerization as exemplified by poly (ethene) and PVC.
- b) recognise the difficulty of the disposal of polyalkenes i.e. non-biodegradability and harmful combustion products.
- c) describe the characteristics of condensation polymerization.
 - i) in polyesters as exemplified by Terylene.
 - ii) in polyamides as exemplified by peptides, proteins, nylon 6 and nylon 66.
- d) predict the type of polymerization reaction for a given monomer or pair of monomers.
- e) deduce the repeat unit of a polymer obtained from a given pair of monomers.
- f) deduce the type of polymerisation reaction which produces a given section of a polymer molecule.
- g) identify the monomer(s) present in a given section of a polymer molecule.

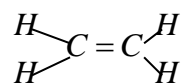
Introduction

As you have learnt small molecules (monomers) can be linked together to form long molecules (polymers). Polymers are either natural or man-made (synthetic). Natural polymers include protein, starch, cotton, wood. However, man-made (synthetic) polymers are now in common use. These include plastics, synthetic rubber and fibres. In this chapter we will focus mainly on condensation and addition polymers. We will discuss how they are made and what properties make them useful.

Addition Polymerisation

In this polymerization, molecules are bonded in long chains. Usually it is the same monomer which contains a double bond.

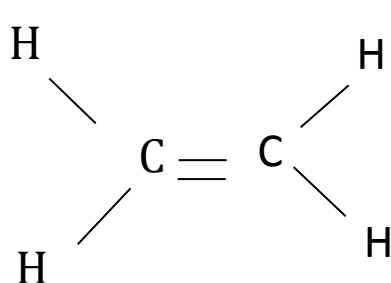
There are two types of addition reaction. One involves the use of catalysts and another involves the production of radicals which propagate the reaction. Let us look at some addition polymers, the simplest of which is poly (ethene). As the name suggests the monomer is the ethene molecule.



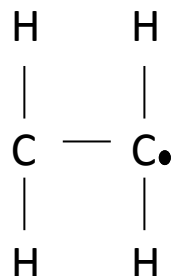
We will also discuss other ethene related polymers, their properties and uses.

Poly (ethene)

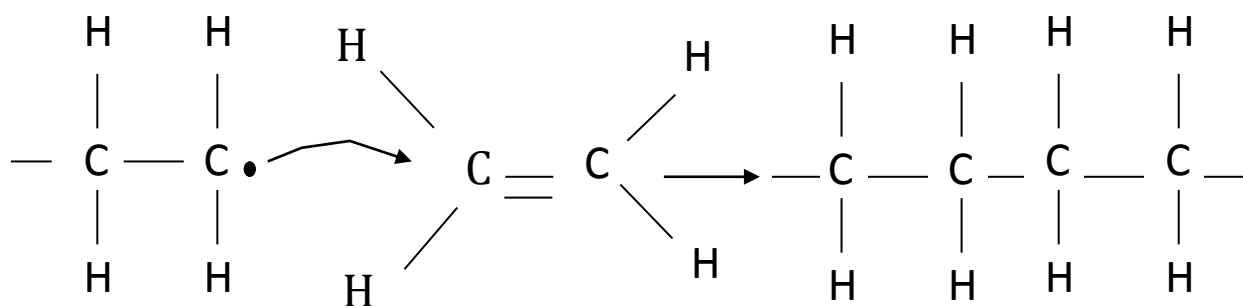
In order for ethene molecules to add to each other in a chain reaction there has to be a chain initiator. This initiator can be a cation, anion or a catalyst. After the reaction has started it will propagate itself as long as monomer radicals continue to be produced.



initiator



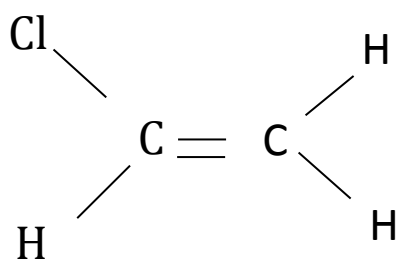
Monomer radical



The process is repeated n times to produce the polymer $(-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-)_n$

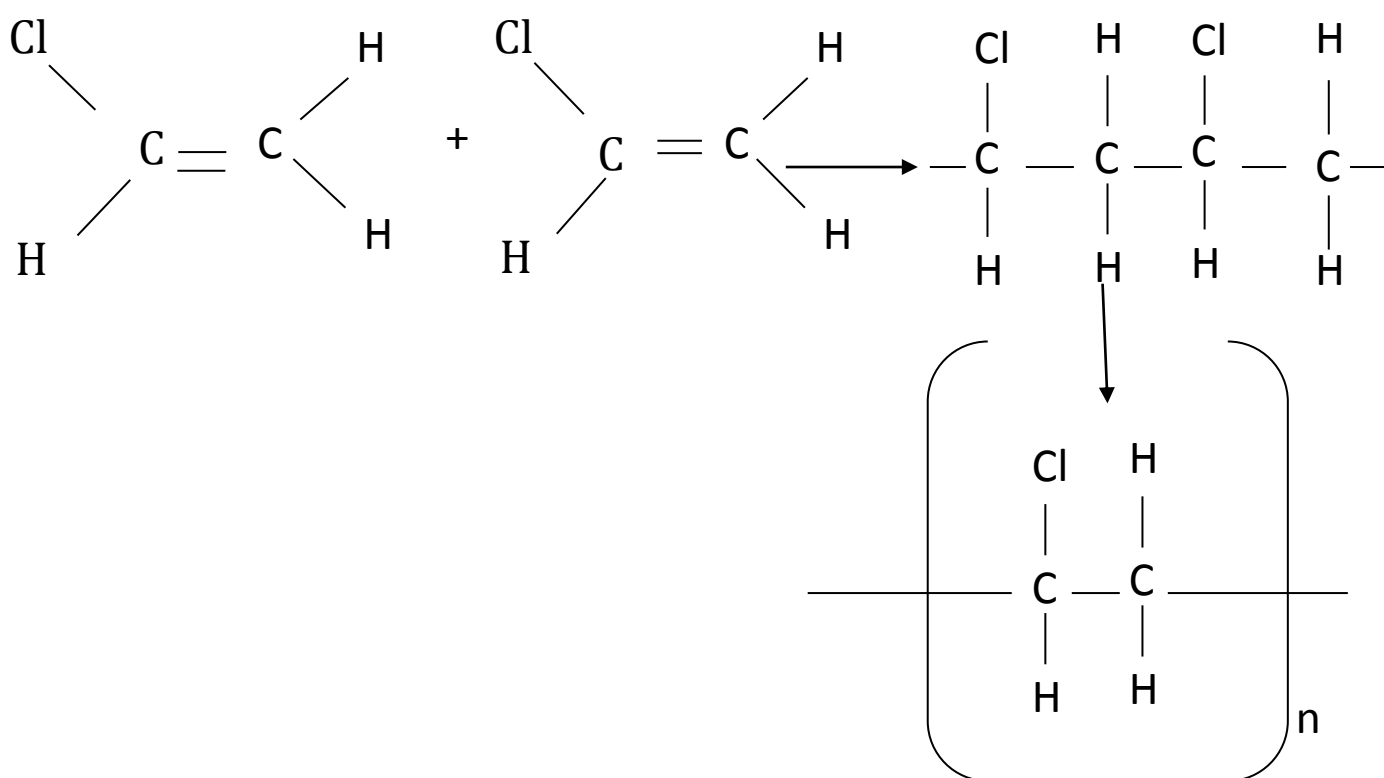
PVC (Polyvinyl chloride)

The monomer is chloroethene



In the presence of a catalyst a molecule of chloroethene can use the π electrons in the double bond to form a covalent bond with another chloroethene molecule.

Catalyst



Characteristics (properties of polythene).

There are two types of polythene, low density and high density polythene. Low density polythene melts at about 105°C and softens when heated gently, but hardens again when cooled. The polymer can be heated repeatedly and moulded into different shapes without degrading. It is an example of a thermoplastic polymer. Heating as you know increases the kinetic energy of the molecules which reduces the intermolecular forces of attraction allowing the molecules to slide over each other. Polythene is also flexible and water resistant. The characteristics referred to above make the polymer useful for making plastic bags, cups and plates. On the other hand high density polythene has greater strength and heat resistance than the low density type and its used to make plastic bottles and kitchen utensils.

Characteristics (properties) of PVC.

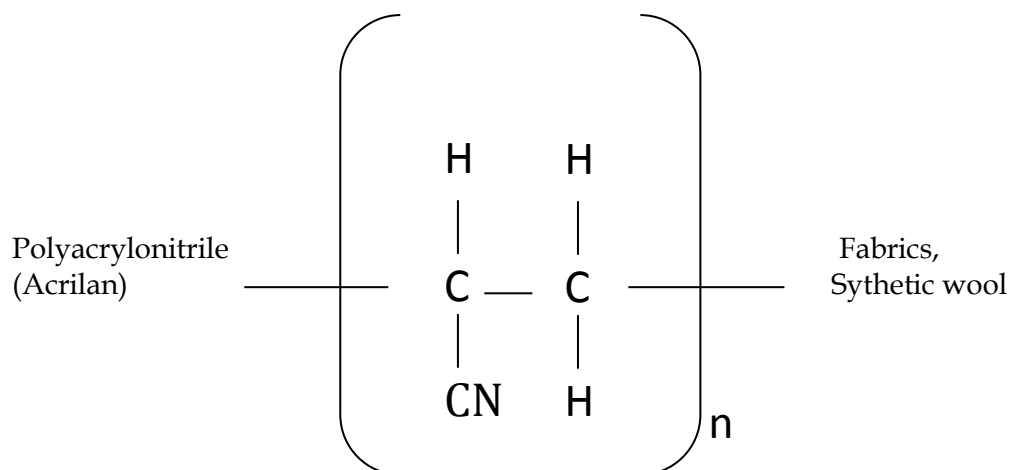
The polychloroethene polymer has $\text{C}-\text{Cl}$ bonds as you saw from its structure. Due to the strong sp orbital overlap, the $\text{C}-\text{Cl}$ sigma bond is very strong making PVC a tough polymer. PVC is fairly rigid but addition of other molecules renders it flexible. Electrically, it is an insulator hence its use as a cover for electrical wires and cables. However, like polythene it is thermoplastic and can be moulded while hot. Its quite stable to environmental agents and this makes it useful for making underground water pipes.

Disposal of polyalkenes

These alkene based polymers are not degradable by bacteria due to strong $\text{C}-\text{C}$ and $\text{C}-\text{Cl}$ bonds. In fact these plastics are a major cause of environmental pollution especially in large cities. Disposal by burial will not solve the pollution problem. Burning them produces gaseous pollutants like carbon dioxide, carbon monoxide and hydrogen chloride gas from polychloro alkenes. As you are aware, carbon monoxide and hydrogen chloride gas are toxic

and carbon dioxide is a green house gas. However, these polymers can be recycled because they can be moulded into other useful articles. Other useful addition polymers and their uses are listed.

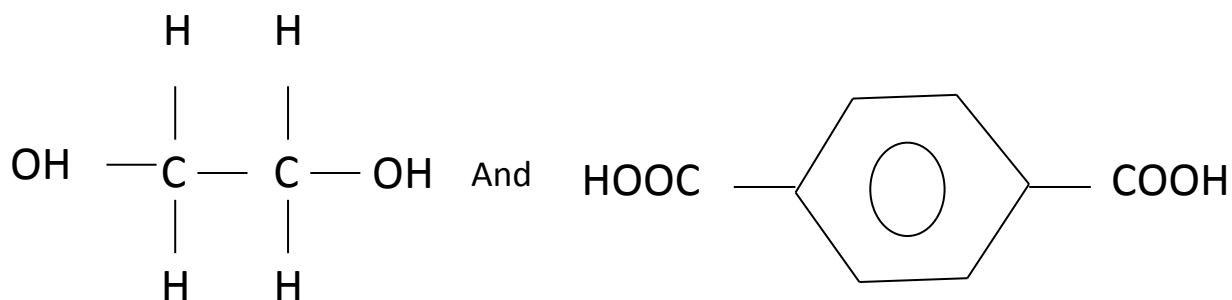
<u>Name of polymer</u>	<u>Structure unit</u>	<u>Uses</u>
Polystyrene		insulating material, cups, packaging material
Polypropylene		pipes, bottles, carpets
Polytetrafluoroethene (Teflon) or ptfe		non- stick pans, electrical insulators, frictionless car parts



Condensation Polymers.

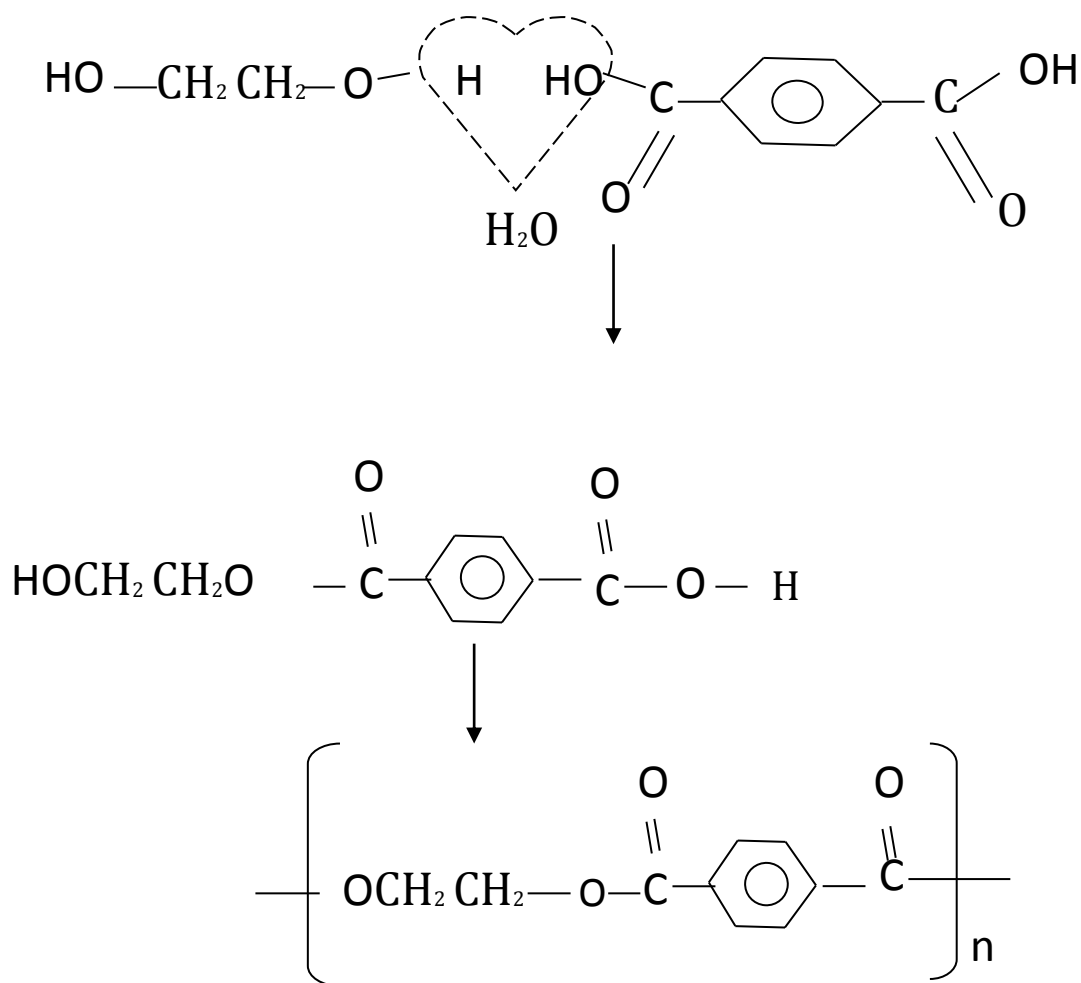
In a condensation reaction as you already are aware, two different molecules combine and a small molecule usually water is removed in the process. The monomers are different and each carries a double functional group which may be an alcohol, carboxylic acid, an amine or an amide, as you saw in the previous chapter. Here we will talk about polyesters and polyamides.

Do you still remember how an ester is formed? You may need to revisit the chapter on alcohols and the previous chapter. In this topic we will discuss one important polymer, polyester. In the previous chapter we discussed the formation of polyamides from diamines and diacids. Polyesters on the other hand are formed by a reaction between a diol and a diacid. Terylene is made from benzene-1,4-dicarboxylic acid and ethane -1, 2- diol.



Notice that each molecule has two functional groups, two -OH groups in one molecule and two -COOH groups in the other molecule.

A water molecule is eliminated at each linkage.



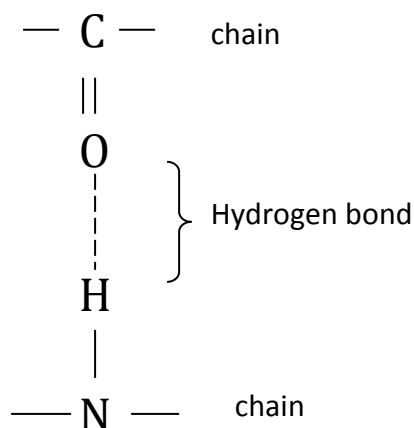
Solid terylene is melted and extruded through small nozzles into fine fibres. The fibres are cooled and woven into cloth. Terylene is wrinkle proof but when heated excessively it shrivels permanently. The material is also “drip dry” or “wash and wear” and does not require ironing. Due to the presence of free flowing electrons the material produces electric discharges.

Polyamides

In this group of nitrogen compounds we find peptides, proteins, nylon 6 and nylon 66.

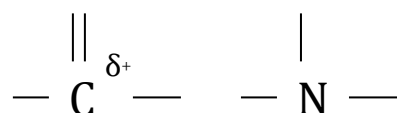
Peptides

We have already dealt with peptides in the previous chapter. Do you remember how they are formed? You will recall that peptides are formed from amino acids. You will also recall that an amino acid molecule has an amine group ($-\text{NH}_2$) at one end and a carboxylic acid at the other end. When two amino acid molecules link up, a peptide bond is formed and a water molecule is eliminated. Several amino acids link up to produce polypeptides.



This hydrogen bonding between peptide groups produces a helical structure of the protein. However, hydrogen bonds are weak and easily broken. This allows changes in the structure where there is no hydrogen bonding.

In the tertiary structure protein chains are folded due to attraction between parts of side chain amino acids. This attraction causes chains to be drawn close together. Other tertiary bonds can be due to hydrogen bonding between side chains. In some cases electrostatic forces of attraction develop between the O and $\text{H}^{\delta+}$ groups.



Yet in other cases attraction and repulsion can occur between non-polar chains due to the polarizing effect of water molecules. The types of bonding referred to above give proteins a 3-dimensional structure. We have seen that proteins are large molecules and as a result they have equally large relative molecular masses. Large as proteins are one would expect them to be insoluble in water. Though many of them are insoluble some are soluble due to the attraction between water molecules and residual acid groups of amino acids. The charge on the peptide side chain depends on the pH of the solution. When the net charge is zero or near zero the protein will not be affected by an electrical potential difference. This happens when the positive charges are counter-balanced by negative charges. However, if the net charge is either positive or negative, the protein will move either to the positive or negative electrode a process called electrophoresis. This method is used to separate different proteins from a mixture.

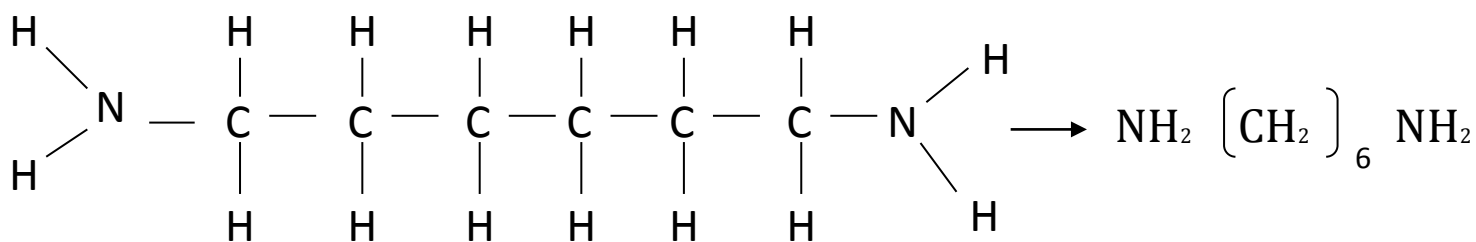
If proteins are subjected to extreme conditions like high pH and high temperature, these conditions tend to disrupt peptide arrangement or hydrogen bonding hence altering the whole protein structure. These changes are referred to as protein denaturation.

Nylon

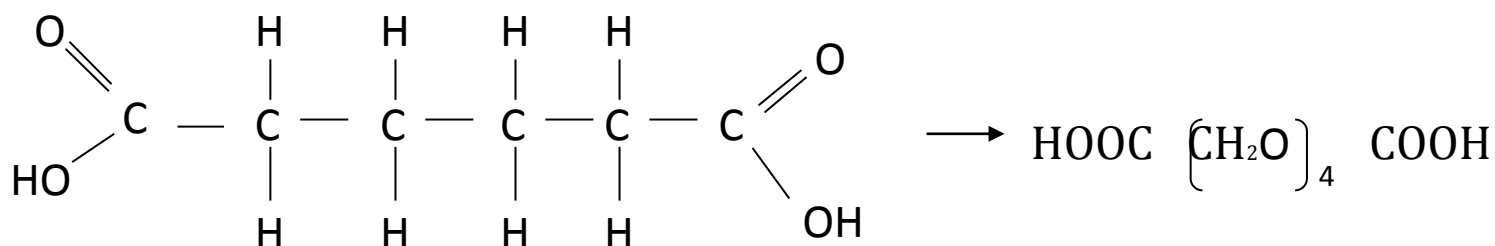
Nylon as you have seen is a condensation polymer belonging to the amide group. We will study two types of nylon; nylon 66 and nylon 6. Both forms of nylon are obtained from two types of monomers, a diamine and a dicarboxylic acid.

Nylon 66

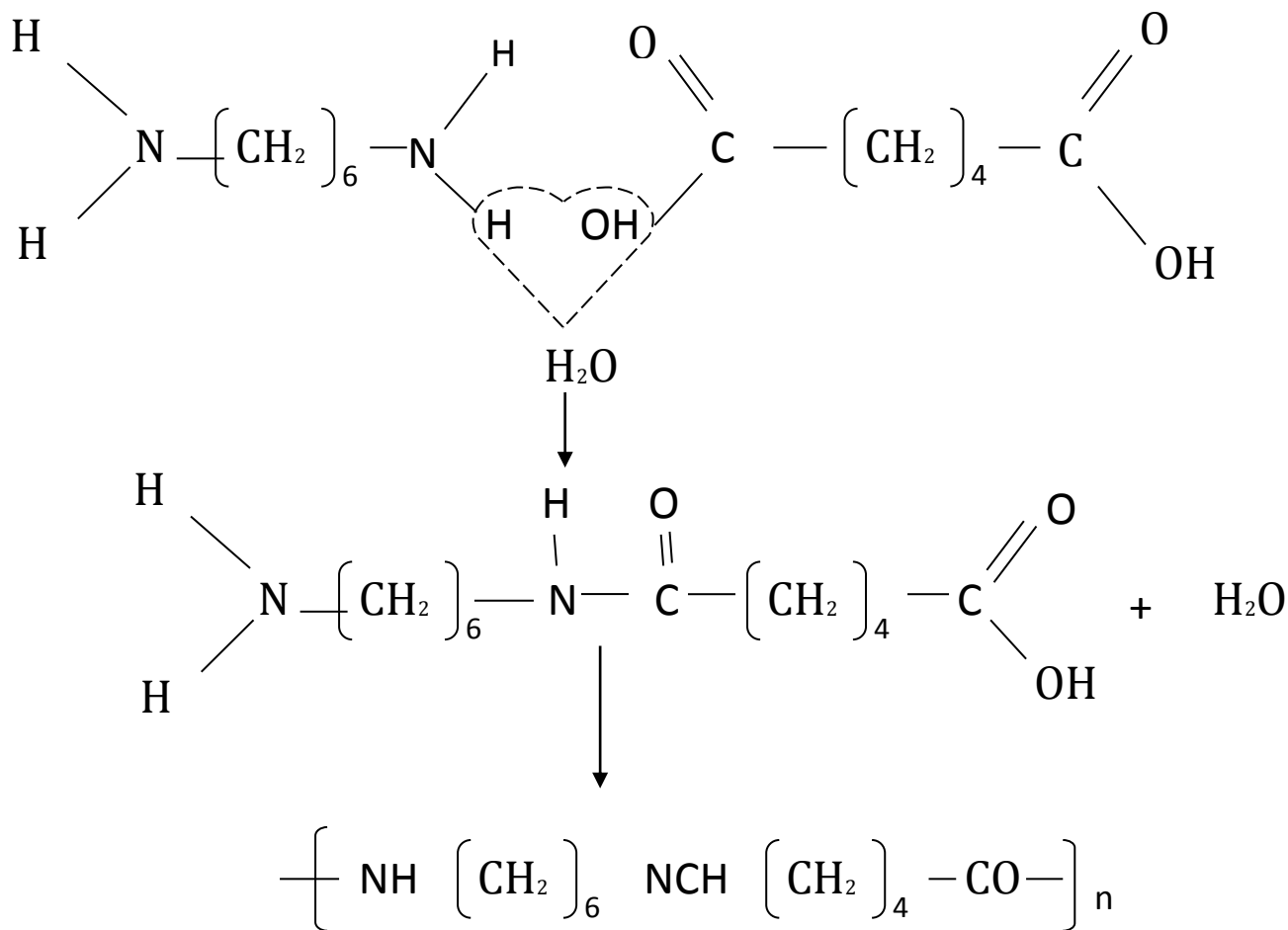
This Nylon is formed from 1,6 diamino hexane



and 1,6- hexanedioic acid



You should be able to work out the product of combining the diamine and the dicarboxylic acid shown below. Try and work out the structure of combining two diamine and two dicarboxylic monomers.



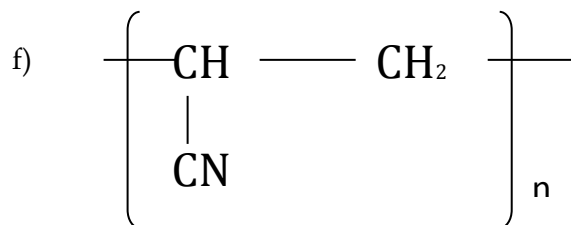
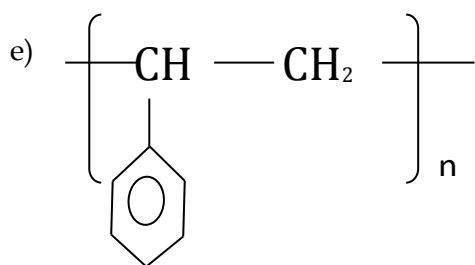
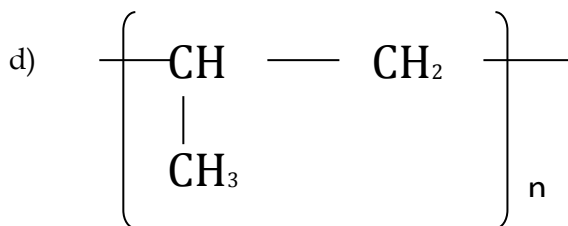
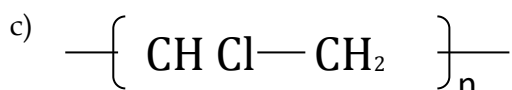
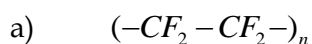
Nylons have a high strength and are scratch resistant and for these reasons they are used for bearings and gears. Nylon fibres are used to make cloth, ropes and stockings, exploiting the elastic properties of fibres which can slide on each other. The nylon cloth like terylene has "drip-dry" properties.

Summary

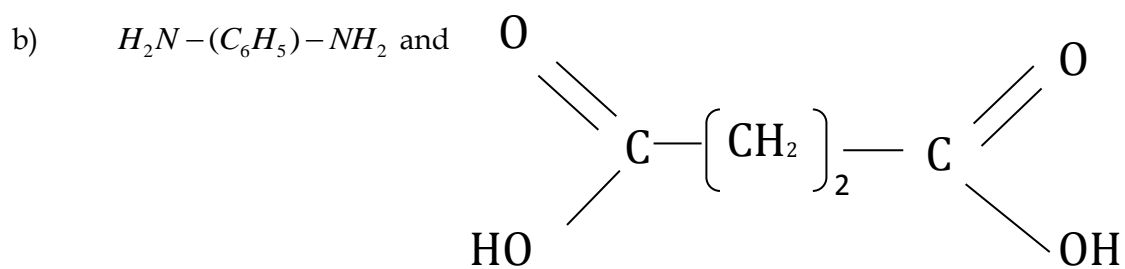
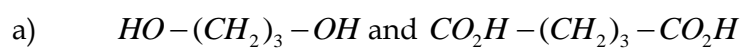
1. Addition polymerisation requires the presence of double (C=C) bonds. Monomers are added together without elimination of atoms or groups of atoms.
2. Polyethene is formed from ethene molecules by uncoupling of (C=C) double bonds.
3. PVC is formed from a chloroalkene.
4. Polythene and PVC are thermoplastics.
5. Polyalkenes are non-biodegradable and burn to produce toxic gases CO_2 , CO , and HCl .
6. In condensation polymerisation water molecules are eliminated.
7. Polyesters are condensation polymers formed from diols and dicarboxylic acids.
8. Amino acids contain a carboxylic acid and an amino group in each molecule.
9. Polyamides are produced from amino acids linked by peptide bonds.
10. Nylons are produced from diamines and dicarboxylic acids.
11. Nylons are strong but elastic materials.
12. Proteins are denatured by high temperature and extreme pH conditions.

Examination Type Questions

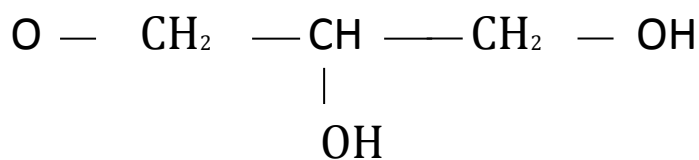
1. Give the structure of the monomer from which each of the following polymers can be made.



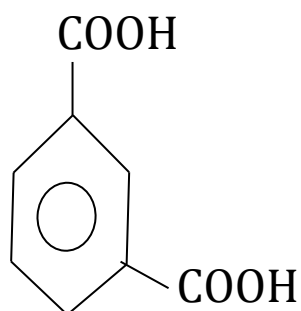
2. Show how a polymer can be formed from the following pairs of monomers and give the repeated structure for n monomer pairs.



3. Dacron is a polymer made from the triol glycerol (1,2,3, propane-triol)
 $HO-CH_2-CH(OH)CH_2-OH$



And



Benzene 1, 3 dicarboxylic acid.

Show step by step how a Dacron structure grows.

References

1. Mc Murray J
Organic Chemistry
Cornell University, USA
Brooks/Cole Publishing Company
Monterey: California USA.
2. Hill G and Holman J.
Chemistry in Context.
Thomas Nelson and Sons Ltd
Surrey UK.
3. Lister T and Renshaw J.
Understanding Chemistry
Stanley Thornes (Publishers)Ltd
Cheltenham England
4. Cambridge 'A' Level Chemistry Syllabus
5. ZimSec "A" Level Chemistry Syllabus.

CHAPTER 10

DISTRIBUTION BETWEEN PHASES

This section explains how the solubility of a gas in a liquid depends on factors such as pressure, temperature and chemical nature of substances. This knowledge is important in instances such as production of carbonated drinks and absorption processes in industry eg. absorption of NO_2 in water to form nitric acid. The section also looks at transformation of compounds from liquid to gas.

Content

- 1.1 Solubility
- 1.2 Henry's law
- 1.3 Solvent extraction
- 1.4 Summary

Learning outcomes

- explain the term solubility.
- explain how the solubility of gas is affected by chemical composition, pressure and temperature.
- state Henry's law.
- use Henry's law in calculations.
- explain the term partition coefficient.
- calculate partition coefficient for a given system.
- describe solvent extraction.
- calculate concentration of a solution after extraction.

Solubility

Solubility refers to the dissolving of a solute in liquid. This process is important in many ways; e.g dissolving of sugar in tea, dissolving of carbon dioxide in water to make soda water and so on.

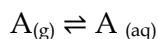
Factors affecting solubility

1. **Chemical nature** An ionic solvent dissolves an ionic solute and a non-polar solvent dissolves a non-polar solute.

Vitamins are either fat soluble or water soluble. Vitamins A, D, E and C are fat soluble. These vitamins are mainly composed of carbon and hydrogen therefore they are non-polar. They will dissolve in non-polar materials such as body fat which is also mainly non-polar. They are not soluble in polar solvents such as water. Vitamins such as vitamin C have polar bonds on them eg. O-H and C-O. These

vitamins are polar. The polar bonds enable them to interact with water which is polar. They are soluble in ionic solvents.

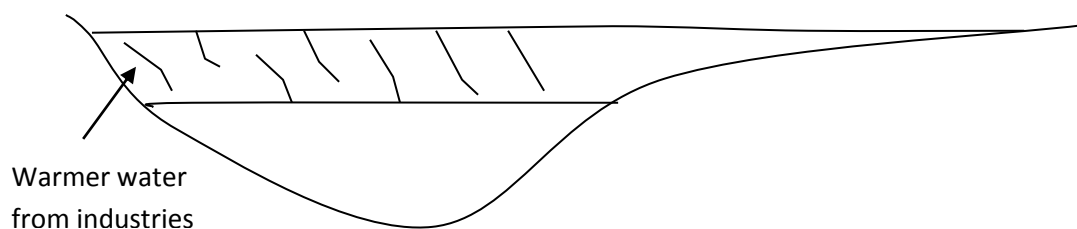
2. **Pressure effects** Pressure has virtually no effect on the solubility of solids and liquids but it significantly affects the solubility of gases. Carbonated drinks are bottled at high pressure so that more carbon dioxide is dissolved in the liquid. Equilibrium exists between the solute in solution and the gas (solute) above the solution. For a gas A;



If pressure is increased, it increases the number of gas particles per unit volume. According to Le Chatelier's principle, pressure can be relieved by a shift to the right of the equilibrium. More gas dissolves at high pressure.

3. Temperature effects

The solubility of gases in water decreases with increasing temperature since dissolution of a gas is exothermic $A_{(g)} \rightleftharpoons A_{(aq)}; \Delta H = -ve$



Water from lakes and rivers is used for industrial cooling. It is returned to its natural source at a temperature higher than ambient. This causes thermal pollution. The warmer water has less dissolved oxygen than normal. It will float on cold water and prevents normal oxygen absorption. The amount of oxygen available for aquatic life is reduced.

Henry's law

The law shows the relationship between gas pressure and the concentration of the dissolved gas.

$$P = K_H X$$

P - Gas pressure in atm

K_H - Henry's law constant (absorption coefficient)

X - Mole fraction of dissolved gas

Henry's Law: the amount of dissolved gas in a solution is directly proportional to the pressure of the gas above the solution.

The law is obeyed by dilute solutions of gases where the gas does not react with the solvent. Henry's law can also be expressed as

$$P = k_H \cdot C$$

Where C is the concentration of the gas in mol/L. k_H can have the units L atm / mol.

The following table lists values of k_H for various gases.

Gas	k_H (atm) (L/atm/mol)
CH_4	$4,13 \times 10^2$
CO_2	$1,64 \times 10^3$
O_2	$4,34 \times 10^4$
CO	$5,7 \times 10^4$

Invalidity of Henry's law

- (1) Different temperatures
- (2) Extremely high concentration or pressure
- (3) Different chemical species in solution

Activity

Comment on whether Henry's law is valid for the solubility of CO_2 in a basic solution.

Solvent extraction

It is the removal of a solute from one solvent into another one which is immiscible with the first one. Usually aqueous and organic phases are used. eg, water and ether. The solute must be soluble in both solvents. The two liquids are shaken together and allowed to settle. The solute distributes itself between the two solvents. Equilibrium is set up ie solute in aqueous phase and in the organic phase.

$$C_{(aq)} \rightleftharpoons C_{(org)}$$

At a given temperature the ratio of $C_{(org)}$ to $C_{(aq)}$ is a constant K

$$K = \frac{C_{(org)}}{C_{(aq)}}$$

K is called the partition coefficient.

Example

After 10, 0 ml of an aqueous solution containing 1.235mg of a drug was extracted with 5.0 ml of toluene, the aqueous layer was found to contain 0,346 mg of the drug compound. Calculate the partition coefficient of the drug between the two solvents.

At equilibrium, organic phase (toluene) contains $1,235 - 0,346 = 0,889\text{mg}$

10ml of the aqueous phase has 0,346mg

$$\text{Concentration in toluene} = \frac{0.889\text{mg}}{5\text{ml}}$$

$$= 0.1778\text{mg/ml}$$

$$\text{Concentration in aqueous phase} = \frac{0.346\text{mg}}{10\text{ml}}$$

$$= \mathbf{0.0346\text{mg/ml}}$$

$$K = \frac{C(\text{org})}{C(\text{aq})} = \frac{0,1778}{0,0346} = 5,14$$

An organic solvent may be used to extract a solute component from an aqueous phase. The concentration of the aqueous phase after extracting n times is given by

$$[A_{aq}]_n = \left(\frac{V_{aq}}{V_{org}K + V_{aq}} \right)^n [A_{aq}]_o$$

$[A_{aq}]_n$ - Final concentration after extraction

$[A_{aq}]_o$ - Initial concentration of aqueous phase

V_{aq} - Volume of aqueous phase

V_{org} - Volume of organic phase used for extraction

n - Number of extractions

K - Partition coefficient

Example

The partition coefficient of I_2 between ether and water is 85, calculate the concentration of I_2 remaining in the aqueous phase after extracting 50ml of 0,001M solution of I_2 using two 25 ml portions of ether.

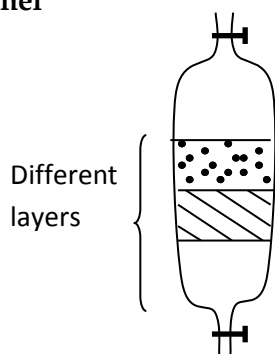
Solution

$$[I_{aq}]_2 = \left(\frac{50}{25 \times 85 + 50} \right)^2 \times 0.001$$

Procedure

Extraction is done using a separating funnel shown below:

Separating funnel



The aqueous layer is put in a funnel. Then a measured volume of the extracting solvent is added. The mixture is shaken thoroughly and then allowed to settle and equilibrium to be achieved. The liquids are immiscible. The lower layer is separated by opening the tap. The layer is then analysed for its concentration.

4.1 Summary

- Solubility refers to the dissolving of a solute into a liquid.
- Solubility is affected by pressure, temperature and chemical composition.
- Henry's law states that the amount of dissolved gas in a solution is directly proportional to the pressure of the gas above the solution.
- The partition coefficient is the ratio of concentration of a component between the two phases (for immiscible liquids).

Examination Type Questions

1. Calculate the solubility of O_2 (oxygen) in water at 25°C at a partial pressure of 120 atm. Henry's law constant for O_2 is $7.8 \times 10^2 \text{ atmL/mol}$. (in the form $P = kC$).
2. If iodine is shaken with 100cm^3 of water and 50cm^3 of an organic solvent, the concentration of iodine in the water layer is $8.0 \times 10^{-3} \text{ mol dm}^{-3}$ and in the organic layer is $1.0 \times 10^{-2} \text{ mol / dm}^{-3}$. What is the partition coefficient of iodine between solvent and water?

CHAPTER 11

PHASE DIAGRAMS

Substances exist either as pure compounds or as solutions of various types. Solutions may be of a solid in a solid (e.g metal alloys), a solid in liquid (salt in water) or liquids in liquids. The state (phase) of a pure compound is determined by conditions of pressure and temperature. It may exist as solid, liquid or gas. A phase diagram shows the states of the compound at particular values of pressure and temperature. For solutions the composition of solution or mixture becomes an important variable. The phase diagram of a solution/mixture is a plot of temperature against composition. The phase of a solution is determined by the temperature. This section looks at the phase diagram for pure compounds and for solutions.

Content

- 1.1 Phase diagrams for pure substances.
- 1.2 Phase diagrams for two component alloys.
- 1.3 Phase diagrams for a salt solution.
- 1.4 Summary.

Learning outcomes

- explain the meaning of phase.
- sketch and interpret phase diagrams of water and carbon dioxide.
- describe the phase changes that take place when pressure or temperature is varied for pure compounds.
- explain the triple point on a phase diagram.
- explain the critical point on the liquid/vapour curve.
- draw the phase diagram for a tin and lead mixture.
- describe an alloy.
- explain the term eutectic mixture.
- describe the phase changes that occur on cooling an alloy liquid mixture.
- describe the effect of temperature on the solubility of a salt.
- draw the phase diagram for a salt solution.

1.0 Meaning of phase

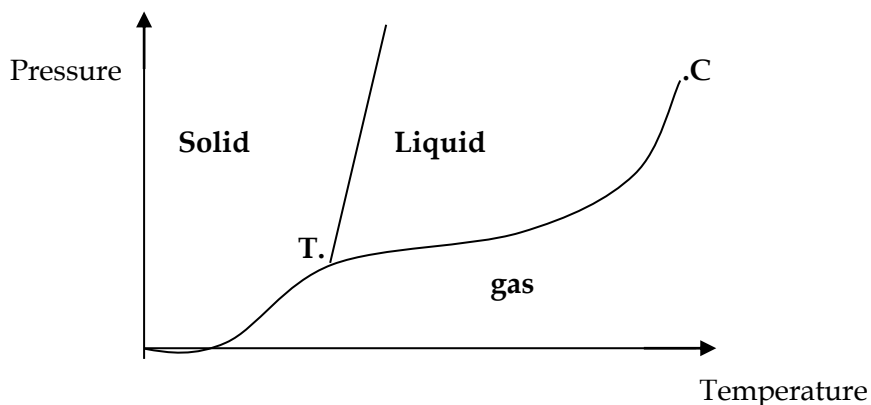
Phase can be the physical state of a substance i.e solid, liquid or gas. It can also refer to a state that is uniform in composition. This means two liquids can be described as two different phases for example a mixture of oil and water. Boundaries exist between phases.

Phase diagrams

These are curves that describe equilibrium conditions between phases. For pure substances the important variables (conditions) are temperature and pressure. For systems with two or more components, temperature and composition become important.

1.1 Phase diagrams for pure substances

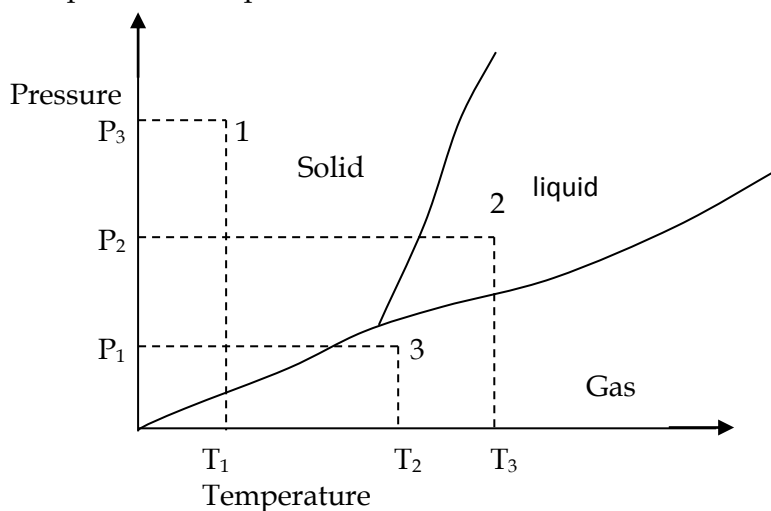
In this case the phases of the pure substance eg. water are solid, liquid and gas. A plot of pressure versus temperature gives the following curves.



The curves represent the equilibrium between the phases of the pure substance which are: solid, liquid and gas. The areas showing these phases are shown in the diagram above. Two other important points are also marked C and T. C is a limit on the curve representing equilibrium between the liquid and gas phases. It is called the critical point. T is called the triple point. It represents the conditions of equilibrium for all the three phases i.e. the condition under which all phases are in equilibrium.

1.1.1. Interpreting the phase diagram of a pure substance

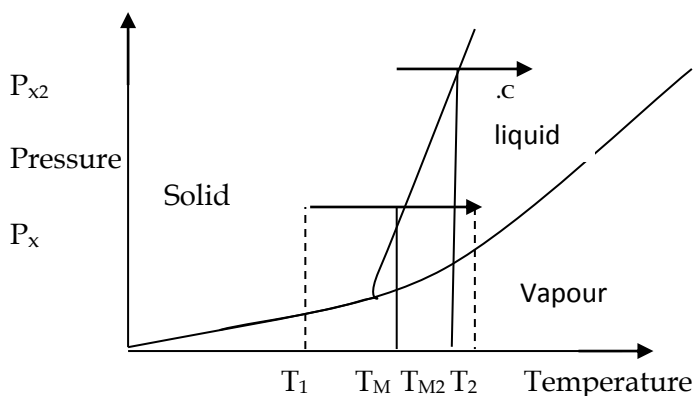
The diagram below shows three conditions of pressure and temperature labelled 1, 2 and 3. The phases of the pure substance can be deduced from the diagram.



At P_3 and T_1 the substance is solid since 1 lies within the solid phase area. At P_2 and T_3 the substance is a liquid as point 2 lies in the area for liquid phase. At point 3 i.e. P_1 and T_2 the substance is gaseous.

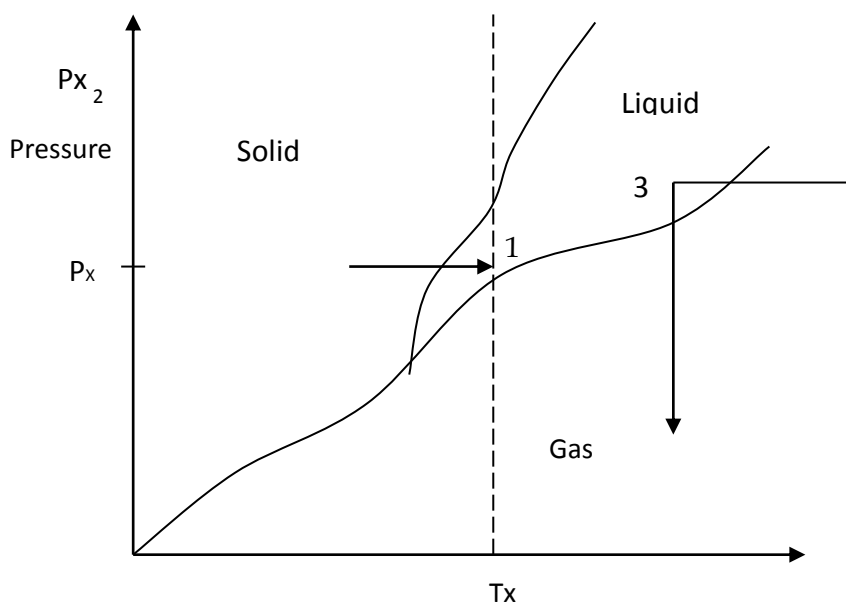
2. Effect of changing temperature

If temperature is increased at constant pressure to a pure substance in solid state, then the effect of change could be deduced from a phase diagram. Let pressure at which temperature is changed be P_x and the temperature be from T_1 to T_2 . The horizontal line from P_x , T_1 to P_x , T_2 shows what happened to the phase of the pure substance.



If temperature is increased from T_1 to T_2 the pure substance changes from solid to liquid. It melts. The substance melts at T_m when pressure is maintained at P_x . If the temperature change is carried out at a higher pressure P_{x2} then the solid would melt at a slightly higher temperature. The phase boundary between solid and liquid has a slight positive gradient.

3. Effect of changing pressure at constant temperature

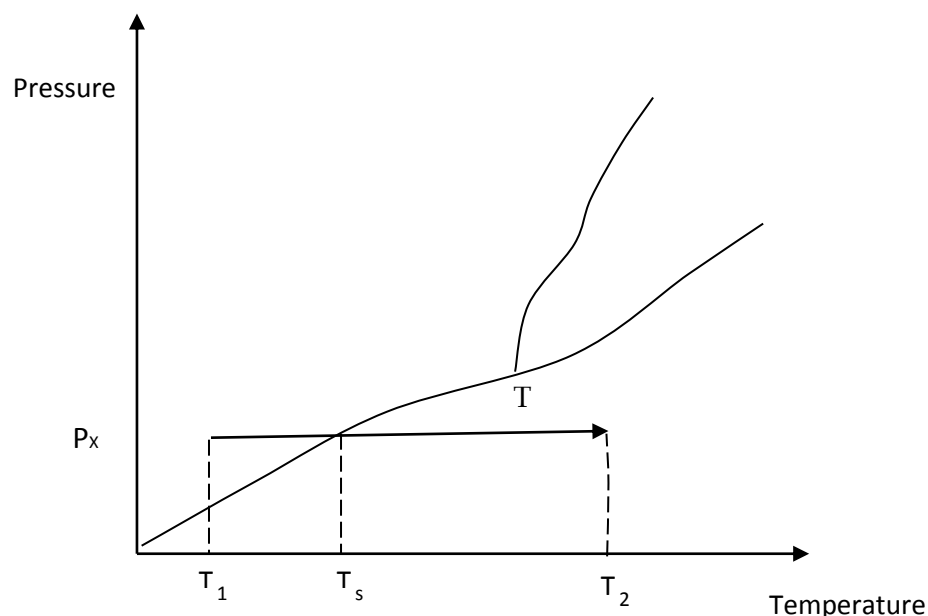


At point 1 the substance is in liquid phase. If its pressure is increased from P_{x1} to P_{x2} at temperature T_x , the substance changes from liquid to solid.

Liquid -gas changes

Point 3 in the phase diagram shows that phase change from liquid to gas can be achieved by either increasing temperature at constant pressure or by reducing pressure at constant temperature. The liquid boils under these conditions. The curve represents the effect of pressure on the boiling point of the pure substance.

Solid -vapour changes



Below the triple point, the solid phase exists in equilibrium with the gas phase. Any changes of phase would be solid to gas or gas to solid without passing through the liquid phase that is, sublimation occurs.

Sublimation can be achieved by increasing temperature at low pressure i.e from T_1 to T_2 . T_s is the sublimation temperature. Sublimation can also be achieved by decreasing pressure at a temperature below the triple point.

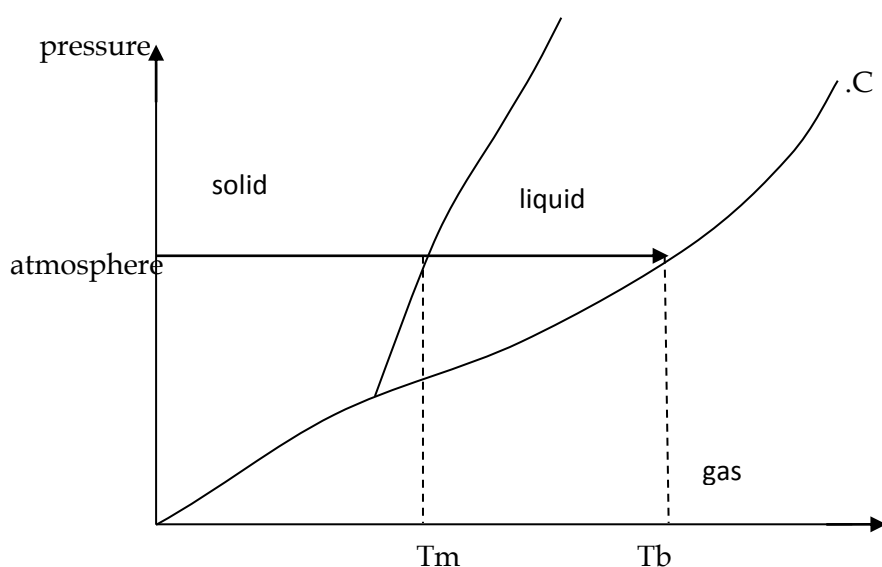
The critical point

The temperature at C is called the critical temperature and the pressure is the critical pressure. Below C, varying temperature or pressure results in a change of phase. Above C, there is no change of phase. At high temperature, particles have enough kinetic energy to prevent them from associating even though pressure may be very high. The critical temperature varies from substance to substance. Substances with strong inter particle interactions have high critical temperatures.

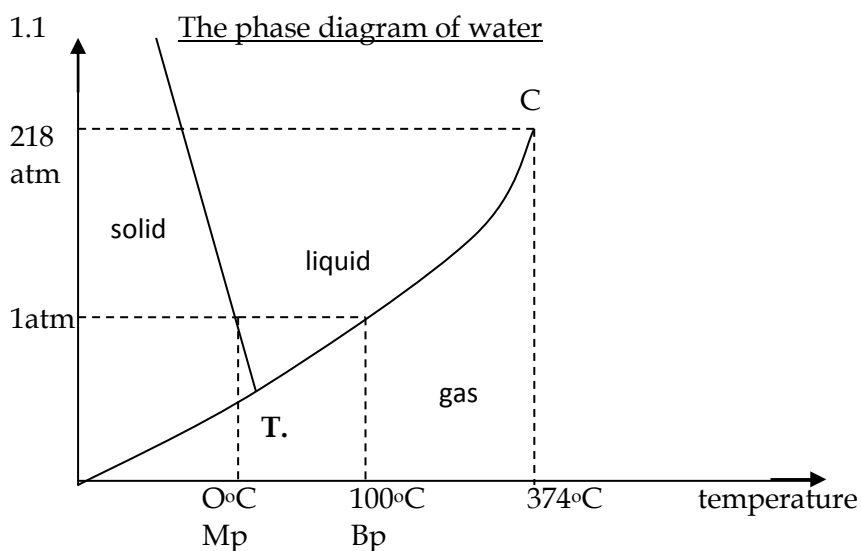
The triple point T

At T all the phases are in equilibrium. Theoretically, all processes would take place i.e melting, boiling, condensation, sublimation e.t.c.

Normal melting and boiling points



The normal melting and boiling points are those at a pressure of 1 atmosphere i.e T_m and T_b . These can be deduced from the phase diagram.



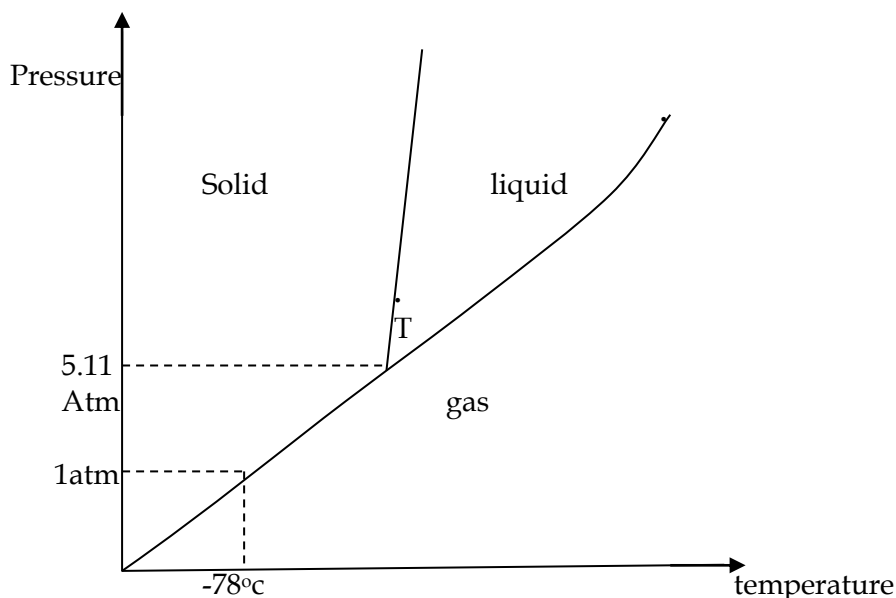
The solid-liquid line has a negative gradient. Increasing pressure lowers the melting point. Equilibrium exists between ice and water.

Ice \rightleftharpoons Water

Ice occupies greater volume than water. This is because ice has an open cage like structure. Increasing pressure to such an equilibrium would favour the direction which results in reduction of volume hence increase in pressure encourages melting.

Above 374°C, it is not possible to convert water from gas to liquid by compression.

1.1.3. Phase diagram for carbon dioxide



The unique feature of this diagram is the position of the triple point which is well above atmospheric pressure. Under normal conditions, only the solid or gas are obtained. Carbon dioxide is used as 'dry ice' since it does not form liquid under normal conditions. It sublimates.

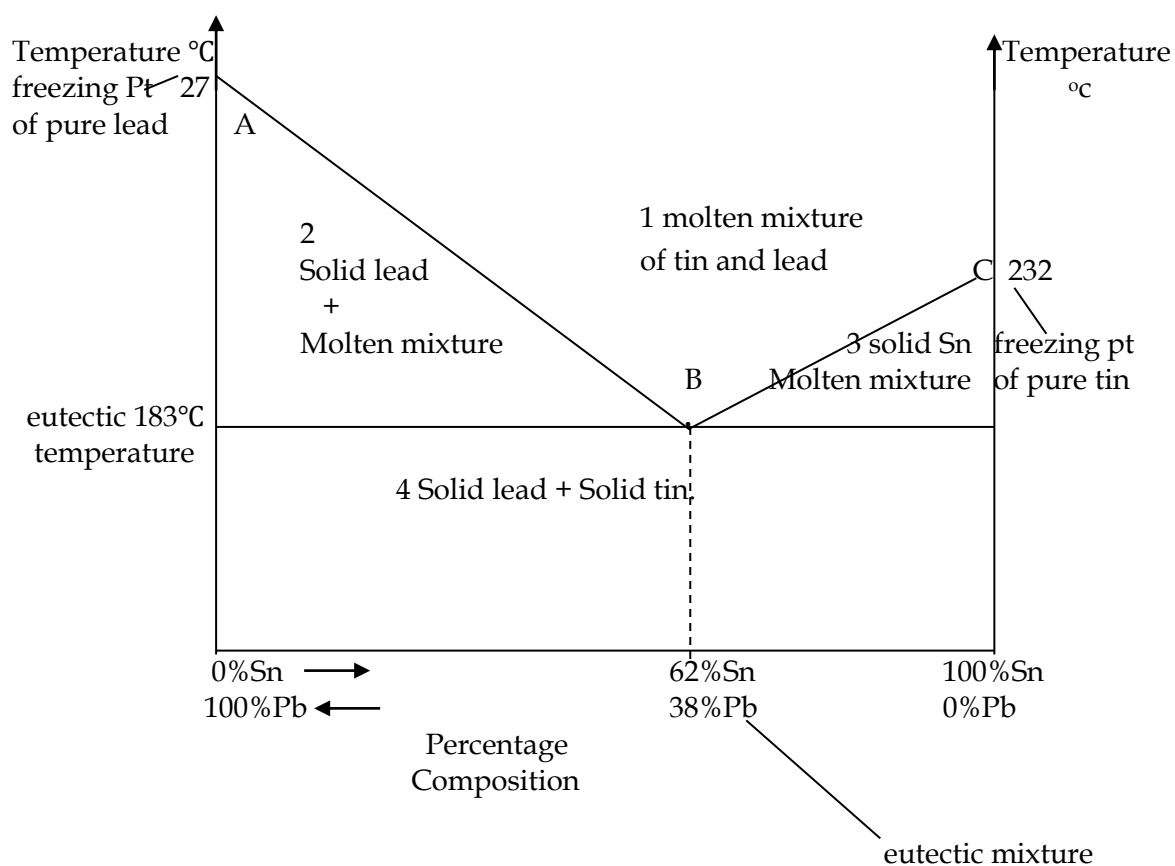
1.2 Phase diagram for a two component alloy

When the number of components is more than one, composition of a mixture becomes an important variable. The phase diagram is now obtained by a plot of composition against temperature. Temperature scale is shown on either side of the diagram.

1.2.1 Tin and lead mixture (diagram)

The freezing point of lead is 327°C and that of tin is 232°C. The addition of tin to lead lowers the freezing point of lead. The less tin present, the smaller the drop in the freezing point of lead. As the proportion of tin increases in the mixture, lead starts to freeze at lower and lower temperatures. The freezing of the whole mixture will occur at 183°C i.e. both lead and tin freeze. The composition of the mixture that freezes at this temperature is 62% tin and 38% lead.

Starting with pure tin whose freezing point is 232°C, the effect of adding lead to tin is the lowering of the freezing point of tin. As more lead is added to tin, the freezing point of tin is lowered more and more until the whole mixture solidifies at 183°C. The composition of the mixture that freezes at 183°C is 62% tin and 38% lead. This mixture is called a eutectic mixture. It has the lowest freezing/melting point.



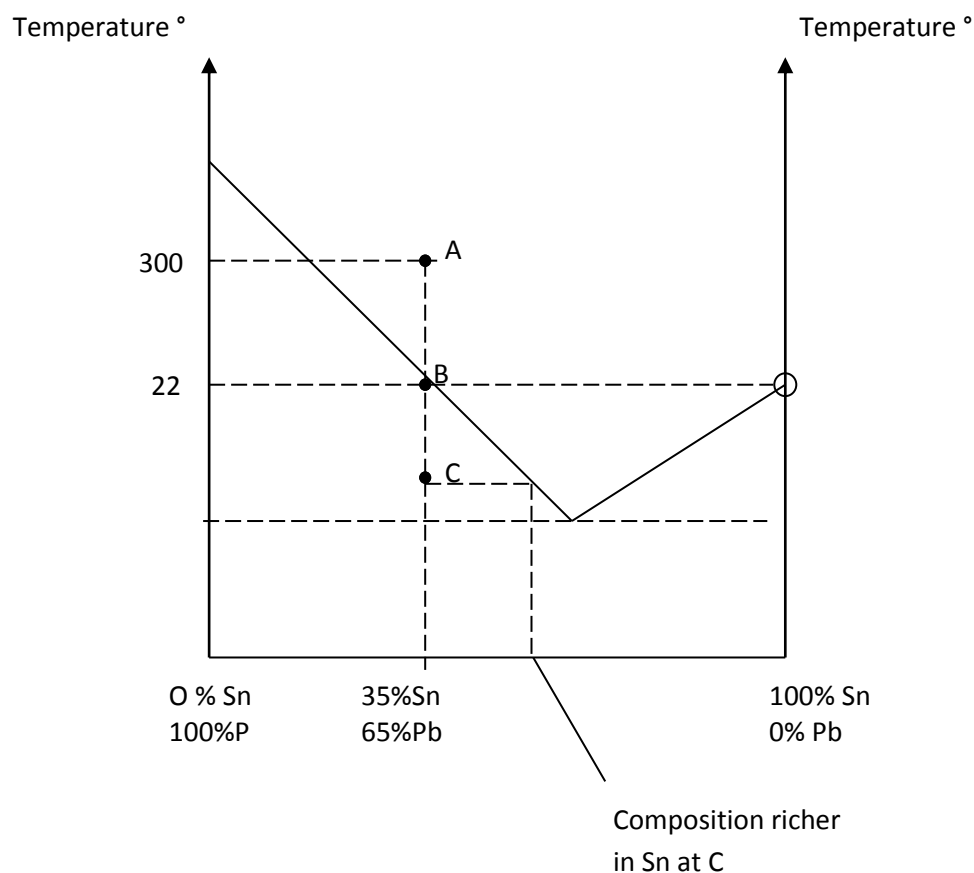
- The line AB shows the variation for the freezing point of leads as the amount of tin in lead is increased
- The line CB shows the drop in the freezing point of tin as the amount of lead in tin is increased.
- Below the temperature 183°C, the mixture solidifies
- At B the molten liquid and the solid have the same composition.

Phases:

- At 1 - Molten mixture of tin and lead
- 2 - Solid lead and liquid mixture
- 3 - Solid tin and liquid mixture
- 4 - Solid lead + Solid tin

1.2.2 Using the phase diagram

A mixture that is 65% in lead and 35% in tin at 300°C falls in the area marked 1 in the diagram above, ie. It is molten lead and tin.



If the mixture above is cooled to about 220°C. The composition as a whole does not change (i.e 65%Pb and 35% Sn). To determine what will be observed at 220°C a tie line (horizontal line) through B is drawn and composition of the mixture is deduced from the ends of the tie line.

Therefore at 220°C the mixture is made up of 100% Pb (left end) which has become solid and on the right end the composition of the mixture is in liquid form.

If mixture is further cooled to C, the liquid remaining after lead solidifies becomes even richer in tin. The liquid moves closer to the eutectic mixture. This continues until the composition of the liquid equals that of the eutectic mixture and solidifies.

Cooling the eutectic mixture

As the eutectic mixture is cooled, the liquid maintains its composition and solidifies on reaching the eutectic temperature.

1.2.3. Tin and lead solder

The alloy is used as a solder. Its composition is 60% tin and 40% lead. This is close to the eutectic composition. It melts with a sharp temperature range. If composition of solder varies greatly from the eutectic composition, it tends to melt over a wide range of temperatures. It may not be useful where quick drying is necessary but it is useful in plumbing where the solder is supposed to be workable for some time.

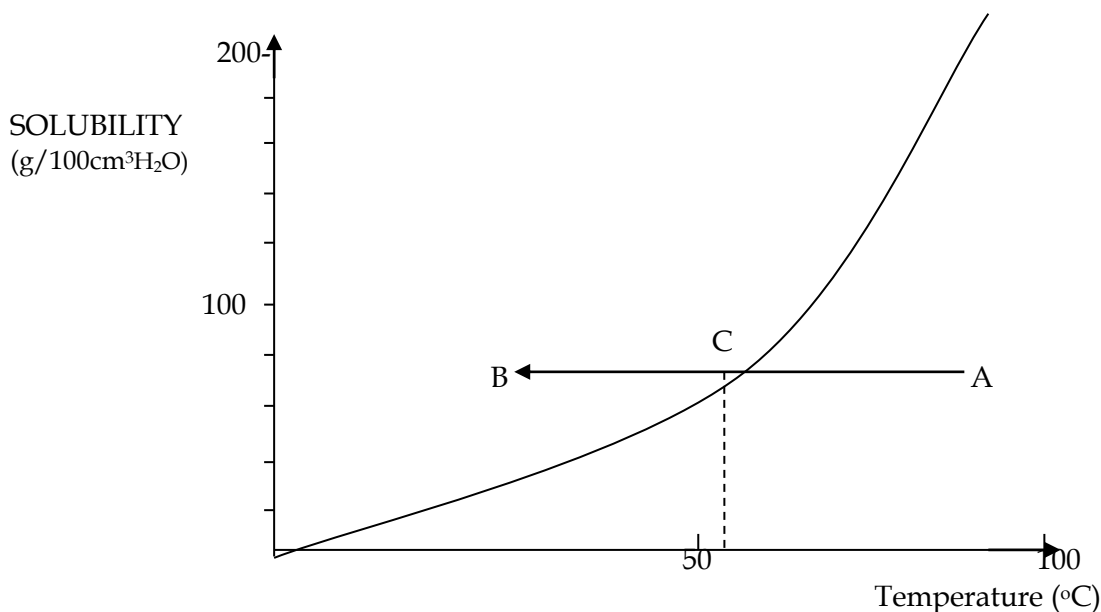
1.3 Phase diagram of salt solution

1.3.1 Solubility curve

The curve shows how temperature affects the solubility of a salt. A solution becomes saturated when no more salt can dissolve. Most substances show an increase in solubility with increasing temperature.

In this case, solubility is given by the mass of salt which saturates 100g of water at a given temperature.

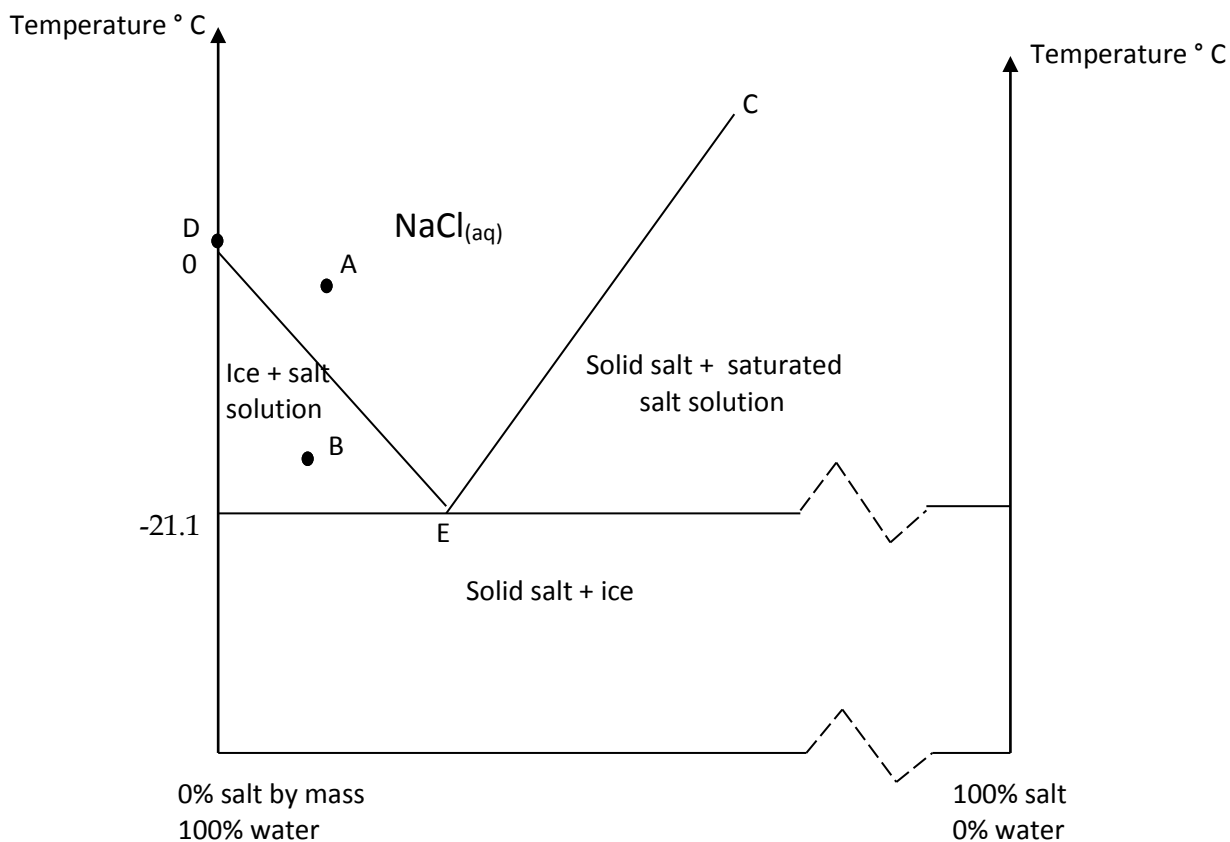
Solubility curve of KNO₃



Interpreting the solubility curve

Consider starting with a solution containing 80g of KNO₃ in 100g water near its boiling point. If the solution is allowed to cool (line AB), it meets the solubility curve at C. This occurs at a temperature just above 50°C. Further decrease in temperature causes potassium nitrate to crystallise out of solution. Two phases now exist i.e liquid solution and solid potassium nitrate.

1.3.2 Phase diagram of sodium chloride



- The temperature range is restricted
- The important changes taking place on the left hand side part of the horizontal scale are missing.
- Below -21.1°C only solid salt and ice exist
- Above -21.1°C salt solution exists (A) and a mixture of ice and salt solution exist at B.
- D E represents the effect of increasing amount of salt on the freezing point of water. The decrease in freezing point continues until 23.3% of salt has been added.
- If a 23.3% salt solution is cooled it forms a solid mixture of same composition
- If a dilute (less than 23.3%) is cooled, ice forms and the remaining solution becomes richer in the salt.
- If cooling is continued, the remaining salt solution achieves a concentration of 23.3% at -21.1°C in which case the mixture solidifies.

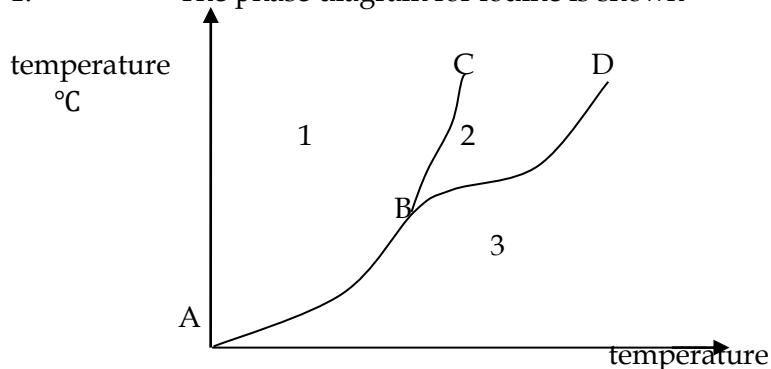
1.4. Summary

- Phase refers to the physical state of substance or a state that is uniform in composition.
- Phase diagrams describe the condition of equilibrium between phases and also areas where a substance exists as a single phase.
- The phase of a pure substance is determined by the conditions of pressure and temperature. When the conditions are changed, a substance may undergo phase change.
- Varying conditions above the critical point will not result in a phase change.

- The triple point is the condition of pressure and temperature where all three states (solid, liquid and vapour) are in equilibrium. Theoretically all change of state should occur at the triple point.
- Alloys are solid- solid mixtures. The melting point of a component is lowered by the presence of a second component.
- The alloy composition that has the lowest melting temperature is called a eutectic mixture
- When a molten alloy is cooled, only one of the components solidifies before the eutectic temperature is reached. At the eutectic temperature the solution solidifies
- The eutectic mixture has the same composition in liquid and solid state.
- The solubility of a salt generally increases as temperature increases.
- When a dilute salt solution is cooled, ice only forms below 0°C due to freezing point depression by salt.
- When salt concentration is 23.3%, the eutectic composition, solution solidifies without change in composition.

Questions

1. The phase diagram for iodine is shown



- Label the areas 1, 2 and 3
- By considering the slope of BC, explain how the melting point of iodine is affected by increasing pressure.
- How is the phase of I₂ affected by increasing pressure and temperature beyond point D?

2. The freezing points of various naphthalene and 4-nitrophenol are given below.

% naphthalene	100	82	70	59	50	40	30	20	10	0
Freezing point/°C	79.5	70	61.5	54.0	44.5	35.0	31.5	39.0	45.5	51.0

- On a graph paper draw the phase diagram of the above mixture and label all regions on the diagram.
- Determine the eutectic temperature.
- What is the composition of the eutectic mixture?

CHAPTER 12

RAOULT'S LAW AND DISTILLATION

Distillation is an important separation process both industrially and on an analytical scale. The ease of distillation depends on the properties of the liquids in a mixture or the mixture itself. Liquid mixtures either obey Raoult's law or show marked deviations from it. Distillation of mixtures that do not obey Raoult's law is not straight forward. This section will describe liquid-liquid mixtures in relation to Raoult's law. It will also describe distillation of various liquid-liquid mixtures. Steam distillation is also outlined.

Content

2.1	Ideal mixtures
2.2	Boiling point- composition diagrams of ideal mixtures
2.3	Fractional distillation of ideal liquid mixtures
2.4	Non-ideal mixtures
2.5	Boiling point- composition diagrams for non-ideal mixtures and distillation
2.6	Fractional distillation in the laboratory
2.7	Steam distillation
2.8	Summary

Learning Outcomes

- explain component interaction in an ideal mixture.
- state Raoult's law.
- explain the effect of adding a non-volatile solute to a liquid.
- describe an ideal mixture.
- draw boiling point-composition diagrams for ideal mixtures.
- describe fractional distillation of ideal mixtures.
- determine the number of theoretical plates in a distillation column.
- describe and explain behaviour of non-ideal mixtures.
- draw boiling point- composition diagram for non- ideal mixtures.
- explain how an azeotrope is formed.
- describe the distillation of a non-ideal mixture.
- describe apparatus used for distillation.
- describe steam distillation.

2.1 Ideal mixtures

Particles in a pure liquid have varying amount of energy. Some of the particles have enough energy to overcome intermolecular forces to form vapour. A liquid with low intermolecular forces easily forms vapour. An equilibrium is set up between the liquid and the vapour.

If a second liquid is introduced to the first one, it will behave similarly. Some of its molecules escape to form vapour. In an ideal mixture, the tendency of molecules to escape to from vapour is the same as in pure liquid. It means that intermolecular forces are the same, i.e between molecules of the liquids and between molecules of the different liquids.

Liquid A	Liquid B	Mixture
Interactions A-A	B-B	A-B

If the interactions are different, the tendency of particles to escape into vapour will be different.

Examples of ideal mixtures

Liquids with similar characteristics approximate an ideal mixture. Examples are:

- Heptane and hexane
- Benzene and methylbenzene
- Propan-1-ol and propan-2-ol

Partial pressure and total vapour pressure.

The pressure of the gas/vapour above the liquid is the total vapour pressure. It is the sum of the partial pressures of gaseous A and gaseous B i.e. P_A and P_B ;

$$\text{Total vapour pressure} = P_A + P_B$$

The partial pressures are proportional to the number of moles of the component in the mixture

$$P_A = X_A x P_A^o$$

$$P_B = X_B x P_B^o$$

X = mole fraction

P^o = Vapour pressure of pure component

In the mixture each gas exerts its own pressure.

Raoult's law

The partial vapour pressure of a component in a mixture is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in the mixture.

$$\therefore P_A = X_A x P_A^o$$

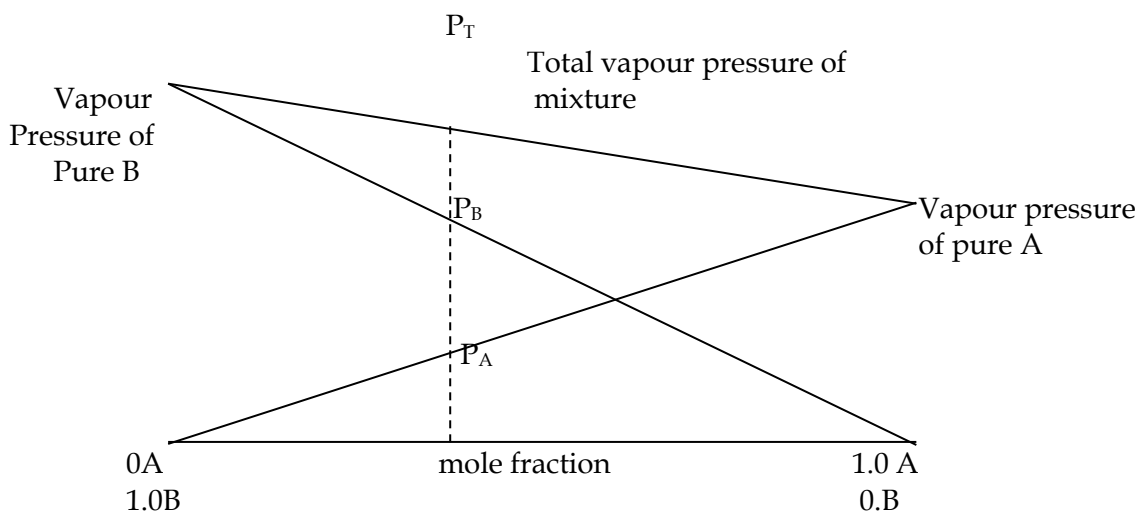
or

$$P_B = X_B x P_B^o$$

The equations are of the form $y = mx + c$, A plot of P_A against X_A gives a straight line. Ideal mixtures obey Raoult's law

Vapour pressure ↑

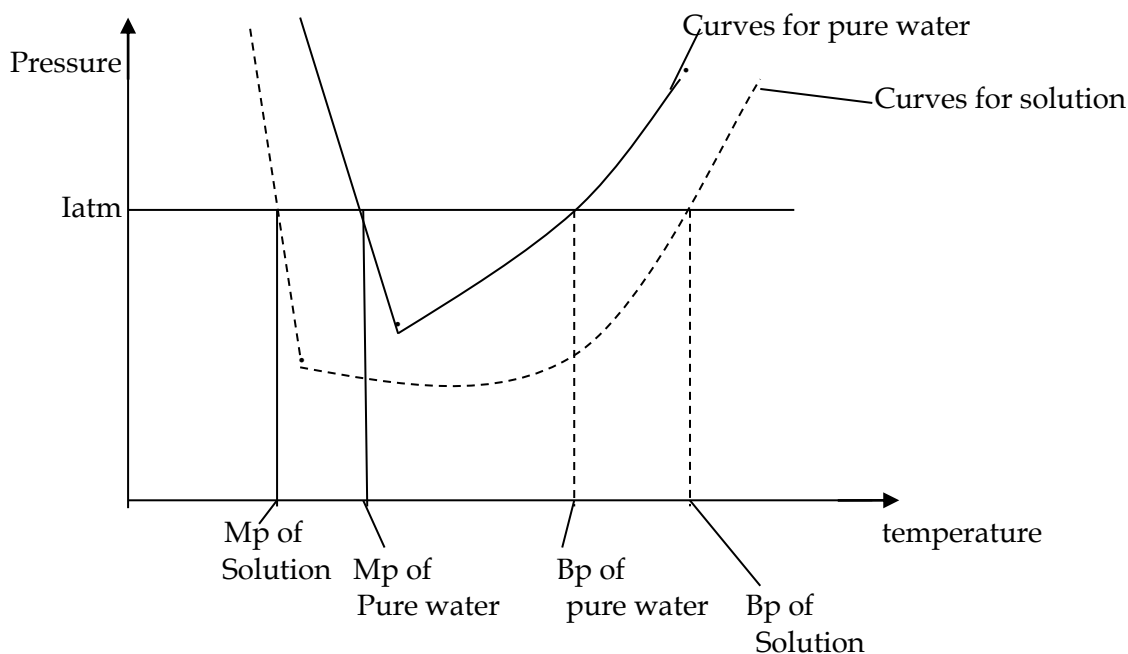
Vapour pressure ↑



To get total vapour pressure of mixture, the values for A and B are added together at each composition $P_T = P_A + P_B$.

Addition of a non- volatile solute to a liquid

The solute reduces the number of liquid (solvent) molecules at the surface. This lowers the tendency of the liquid molecules to form vapour. The vapour pressure of the solvent is lowered. If the solvent is water the effect of a solute on freezing and boiling points can be deduced from the phase diagram of pure water.

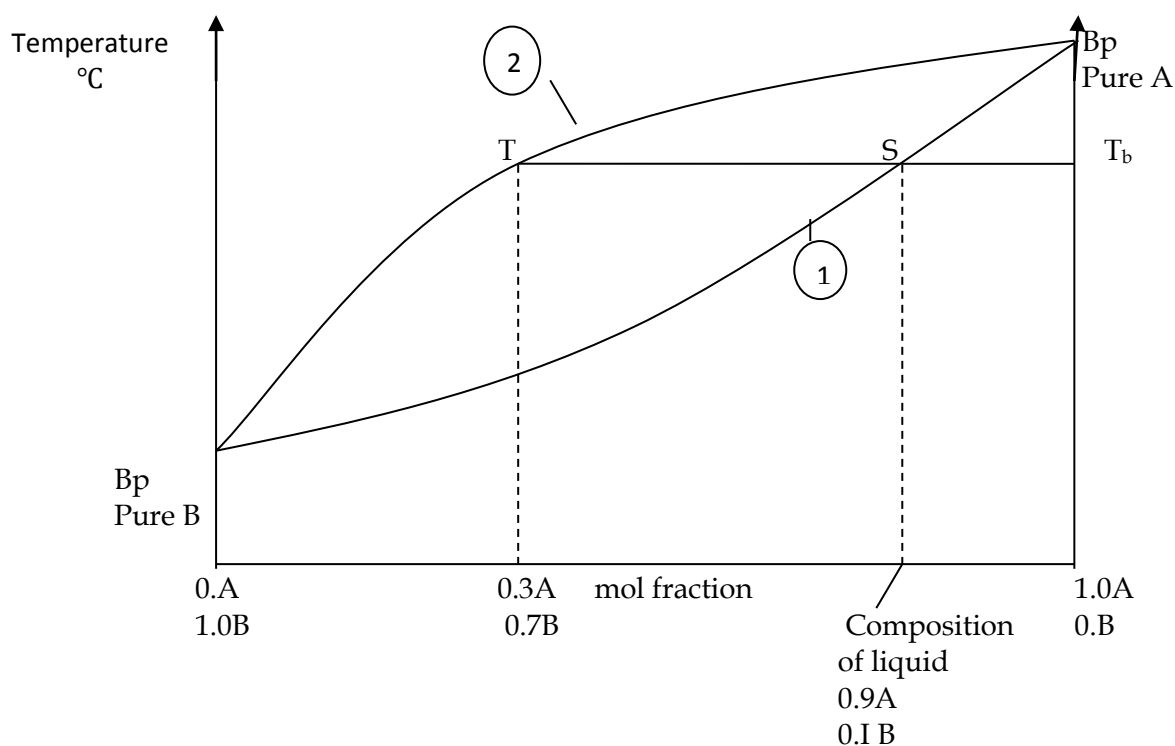


The presence of solute lowers the melting point and elevates the boiling point.

2.2 Boiling point-Composition diagram for ideal mixtures.

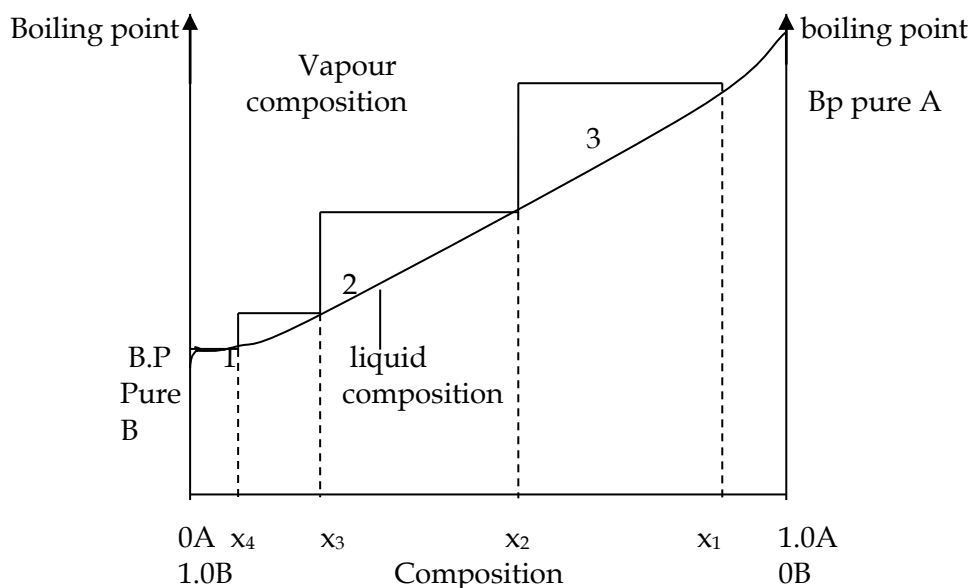
For the components A and B in a mixture where B has a higher vapour pressure than A, it follows that B has the lower boiling point and A has higher boiling point. The boiling points of pure components are marked on a boiling point- composition diagram.

If the boiling points are plotted against composition of mixture a curve (1) is obtained. It shows the composition of the liquid mixture. Each composition of mixture of the liquid is in equilibrium with vapour of a particular composition. If vapour phase composition is plotted against boiling point, another curve is obtained.



If a liquid mixture has composition 0.9 A and 0.1B, it will boil at temperature T_b. The line ST links the liquid composition curve and the vapour composition curve. The liquid at S produces a vapour with the composition at T, that is 0.3A and 0.7B. The vapour is rich in B.

2.3 Fractional distillation of ideal liquid mixtures



If liquid of composition x_1 is boiled, it gives off vapour of composition x_2 . If the resulting vapour is cooled, it gives liquid of same composition. If liquids of composition x_2 is boiled, it gives off vapour of composition of x_3 . Again if the vapour is cooled, a liquid of same composition is formed. When liquid of composition x_3 is boiled, a vapour with composition x_4 is produced. If the vapour is cooled a liquid with composition very close to pure B is obtained, Hence A is separated from B. Separation is achieved by a series of boiling - condensing and reboiling processes.

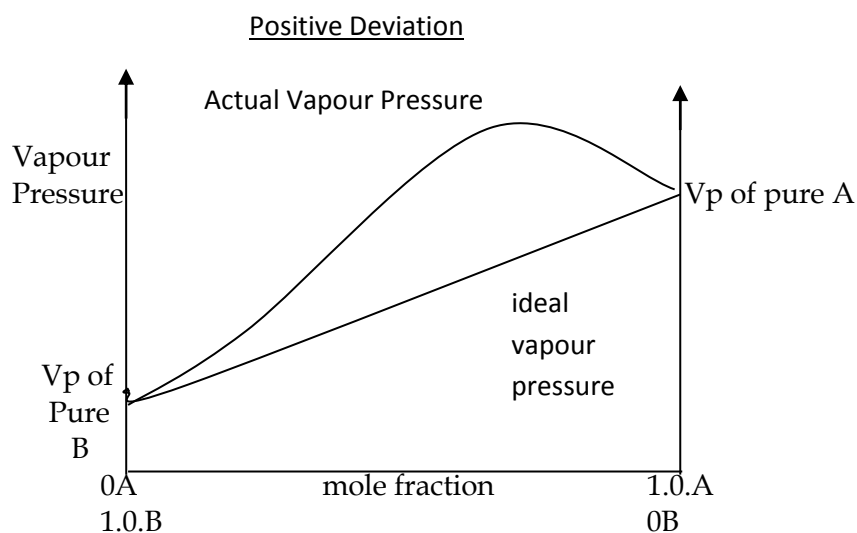
Theoretical plates

From the diagram above, the steps 1, 2, 3 represent the theoretical stages or plates required to effect a separation of a mixture with composition of X_1 practically the number of plates is slightly different.

2.4. Non- ideal mixtures

Deviations from Raoult's law

Positive deviations: The vapour pressure off the mixture is always higher than that expected from ideal.



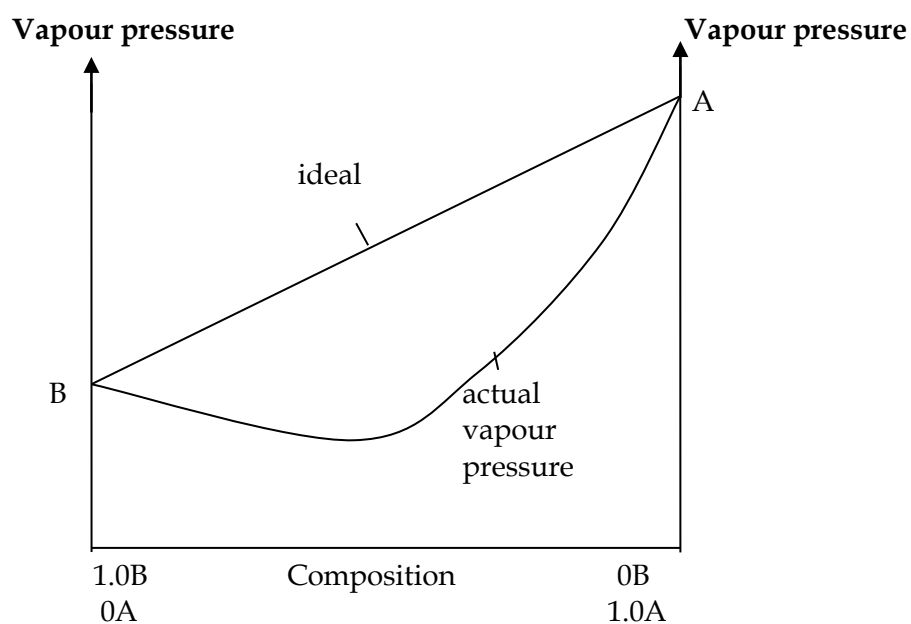
The mixture in this case shows a very large deviation (positive). It forms a maximum higher than both vapour pressures of A and B.

Positive deviations imply that molecules are leaving the liquid more easily than a pure liquid. Interaction between A and B are less than in pure liquids. Such interaction produces very little heat on mixing A and B than energy absorbed to break original associations. The overall energy change is endothermic.

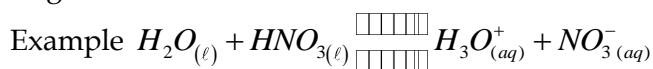
Ethanol and water form a non-ideal mixture that exhibits a large positive deviation from Raoult's law.

Negative deviations

Vapour pressure is less than that expected for an ideal mixture. Greater deviation results in the formation of a minimum or the curve lower than that of either pure components.



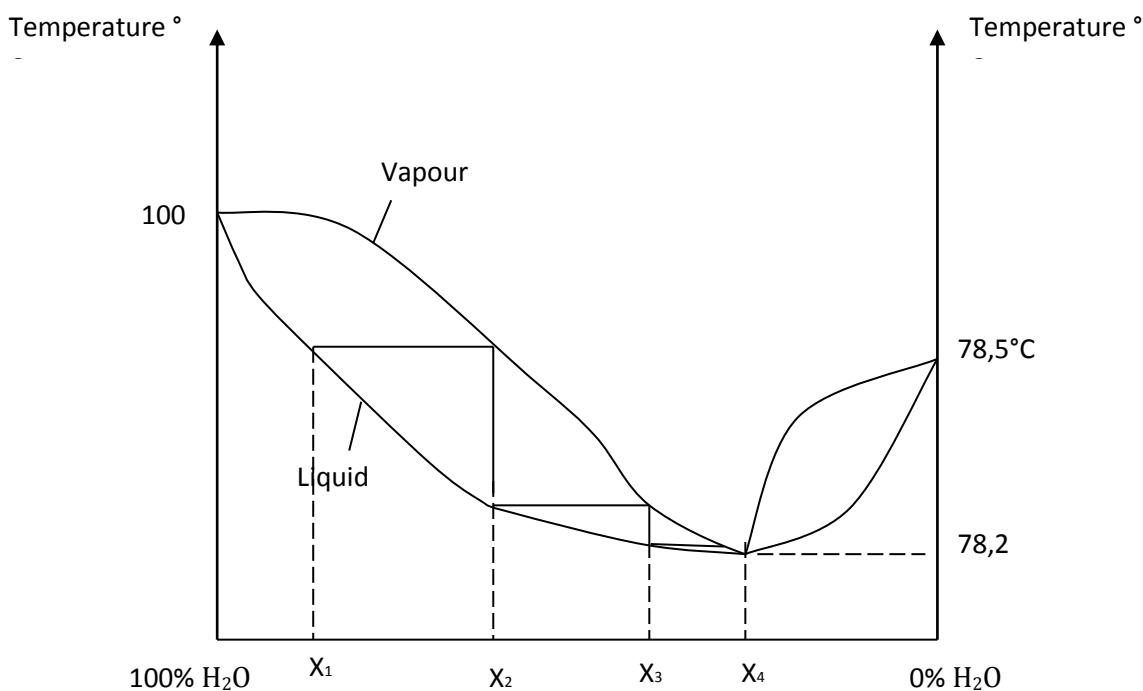
Negative deviations indicate that molecules do not easily leave the liquid phase than they do in pure liquids. The overall process is exothermic because, the bonds formed are stronger. More energy is given out in the formation of new bonds than was taken in breaking the original ones.



2.5 Boiling point- composition diagrams for non-ideal mixtures and distillation

Ethanol- water mixture

- It has a large positive deviation from Raoult's law.
- It produces a maximum on the vapour pressure curve
- The boiling point/composition curve will have a minimum value lower than boiling points of pure components for ethanol/water mixture. The minimum occurs with 95,6% by mass of ethanol. The boiling point of water is 100°C and that of ethanol is 78,5°C. The mixture with 95,6% ethanol boils at 78,2°C.

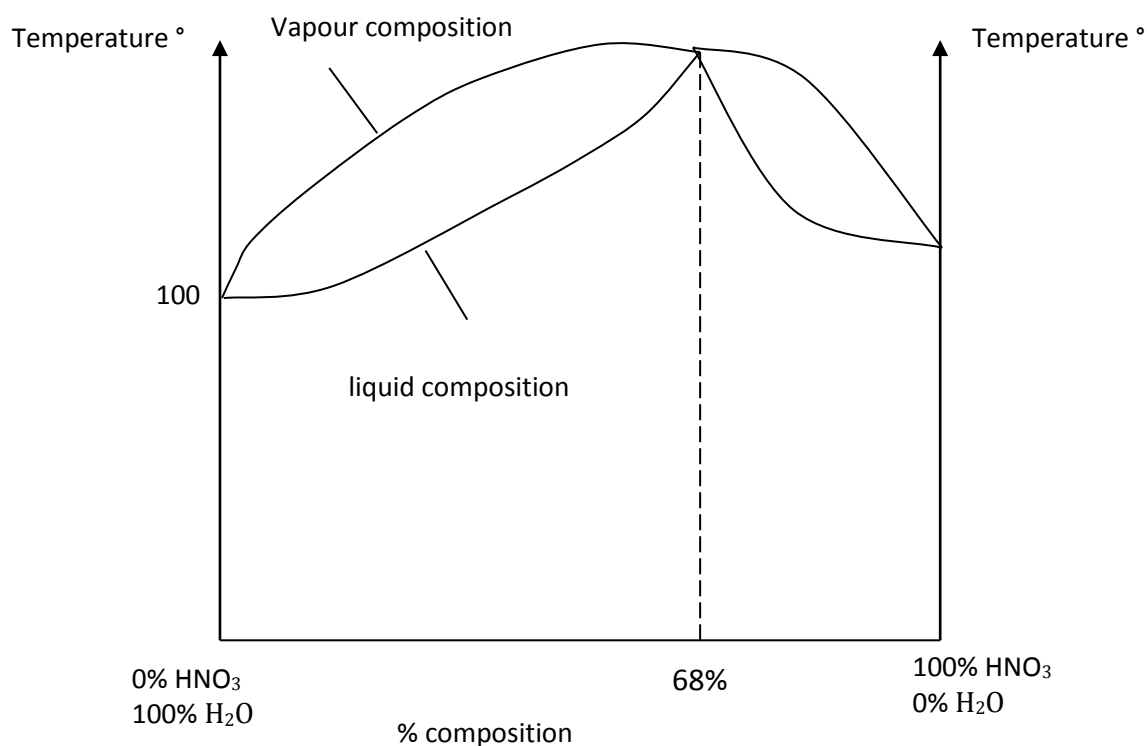


Azeotrope mixture

Boiling an ethanol-water mixture with composition x_1 gives vapour of composition x_2 . If the vapour is cooled, liquid of composition x_2 is formed. This is repeated until liquid of composition x_4 is produced. If this liquid is boiled it produces vapour of same composition. Separation of ethanol and water is not possible at this composition. The mixture has a composition of 95,6% ethanol (by mass). The mixture is called an azeotrope. It prevents further separation of the mixture.

Nitric acid-water mixture

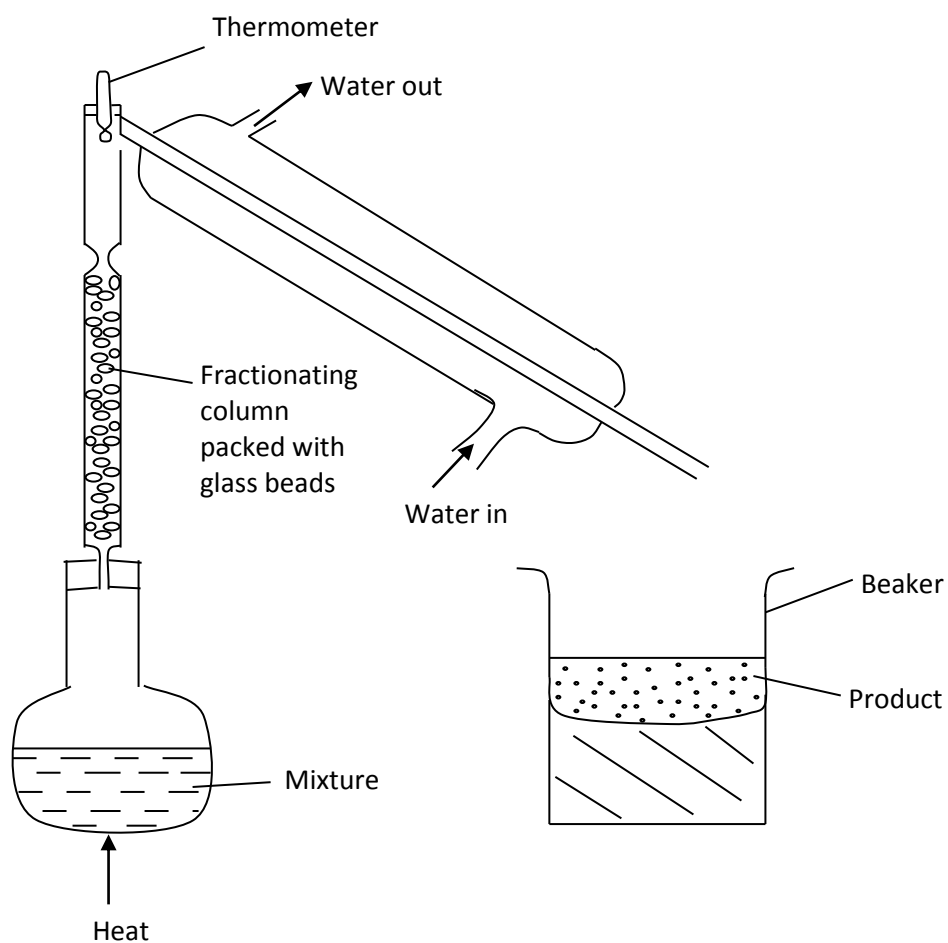
It shows a large negative deviation. It forms an azeotrope at 68% by mass nitric acid with a boiling point of 120°C.



Distillation of Nitric acid produces 68% as final product.

2.6 Fractional distillation in the laboratory

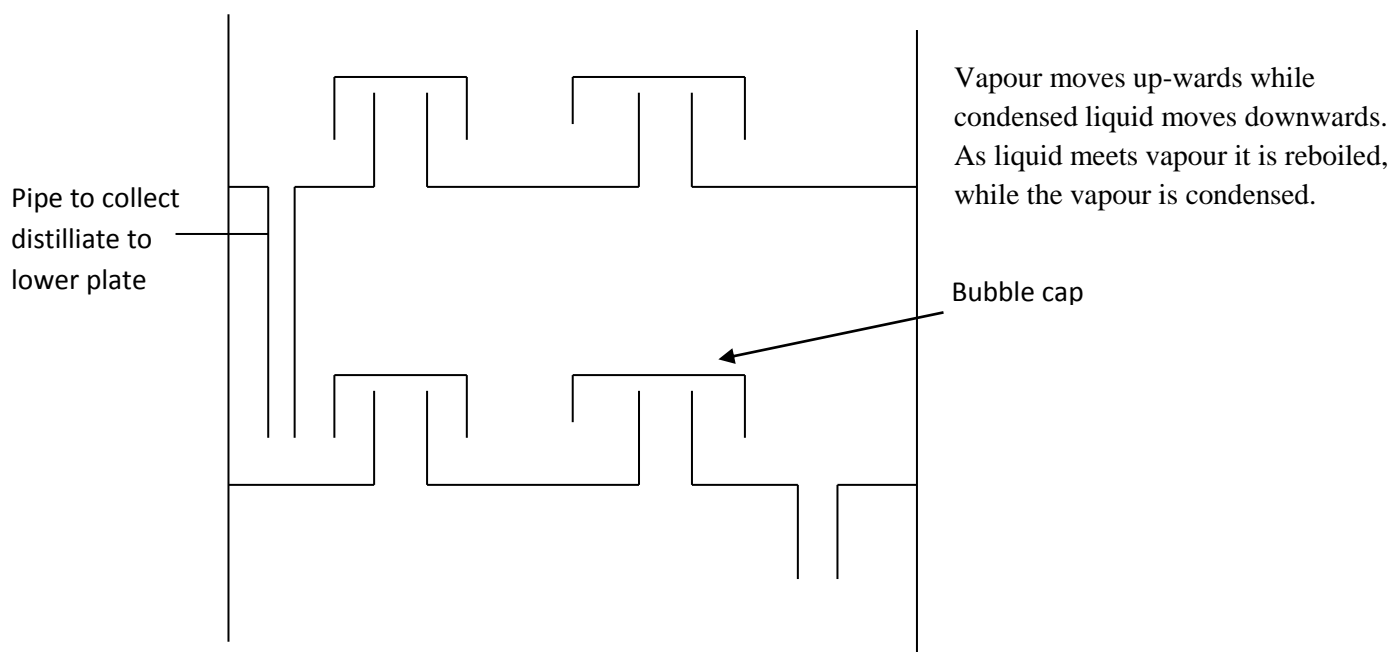
The apparatus are show below:



- Glass beads-provide large surface area for vapour to condense on.

- The temperature is maintained at the boiling point of the more volatile components.
- The vapour is richer in the more volatile component and the liquid remaining in the flask becomes richer in the other component.
- Reboiling and condensing is achieved by presence of packing material

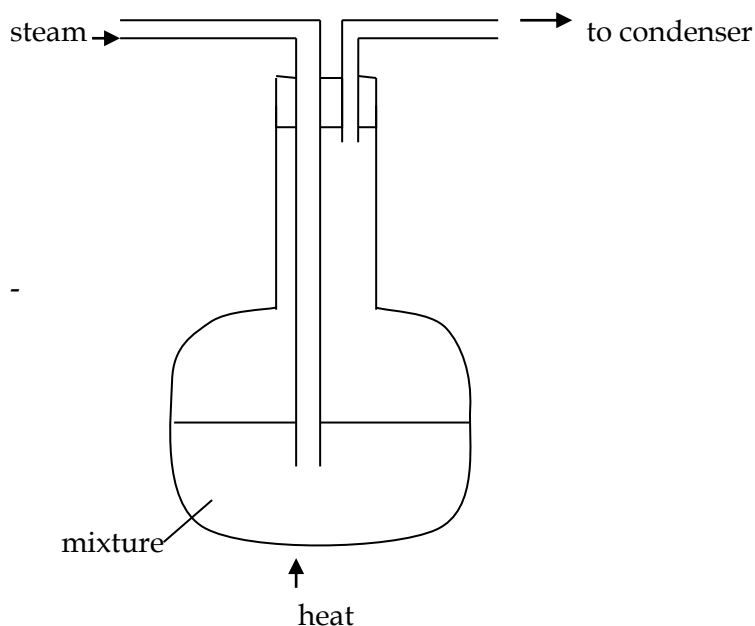
Industrially, distillation columns are used for fractional distillation. These have stages or trays over which reboiling and condensation occurs. A section of a table cap column is shown below.



2.7 Steam distillation

It is used for distillation of immiscible mixtures, particularly those immiscible with water. In the presence of water, the other component boils far below its normal boiling point. Normal distillation of such components would require high temperatures. But high temperature would decompose the components. When distilled in the presence of water, temperature is kept low.

Apparatus



Steam is generated in a separate flask. As steam passes through the mixture, it condenses, releasing heat. The heat released is enough to boil the mixture.

Steam distillation can be used to extract products such as eucalyptus oil and citrus oils from lemon orange peels.

2.8 Summary

- In an ideal liquid-liquid mixture the tendency to form vapour is the same as in a pure liquid. All intermolecular forces are the same.
- Raoult's law states that the partial pressure of a component in a mixture is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in the mixture.
- Addition of a non-volatile solute to a liquid lowers the freezing point of the liquid and elevates its boiling point.
- Non-ideal mixtures show positive or negative deviations from Raoult's law.
- The vapour curve and liquid curve for a non-ideal mixture converge at composition called an azeotrope.
- Further separation of a non-ideal mixture is not possible beyond the azeotrope mixture.
- Steam distillation is used to distil components that are decomposed by excess heat. The presence of water in the mixture lowers the boiling point of the component to be distilled.

Examination Type Questions

1. A mixture of two miscible liquids A and B was distilled under reflux. The composition of the vapour in equilibrium with the liquid was determined. This was repeated several times with mixtures of different compositions. The results are shown below.

BP of mixture in °C	100.0	90.8	83.8	79.0	77.8	78.6	81.2	85.0
Mole fraction of A in liquid mixture	0	0.20	0.40	0.60	0.70	0.80	0.90	1.0
Mole fraction of A in Vapour	0	0.38	0.58	0.68	0.70	0.72	0.80	1.0

- (a) On a graph draw the curves for boiling point against composition for both liquid and vapour.
- (b) By considering the shape of the curves, explain the nature of the mixture (ideal or non-ideal).
- 2.(a) State Raoult's law as it applies to a mixture of two miscible liquids.
- (b) Sketch a boiling/composition diagram for a mixture of two liquids which obey Raoult's law labelling the liquid and vapour curves.
- c) Use the curves to explain fractional distillation.

CHAPTER 13

SEPARATION TECHNIQUES FOR ANALYSIS: CHROMATOGRAPHY AND ELECTROPHORESIS

The reagents that are used in analysis may not be specific which renders the process difficult. It is sometimes necessary for components of a mixture to be separated so that they are analysed individually. Chromatography and electrophoresis are some of the methods used to separate compounds of a mixture for analysis. Modern technology makes it possible to automatically separate and detect the compounds of a mixture. Suitable output enables identification of components and their qualification. The section discusses chromatographic and electrophoretic methods.

Content

- 1.5 Chromatographic methods
- 1.6 Electrophoresis
- 1.7 Summary

Learning outcomes

- on completion of this section candidates should be able to :
- describe chromatographic methods of separation.
- explain qualitatively chromatographic methods.
- describe electrophoresis.
- explain use of electrophoresis to separate charged species.
- explain the analysis of genes.

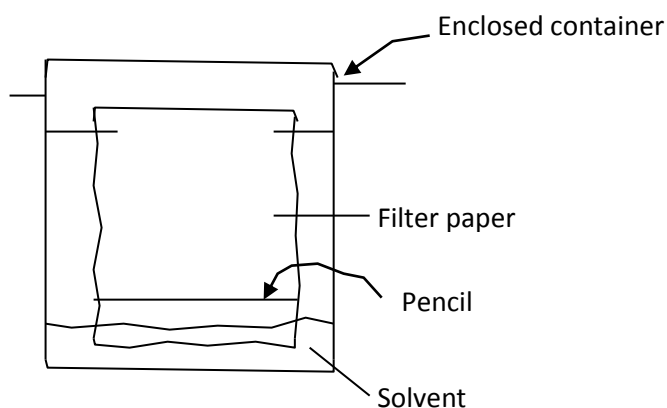
Chromatographic methods

4.1.1 Paper chromatography

The method is used to separate and identify compounds in a small sample of a mixture eg. Chlorophyll and amino acids produced by the hydrolysis of proteins.

4.1.2 Procedure

A thin pencil line is drawn near one edge of a rectangular filter paper parallel to the edge. The sample mixture in a solution is applied as a drop on the pencil line. Pure amino acid samples are placed as droplets on the pencil line as regular individuals, for the purpose of identifying amino acids.



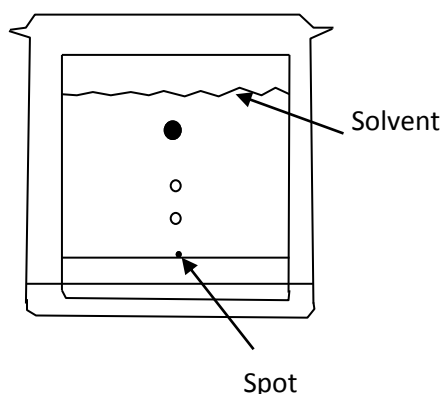
The filter paper is lying in an enclosed glass container with the bottom edge of the filter paper immersed in a solvent. The pencil line will be just above the solvent surface. The container is sealed to prevent evaporation of solvent.

As the solvent moves upwards it carries the components in the sample and the pure sample, at different rates. Before the solvent reaches the top the paper is removed from the container and allowed to dry. A staining agent is sprayed on the whole paper which is warmed in an oven. This enables individual amino acids to show up as blue spots.

The individual amino acids can be characterised through the use of R_f factors / values.

$$R_f = \frac{\text{distance moved by the pure substance}}{\text{distance moved by the solvent front}}$$

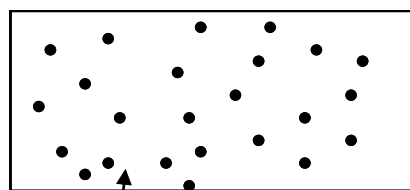
The value of R_f depends on solvent used and the temperature. The chromatogram below is produced.



Spots with equal R_f can be regarded as identical – in the chromatogram above, the sample has the three amino acids, X, Y and Z .

4.1.3. Thin layer chromatography

This is very similar to paper chromatography. It consists of a thin film (stationery phase) on a support. It has the advantage that a variety of materials can be used as the thin layer depending on the nature of the substance to be separated. Thin layer chromatography is faster than paper chromatography.



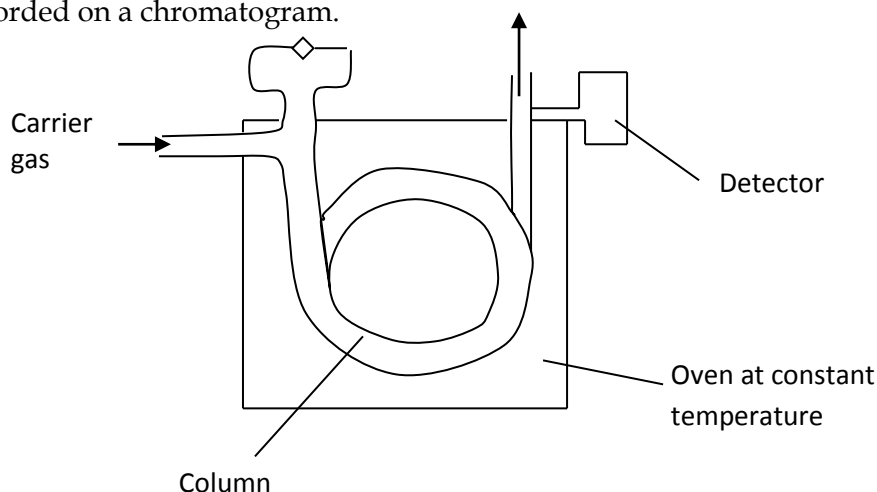
Slide with solid Al_2O_3 paste. (thin film)

The solvent moves upwards the slide carrying with it sample components. The later move up at different rates. This is because the components continuously distribute themselves between the mobile and stationary phases. The chromatogram is very similar to the one produced in paper chromatography so is its interpretation.

4.1.4 Gas - liquid chromatography

The process is employed to separate mixtures of gases/liquids and volatile solids. The mobile phase is a gas which does not interact with components to be separated. It is called the carrier gas. The gas passes through a column containing the stationary phase.

The mixture to be separated is injected at the top of the column. Partition of the components occurs between mobile and stationary phases so that the components emerge at the end of the column at different times. A suitable detector senses the different components as they emerge and generates signals that are amplified and recorded on a chromatogram.



The different components (A, B, C and D) reach the detector at different times (retention times). The retention time can be used to identify a specific component. The area under each peak gives the quantity of the component. The method provides both qualitative and quantitative information. It can be applied to the quantity control of products.

4.1.5 High performance liquid chromatography

It is based on column chromatography. The stationary phase is contained in a glass or metal tube. The liquid mobile phase is forced through the stationary phase. Separation is achieved because solutes are partitioned between the mobile and the stationary phase. The equilibrium constant (Partition coefficient) is given by:

$$K = \frac{C_s}{C_m}$$

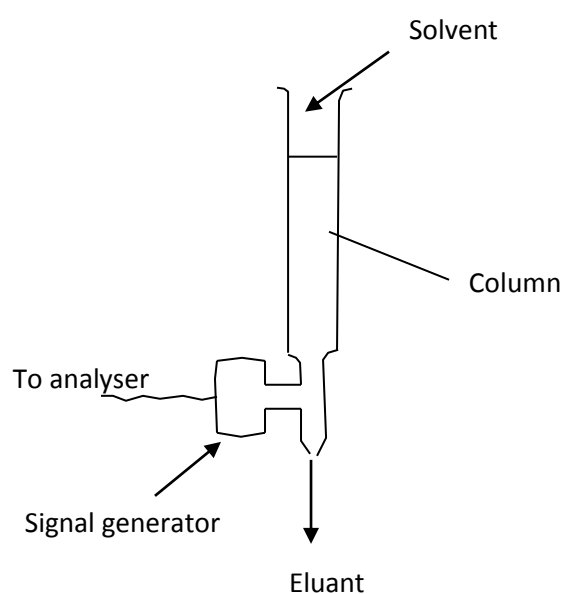
C_s - concentration of solute in the stationary phase

C_m - concentration of solute in the mobile phase, K is constant at a given temperature, therefore there is a linear relationship between C_m and C_s i.e. $C_s = KC_m$

Hence the process is referred to as linear chromatography.

Elution

A sample portion is introduced at the head of the column. When solvent (mobile phase) is introduced, the solute distributes itself between the mobile and stationary phases. Introduction of further portion of mobile phase (eluant) forces the solvent containing part of the solute to move down the column. At the same time, the solute on the stationary phase is partitioned between the stationary phase and fresh solvent. Continued addition of mobile phase carries solute down at different rates. The component that is more soluble in the mobile phase elutes faster than one that strongly interacts with the stationary phase. The end of the column has a device to detect the components as they reach the column end. Signals are generated which enable identification of the components.



The charge on such a molecule depends on the acidity of the solution.

At the iso- electric point the charges are balanced in an acidic environment. Positive charges exceed negative charges. In a basic environment the negative charges are more than positive charges. In the peptide, the relative proportions of acidic and basic groups are different, and the peptides have different isoelectric points. This in addition to size and shape makes peptides to have different mobilities in an electric field.

4.2.5 Gene analysis

DNA material contain the four bases; adenine (A), cytosine (C) , guanine (G) and thymine (T). The sequence or order of occurrence of the four bases defines an individual's genetic make up. This forms the basis of forensic analysis and other tests. Capillary electrophoresis enables DNA sequence analysis.

4.3 Summary

- Chromatographic methods are based on the partition of a solute between a mobile phase and a stationary phase.
- In linear chromatography the ratio of the concentration of a solute in the stationary phase and in the mobile phase gives the partition coefficient.

$$K = \frac{C_s}{C_m}$$

- Electrophoresis enables separation of components on the basis of charge , size and shape of the components.
- The pH of a solution may affect the relative proportions of positive and negative charges in a solution.
- The isoelectric point is the pH at which the number of positive charges is equal to the number of negative charges.

CHAPTER 14

COMPLEXES

Complexes are coordination compounds formed between metal ions and ligands. This section explains formation and stability of complex molecules. The nature of ligands is outlined. The geometry of coordinate compounds as well as the types of isomerism is also described. These complexes show unique characteristics such as presence of colour in ions and compounds and magnetic properties. The origin of such properties is explored.

Content

- 1.0 Complexes
- 1.1 Ligands
- 1.2 Bonding in complexes
- 1.3 Colour; magnetism

Learning outcomes

On completion of the section, students should be able to:

- describe a complex as resulting from the bonding of a metal ion and ligands.
- describe neutral and anionic ligands.
- explain how a coordinate bond is formed.
- name complex compounds according to set rules.
- explain coordination in complexes.
- describe the shapes of 2,4 and 6 coordinated complexes.
- describe structural and optical isomerism in complexes.
- explain ligand exchange in terms of competing equilibria.
- explain ligand exchange in terms of stability constants.
- explain how ligand exchange and complex formation equilibria affect solubility of compounds.
- predict the feasibility of a complex reaction using standard electrode potential values.
- explain the effect of ligand exchange on E^θ values.
- explain the origin of colour in complexes.
- explain magnetic properties of transition metals and their complexes in terms of paired and unpaired electrons.

1.0 Complexes

A complex is formed by the combination of a central metal ion surrounded by, and bonded to, neutral molecules or ions acting as 'ligands'.

1.1 Ligands

A **ligand** is an atom, ion or molecule with a lone pair or pairs of electrons that it can use to bond to a central ion. The ligand donates a pair of electrons to an empty orbital on a metal ion. **The central metal ion** accepts electrons from ligand using vacant 3d, 4s, 4p and even 4d orbitals for the 3d-block transition elements. The lone pair donation is usually from an O, N or halogen atom of the ligand. The bond formed is a dative or coordinate covalent bond.

1.1.1 Types of ligands

There are two types of ligands:

neutral ligands without an overall charge and anionic which are negative

Examples of neutral ligands:

<u>Formula of ligand</u>	<u>Name used in complex</u>
H ₂ O	aqua
NH ₃	amine
CH ₃ NH ₂	methylamine
CO	carbonyl
NO	nitrosyl

Examples of anionic ligands:

<u>Formula of ligand</u>	<u>Name used in complex</u>
F ⁻	Fluoro
Cl ⁻	Chloro
Br ⁻	Bromo
I ⁻	Iodo
OH ⁻	Hydroxo
CN ⁻	Cyano

1.1.2 Number of bonding sites on ligands

Six coordinate bonds are formed by electron pair donation to 3d, 4s and 4p orbitals that are empty



The diagram above shows a complex ion. The negative cyanide ions form one bond per ligand and donate an electron pair (dotted arrows) into a vacant 3d, 4s or 4p orbital in the iron(III) ion to form six dative covalent bonds. The resulting ion has the formula $[\text{Fe}(\text{CN})_6]^{3-}$, 3- is the net charge between the 3+ charge on the metal ion and the 6 - charge of the ligands

The co-ordination number of the complex above is 6, which means there are 6 coordinate bonds between metal and the ligands. A co-ordination number of 6 can be achieved from three co-ordinated bidentate ligands, two tridentate ligands or one hexadentate ligand.

1.3.2 Naming complexes

The following steps apply to the naming of complexes;

The ligand is named before the metal ion.

'o' is added to the root name of the ligand if it is an anion e.g chloro-, cyano- e.t.c. (see table in section 1.1.1)

For neutral ligands, the name of the molecule is used e.g methylamine. But the following ligands, H_2O , NH_3 , NO and CO special names are used (see table in 1.1.1)

The number of binding sites are indicated by prefixes such as mono (1), di-(2), tri-(3), tetra-(4), hexa-(6) e.t.c.

The oxidation state of the metal ion is shown using bracketed Roman numerals e.g (III) indicates an oxidation state of +3.

If there are different types of ligands on a complex, alphabetical order is used.

The suffix -ate is added to the name of the metal if the complex is negative.

Activity

1. Name the following complexes



2. Give the formula of the following complex ions

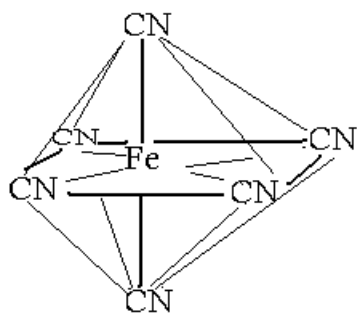
i. tetrachloroferrate (II) ion

ii. amminetrichloroplatinate(II) ion

1.3.3 Coordination number and shapes of complexes

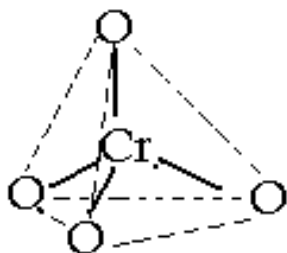
Complexes with a coordination of 6 are octahedral while complexes with a coordination of two are linear. The coordination of four can give rise to tetrahedral or square planar shapes.

Shapes of complexes depend on the nature of hybridisation on the central metal ion. An octahedral shape is formed when the metal ion has the hybridisation d^2sp^3 . In the complex $[\text{Fe}(\text{CN})_6]^{3-}$, six empty orbitals are required on the Fe^{3+} ion to accept the six pairs of electrons from the ligand. Six equal orbitals are created in Fe^{3+} , i.e. two 'd', one 's' and three 'p' orbitals capable of accommodating 6 pairs of electrons thus a coordination of 6 is achieved e.g.



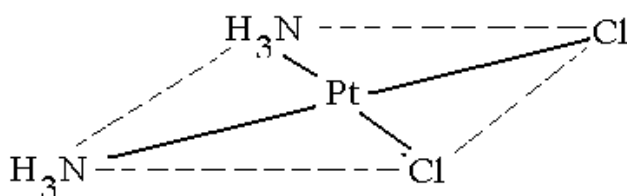
There are two ways (in terms of hybridisation) by which the coordination of four could be achieved. 1. by sp^3 hybridisation or 2. by dsp^2 hybridisation. In sp^3 hybridisation the orbitals are directed at the corners of a tetrahedron giving rise to a tetrahedral complex

e.g



dsp^2 hybridisation has orbitals directed at the corners of a square and complexes with such hybridisation form square planar shapes.

e.g.



sp hybridisation has two orbitals at an angle of 180° . If the complex contains two ligands, the possible shape is linear.

e.g. $[Ag(NH_3)_2]^+$.



1.3.4 Isomerism in complexes

Complexes show two types of isomerism: structural and stereoisomerism.

(a) Structural Isomerism

Two forms of structural isomerism occur, coordination isomerism and linkage isomerism. In coordination isomerism, complexes differ in terms of composition;



In A, SO_4^{2-} is coordinated to Fe^{3+} and Br is the counter ion while in B, their roles are reversed. In linkage isomerism, complexes are the same except that one of the ligands is attached to the central metal through a different atom. e.g. NO_2^- can attach to the central metal through N or through O.

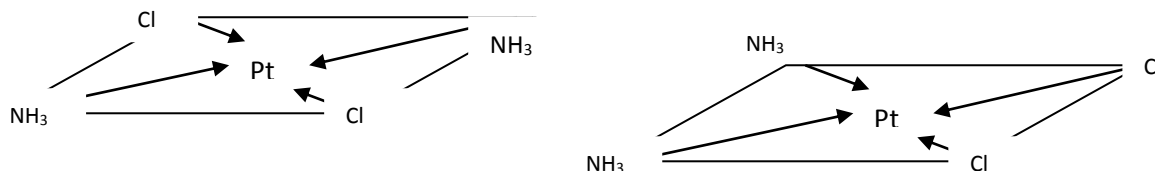


Tetraamminechloronitrocobalt(III) chloride (bonding through lone pairs on nitrogen) and Tetraamminechloronitritocobalt(III) chloride (bonding through lone pairs on Oxygen)

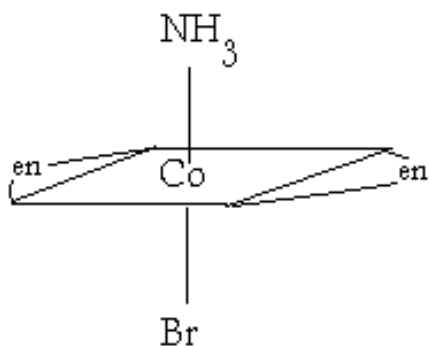
(b) Stereoisomerism

Complexes have the same types of bonds but differ in arrangement in space. Two forms of stereoisomerism are exhibited namely geometrical and optical isomerism.

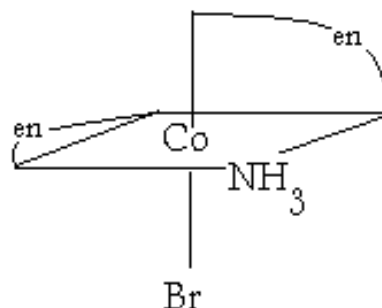
In geometric isomerism atoms or groups occupy different positions in the complex. e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has a square planar arrangement, two possible arrangements being



Trans-isomer (similar groups on opposite sides) Cis-isomer (similar groups on same side)
Geometrical isomerism in octahedral complexes,

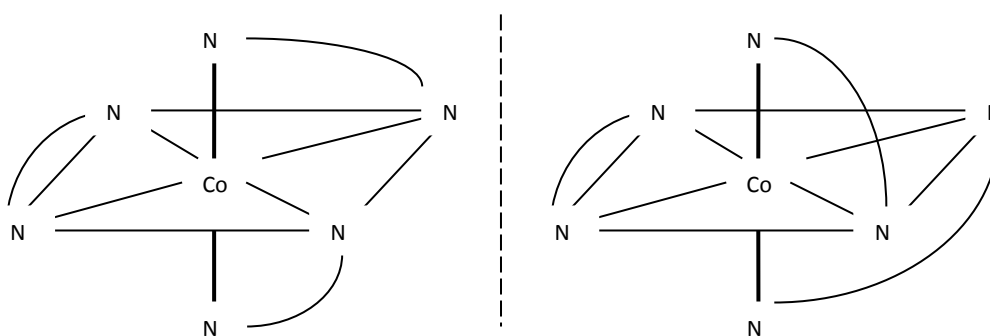


Trans -isomer



Cis-isomer

In *optical isomerism*, complexes are mirror images of each other



Mirror line

Isomer I

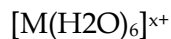
Isomer II

The isomers are mirror images of each other. They are not superimposable on each other. Such images are also said to be chiral or enantiomers. Enantiomers rotate plane polarised light in opposite directions. The ligands in the complexes above are bidentate.

1.3.5 Complex stability

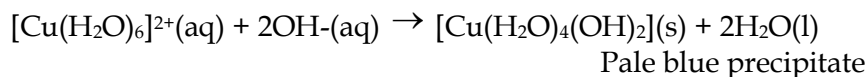
One ligand can replace another depending on the relative bond strengths in a ligand exchange reaction. If the ligands are easily exchanged, the complex is described as 'unstable' and if the ligands are more strongly bound, the complex is stable

Transition metal ions are generally complexed with six water molecules in solution.



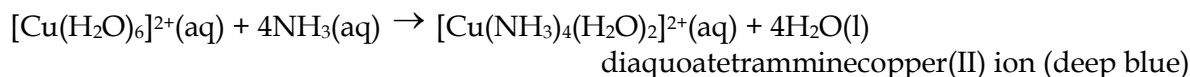
If another ligand is added to an aqueous solution of a transition metal, water molecules may be replaced. Water and the new ligand compete for the metal ion. If the new complex is more stable than the aqueous ion, ligand exchange occurs.

When alkaline aqueous ammonia is added to a blue hexa-aqua copper(II) ion solution, initially a gelatinous blue precipitate of the hydroxide is formed.



The reaction above shows a precipitation reaction involving ligand displacement.

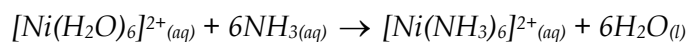
With excess ammonia, a deep blue solution is formed. The overall change can be expressed as:



The co-ordination number remains at 6, both octahedral complexes, both ligands are neutral, the overall charge of the complex remains at +2, and substitution is incomplete.

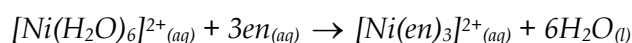
$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2]^{2+}}{[Cu(H_2O)_6]^{2+}[NH_3]^4} = 1.0 \times 10^{12} \text{ dm}^{12}$$

When a bidentate or polydentate ligand is added to a complex of monodentate ligands, a more stable complex will be formed. With excess aqueous ammonia the blue hexa-ammine complex ion is formed:



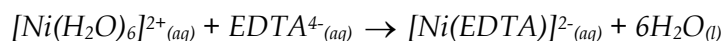
$$K_{stab} = \frac{[Ni(NH_3)_6]^{2+}}{[Ni(H_2O)_6]^{2+}[NH_3]^6} \quad K_{stab} = 4.8 \times 10^7 \text{ mol}^{-6} \text{ dm}^{18}$$

The hexa-aquanickel(II) ion forms complexes with other ammine ligands e.g. the bidentate ligand 1,2-diaminoethane ($H_2N-CH_2-CH_2-NH_2$, abbreviated **en**)



$$K_{stab} = 2.0 \times 10^{18} \text{ mol}^{-3} \text{ dm}^9$$

The complex with EDTA is also readily formed.

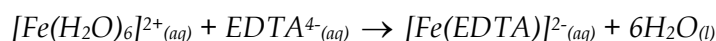


$$K_{stab} = 1.0 \times 10^{19} \text{ mol}^{-1} \text{ dm}^3$$

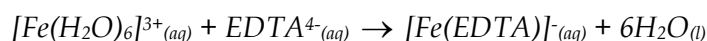
K_{stab} for the same ion tends to increase the greater the chelating power of an individual ligand. e.g. for nickel(II) ion $K_{stab}(EDTA) > K_{stab}(en) > K_{stab}(NH_3)$

Effect of metal ion charge on complex stability

Both the hexa-aqua ions of iron (II) and iron (III) readily complex with EDTA



$$K_{stab} = 2 \times 10^{13} \text{ mol}^{-1} \text{ dm}^3$$



$$K_{stab} = 1.3 \times 10^{25} \text{ mol}^{-1} \text{ dm}^3$$

The more highly charged Fe^{3+} ion forms a stronger complex than the Fe^{2+} ion.

1.3.6 Effect of complexing on standard electrode potentials

For ions of the same metal in different oxidation states, the effect of ligand exchange on electrode potentials depends on the stabilities of the complexes formed relative to their aqua complexes. The complex with the metal ion in its higher oxidation state forms the more stable complex. The electrode potential becomes more negative.

Electrode reaction	E° / V
$Ag^+_{(aq)} + e = Ag_{(s)}$	+0.80
$Ag(NH_3)_{2(aq)} + e = Ag_{(s)} + 2NH_{3(aq)}$	+0.37
$Ag(CN)_{2(aq)} + e = Ag_{(s)} + 2CN^-_{(aq)}$	-0.38

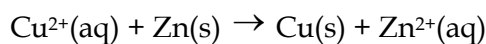
$Ag(CN)_2$ is more stable than $Ag(NH_3)_2$.

E° values can be used to theoretically predict the feasibility of a reaction. E° values for a complete reaction is given by:

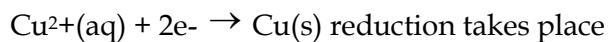
$$E^\circ_{\text{cell}}(\text{reaction}) = E^\circ(\text{reduction}) - E^\circ(\text{oxidation})$$

which is the difference between the half-cell potentials

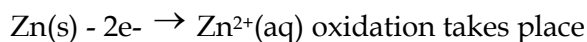
For the copper-zinc cell, the overall reaction is:



$E^{\circ}(\text{red})$ is the most positive or the least negative = the strongest oxidising agent or electron acceptor of the two half-cell systems.



$E^{\circ}(\text{ox})$ is the least positive or the most negative = the strongest reducing agent or electron donor of the two half-cell potentials.



Calculating the voltage-EMF for the copper-zinc cell:

$$E^{\circ}(\text{red}) = +0.34\text{V},$$

$$E^{\circ}(\text{ox}) = -0.76\text{V}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{red}) - E^{\circ}(\text{ox}) = +0.34\text{V} - (-0.76) = +1.10\text{V} \text{ (feasible!)}$$

When E°_{cell} is positive, the reaction is feasible and when E°_{cell} is negative the reaction is not feasible.

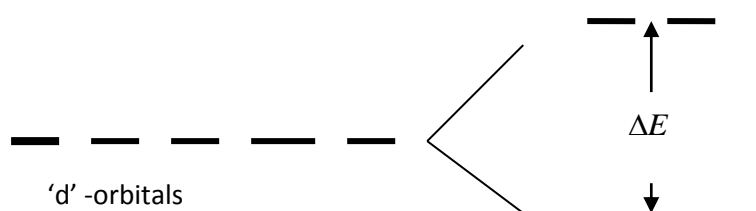
1.4 Colour in complexes

Colour in complexes is due to the following:

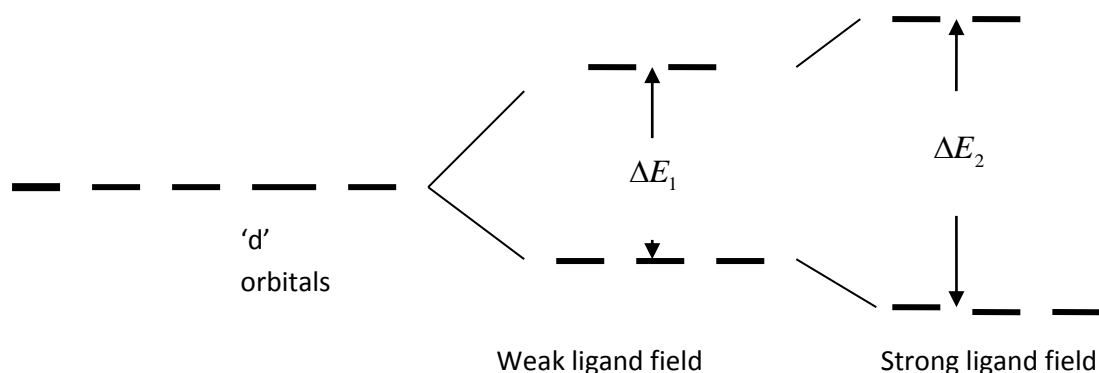
Colour arises from incomplete 'd' orbitals. Incomplete 'd' orbitals contain from one to nine electrons.

The nature of the ligands attached to a metal ion.

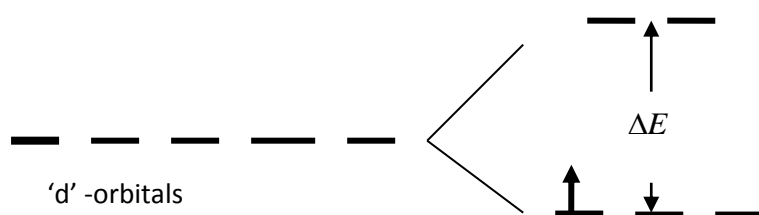
According to the crystal field theory, the degenerate (equal energy) 'd' orbitals are split in a ligand field. When 'd' orbitals are approached by six ligands octahedrally, two of the five 3d orbitals, experience more repulsion than the other three. The two orbitals will be of higher energy.



ΔE is the energy difference between the lower and higher orbitals. Its magnitude will depend on the metal ion and the ligand. For the same ion, the split in a weak ligand field and in a strong ligand field the split is as follows:



In the case of the metal ion, the size of the split is determined by the charge on the metal ion. The split is bigger for a metal ion M^{3+} than it is for M^{2+} . For the ion $Ti^{3+}_{(aq)}$, there is one electron in the 'd' orbitals.



It will occupy the lower orbitals. To move this electron to higher orbitals, radiation of a particular energy must be absorbed. Green light (wavelength 500nm) is absorbed. The remaining colours of the visible spectrum give the characteristic colour of the $Ti^{3+}_{(aq)}$ ion. The remaining colours result in a purple colour. $Ti^{3+}_{(aq)}$ is purple. The relationship between ΔE and the frequency of light absorbed is given by

$$\Delta E = h\nu$$

Where h is Planck's constant and ν is the frequency of light absorbed.

$$\nu = \frac{c}{\lambda}$$

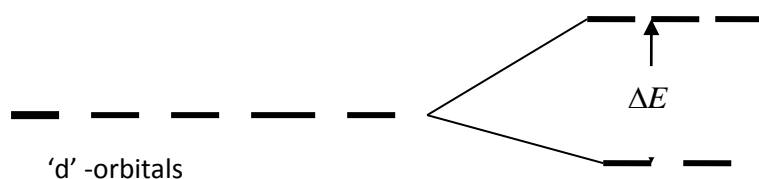
c is the speed of light and λ is the wavelength of radiation

$$\therefore \lambda = \frac{c}{\nu}$$

$$\lambda = \frac{hc}{\Delta E}$$

Ligands will produce different values of ΔE , hence they will absorb radiation of varying wavelength. Their complexes have different colours.

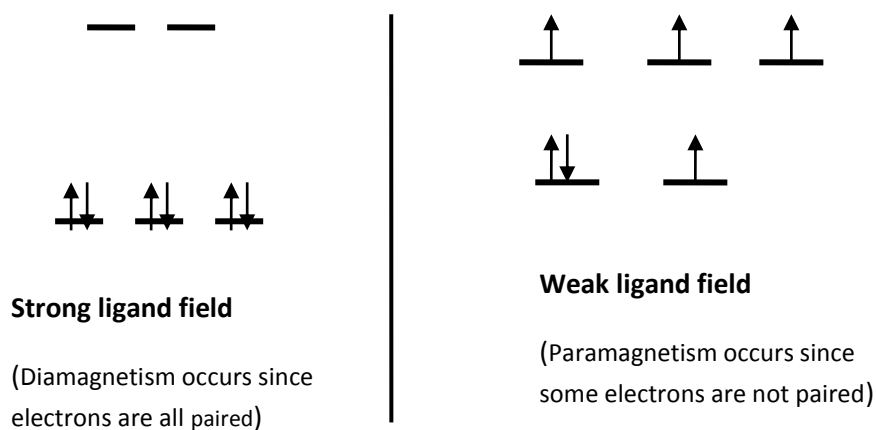
In a tetrahedral environment the split of the 3d orbitals are as follows:



For the same ligand, the split ΔE is bigger for octahedral split than for a tetrahedral split.

1.5 Magnetism

Electrons in split 3d orbitals can be arranged in two ways giving either diamagnetic or paramagnetic complexes. Diamagnetic substances move away from a magnetic field and paramagnetic substances are attracted to a magnetic field. In a strong ligand field the orbital split is octahedral and electrons are paired up in the lower energy orbitals. If all electrons are paired, a diamagnetic complex is formed. In a weak ligand field, electrons occupy all the five orbitals before pairing up. If some of the electrons are not paired, paramagnetism occurs. For Co^{3+} ,



1.6 Summary

- A complex is formed by the bonding of a metal ion and electron pair donors (ligands) through dative covalent bonds (coordinate bonds).
- Neutral ligands consist of molecules e.g NH_3 , H_2O e.t.c.
- Anionic ligands are negatively charged ions e.g Cl^- , CN^- e.t.c
- A coordinate bond is formed when ligands donate a pair/s of electrons into vacant orbitals on a central metal ion. The electrons are shared to form a bond.
- The coordination number is the number of coordinate bonds formed by a metal ion. Common coordination numbers are 2, 4 and 6.
- Complexes exhibit the following types of structural isomerism: coordination and linkage isomerism.
- Complexes also show the following types of stereoisomerism: geometrical and optical isomerism.
- Ligand exchange occurs if the incoming ligand forms a more stable complex.
- The addition of a ligand which forms a stable complex with a metal ion from an insoluble compound causes the compound to dissolve.

- The feasibility of a complex reaction can be predicted from a calculation of overall cell potential ($E^{\ominus}_{\text{cell}}$). If $E^{\ominus}_{\text{cell}}$ is positive then the reaction is feasible and if negative the reaction is not feasible.
- The value of an electrode potential becomes more negative as a complex becomes stable.
- When all 'd' electrons in a complex or metal are paired, diamagnetism is exhibited (repulsion from a magnetic field).
- If there are unpaired electrons in a metal or ion, then paramagnetism is exhibited (attraction to an electric field).

Examination Type Questions

1. Cobalt forms an ion of formula $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.
 - i) What is the oxidation number of cobalt in this ion?
 - ii) State the type of isomerism shown by this ion.
 - iii) Draw and label the isomers formed by the ion.
2. Describe and explain what happens when dilute aqueous ammonia is gradually added to an aqueous solution containing $\text{Cu}^{2+}_{(\text{aq})}$, followed by an aqueous solution of EDTA.
3. Many transition metal complexes are coloured. Explain the origin of colour in complex compounds.

CHAPTER 15

CHEMISTRY OF TRANSITION ELEMENTS

Introduction

Transition elements are important as structural metals. Their comparable atomic sizes enable alloys to be formed. The variable oxidation states give a variety of differently colored ions with varying stabilities. Some of the elements are part of important biological molecules. The section looks at the chemistry of each element in relation to the aspects mentioned above.

Contents

2.1	Vanadium
2.2	Chromium
2.3	Manganese
2.4	Iron
2.5	Cobalt
2.6	Nickel
2.7	Copper

Learning outcomes

On completion of this section, students should be able to:

- describe and explain the use of vanadium in hardening of steel.
- describe the stability of vanadium in the oxidation states of +2, +3, +4 and +5.
- describe the colours of vanadium ions and their compounds.
- describe the use of chromium in hardening steels.
- compare the stability of +3 and +6 chromium ions and their compounds.
- describe the colours of chromium ions and their compounds.
- explain the oxidising properties of dichromate (VI).
- describe and explain the inter-conversion between chromate (VI) and dichromate (VI).
- compare the stability of +2, +4, +6 and +7 oxidation states of manganese.
- describe the colour of manganese in various oxidation states.
- describe redox reactions involving MnO_2 , MnO_4^{2-} and MnO_4^- .
- explain the biological importance of iron.
- explain how rusting occurs.
- describe methods of preventing rust.
- describe role of iron in homogeneous and heterogeneous catalysis.
- compare the stability of +2 and +3 oxidation states of iron.

- describe the colours of iron ions in the +2 and +3 oxidation states.
- describe tests to distinguish between Fe²⁺ and Fe³⁺.
- explain the biochemical importance of cobalt.
- compare stability of cobalt ions and compounds in the oxidation states of +2 and +3.
- describe the use of cobalt(II) ions to test for the presence of water.
- explain the effect of ligand or temperature on stability and geometry of cobalt complexes.
- describe the use of cobalt in alloys.
- describe the extraction and purification of nickel.
- describe the use of nickel in alloys.
- explain catalytic properties of nickel.
- describe the extraction and purification of copper.
- describe the alloys of copper.
- describe and explain the stability of copper in the +1 and +2 oxidation states.
- explain the use of copper ions in testing for aldehydes and reducing sugars.
- describe the reaction of Cu²⁺ and I⁻ ions.

2.1 Vanadium V,

2.1.1 Uses

Small amounts of vanadium are added to steel to strengthen it. Vanadate ((VO_3^-)) is added to steel to protect it from rust and corrosion.

2.1.2 Relative stability and colour of ions and compounds

Vanadium shows variable oxidation states of varying colours

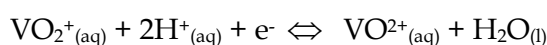
Oxidation states: +2, +3, +4, +5.

When a solution of e.g. ammonium vanadate(V), is reduced by zinc in dilute sulphuric acid, Vanadate(V) ions change into VO₂⁺ (**pale yellow**). Vanadium oxidation state is still +5.



Three successive reduction steps then follow to eventually give V²⁺ ions, shown as half-cell equations:

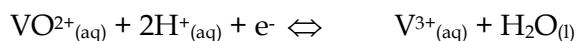
(i) Vanadium(+5) ⇒ Vanadium(+4):



Pale yellow

blue oxovanadium(IV) ion

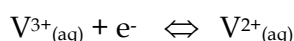
(ii) Vanadium (+4) \Rightarrow Vanadium(+3):



Blue **green** vanadium (III) ion

Vanadium (IV) and Vanadium (III) species undergo aerial oxidation back to the Vanadium (V) compound in acid solution

(iii) Vanadium (+3) \Rightarrow Vanadium (+2):



Green **purple-violet** vanadium (II) ion (hexaaquavanadium(II))

V^{2+} is a powerful reducing agent. It is oxidised by oxygen back to vanadium (III) cation. The +3 and +5 oxidation states are stable.

2.2 Chromium

2.2.1 Uses

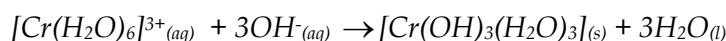
Chromium is a hard white metal. It is used to produce hard steel alloys for making ball bearings and for coating steel articles for corrosion protection. It resists chemical attack at room temperature. Chromium metal is a component of 'stainless steel'.

2.2.2 Chemistry

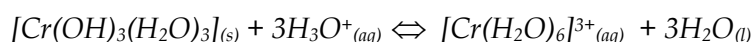
Oxidation states of importance are +2, **+3**, +6.

Chromium (III) ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (green)

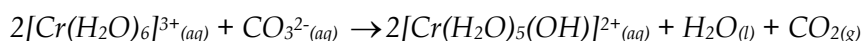
With aqueous ammonia (alkaline) or sodium hydroxide, green chromium (III) hydroxide is precipitated.



The hydroxide readily dissolves in acids to form salts,



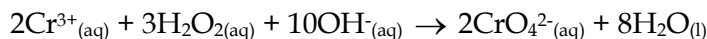
With aqueous sodium carbonate the hydroxide precipitate is formed and **carbon dioxide** because of the acidity of the hexaaquachromium(III) ion



Chromium (III) complexes are extremely numerous and varied.

Chromium (VI)

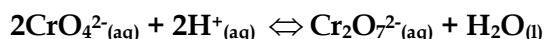
When hydrogen peroxide is added to an alkaline chromium(III) solution, oxidation occurs to give the yellow chromate (VI) ion CrO_4^{2-} .



Green

yellow Cr (VI)

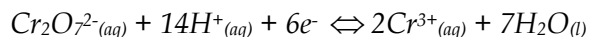
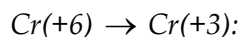
When the resulting solution from the reaction above is acidified with dilute sulphuric acid, the orange dichromate (VI) ion $\text{Cr}_2\text{O}_7^{2-}$ is formed.



(no change in oxidation state)

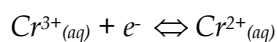
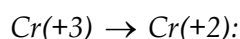
The equilibrium is pH dependent. In more acidic solution, more concentration of H^+ , pH decreases. Equilibrium shifts to the right, formation of dichromate is favoured (solution becomes more orange). In more alkaline, less H^+ (removed by OH^-), pH increases and equilibrium shifts backwards. Solution becomes more yellow.

The dichromate (VI) ion is reduced in two stages by a zinc/dilute sulphuric acid mixture.



Orange

green



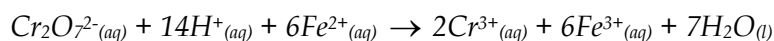
Green

blue

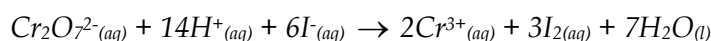
$\text{Cr}(\text{II})$ is readily oxidised by dissolved oxygen

Potassium dichromate (VI), $\text{K}_2\text{Cr}_2\text{O}_7$, can be crystallised to high purity without water of crystallisation, and is used as a standard in redox volumetric titrations. The dichromate (VI) ion is a strong oxidising agent. Examples of its oxidising action are:

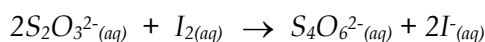
- Oxidation of iron (II) ions.



- It oxidises iodide ions to iodine.



The released iodine can be titrated with standard sodium thiosulphate solution using starch indicator.



Black/brown **colourless endpoint**

The reaction of iodine and sodium thiosulphate can be used to estimate oxidising agents like dichromate (VI) ions. The iodine is titrated with standardised sodium thiosulphate using starch as an indicator. Iodine gives a blue colour with starch; the end-point is very sharp change from blue to colourless.

Chromium (II)

The **blue** hexaaquachromium(II) ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$, is formed by reducing chromium(III) salt solutions with zinc and hydrochloric acid but it is unstable and is rapidly oxidised back to green chromium(III) ions by dissolved oxygen.

2.3 Manganese

2.3.1 Uses

It is a hard brittle metal but is the most important metal in steels. Ferromanganese (80% Mn, 20% Fe) is used in making alloy steels. The presence of manganese imparts hardness and resistance to wear.

2.3.2 Chemistry

Important oxidation states are: +2, +4, +6, +7

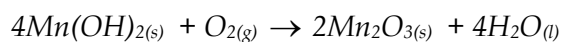
Manganese (II) ion $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ **pale pink**

The hexaaquamanganese (II) is stable in aqueous solution.

The alkalis sodium hydroxide or ammonia, produce the hydrated manganese (II) hydroxide precipitate. There is no further reaction with excess of either.



The hydroxide is almost **white** if oxygen is excluded, but it turns **brown** to form hydrated manganese (III) oxide.



Oxidation of the manganese(II) ion

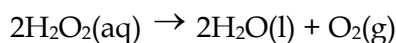
Acidified Mn^{2+} is not oxidised by hydrogen peroxide H_2O_2 , but alkaline $\text{Mn}(\text{OH})_2 + \text{H}_2\text{O}_2$ gives brown Mn_2O_3 or $\text{MnO}(\text{OH})$, a hydrated manganese(III) oxide/hydroxide.

Manganese (III) $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ violet

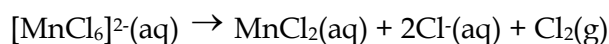
The $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ ion is unstable in aqueous solution.

Manganese (IV)

The important manganese (IV) compound is MnO_2 (solid black oxide). It is an excellent catalyst for the decomposition of hydrogen peroxide.



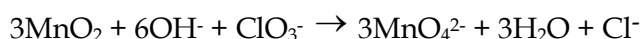
If $[\text{MnCl}_6]^{2-}$ is warmed, chlorine is formed as the complex decomposes to Mn(II) compounds.



The +4 oxidation state is less stable compared to the +2.

Manganese (VI) MnO_4^{2-} (dark green)

A solution of the dark green manganate(VI) ion, MnO_4^{2-} can be made by strongly heating a mixture of manganese(IV) oxide, potassium hydroxide and potassium chlorate(V) in a crucible and extracting the manganese(VI) compound with water.



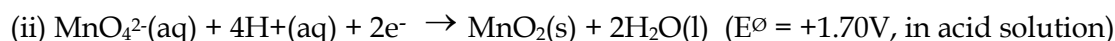
The manganate(VI) ion, MnO_4^{2-} is unstable in acid solution, and slowly disproportionates. The green solution changes to purple and a black precipitate is formed.



The oxidation state changes are (+6) \rightarrow (+7) and (+4),

Explaining disproportionation using E^\ominus values

The obviously feasible and spontaneous disproportionation reaction can be explained by considering the standard electrode potentials (standard reduction potential) involved (quoted as half-cell reductions, as is the convention).



(ii) has the more positive potential, so this will be the reduction half-cell reaction.

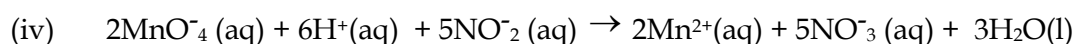
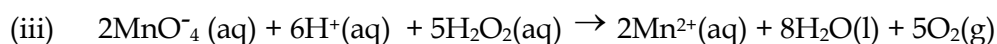
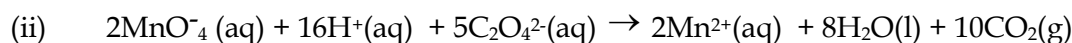
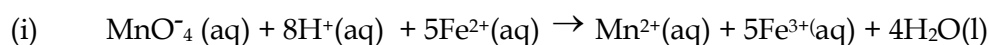
(i) has the less positive potential, so this will be (reversed) the oxidation half-cell reaction.

$E^{\ominus}\text{reaction} = E^{\ominus}\text{reduction} - E^{\ominus}\text{oxidation} = (+1.70) - (0.56) = +1.14\text{V}$, well over 0V , therefore reaction is feasible.

Manganese (VII): MnO_4^- (Purple)

The manganate(VII) ion, MnO_4^- , is intensely coloured and very stable complex ion.

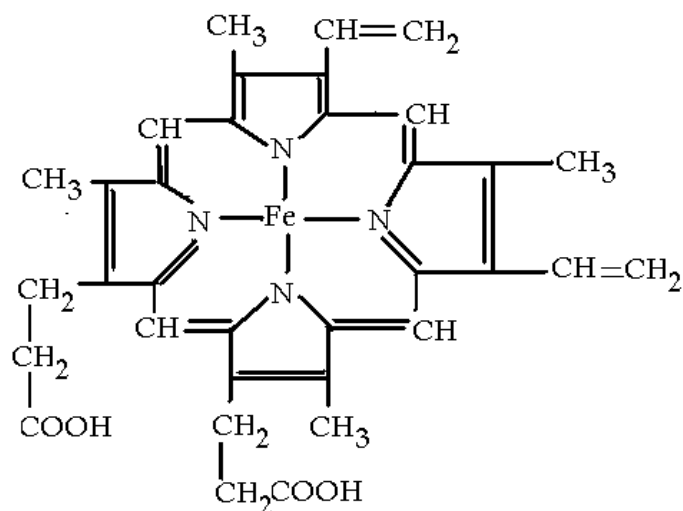
Potassium manganate(VII), KMnO_4 , is oxidising and is used to titrate (i) iron(II) ions, (ii) ethanedioates, (iii) hydrogen peroxide and (iv) nitrate(III) ions.



Iron

2.4.1 Biological importance of iron

Iron plays an important role in the process of respiration in living organisms. Respiration makes available energy for various activities through the breakdown of food substances. The food is oxidised by oxygen indirectly. The electrons are transferred from food to the oxygen along a chain of complex molecules in a respiratory chain. The main electron transfer molecules are cytochromes. These are iron containing species. They have two main parts: haeme, (an iron complex shown below) and a protein.



The iron shifts between +2 and + 3 oxidation states. Iron also transports oxygen and stores oxygen in mammalian blood. Oxygen is stored in a molecule called myoglobin which has a structure very similar to cytochromes. The transport of oxygen is carried out by haemoglobin which consists of four myoglobin -like units capable of binding four O₂ molecules. The complex formed is bright red in colour. It is called oxyhaemoglobin.

Carbon monoxide toxicity

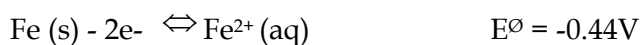
Carbon monoxide has a much greater affinity for Fe²⁺ than oxygen. Thus carbon monoxide combines with haemoglobin forming a more stable complex carboxyhaemoglobin. This prevents haemoglobin from carrying out its normal function. The body is deprived of oxygen.

2.4.2 Rusting of iron

Rust refers to a number of iron oxides: hydrated iron (III) oxides Fe₂O₃.nH₂O and Iron (III) oxide-hydroxide (FeO(OH),Fe(OH)₃)

Electrochemistry of rusting

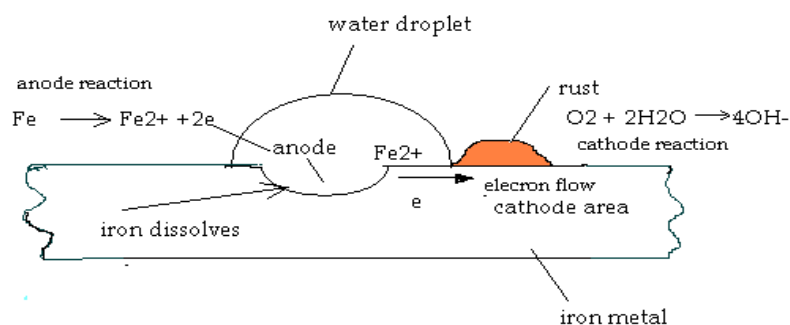
The half-cell of oxidation of Fe to Fe²⁺ occurs in regions of low oxygen concentration, Iron reacts and goes into solution as ions;



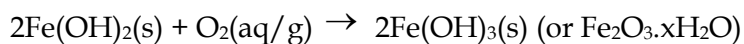
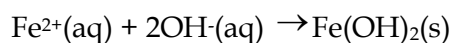
The half-cell reduction is



It occurs in the oxygen richer regions, using electrons that flow through the iron from the oxidised iron.



The result is iron (II) hydroxide, which is then oxidised to iron (III) hydroxide or hydrated iron (III) oxide, orange-brown rust!



2.4.3 Factors affecting rate of rusting

The following all speed up rusting:

Decreasing pH : $\text{H}^{+}(\text{aq})$ ions remove $\text{OH}^{-}(\text{aq})$ formed from the reduction of $\text{O}_2(\text{g/aq})$.

Increased concentration of any ions improves the electrical conductivity of the aqueous media, which is part of 'redox circuit'. corrosion rates increase, because the iron is preferentially oxidised with the more negative half-cell potential.

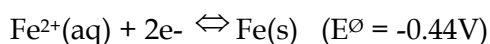
2.4.4 Rust protection/inhibition

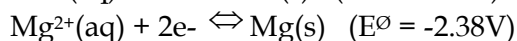
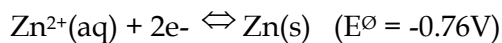
A plastic or paint- forms physical barrier to exclude water and oxygen (air),

Plating: either by (i) dipping in molten zinc, or (ii) electrolysis with $\text{Zn}^{2+}(\text{aq})$ solution and the iron/steel object as the cathode. Galvanising with Zn layer results in the formation of ZnO that is protective. Even if scratched, the Zn with a more negative half-cell potential is preferentially oxidised.

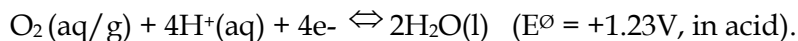
Sacrificial corrosion with blocks of Zn or Mg

Zinc and Magnesium have more negative half-cell potentials than iron. They are preferentially oxidised.





The reduction of oxygen to water is a positive redox potential.



The oxidation of all metals is feasible. However, the metal with the most negative potential will be preferentially oxidised i.e. $\text{Mg} > \text{Zn} > \text{Fe}$.

Alloying: Stainless steel contains Cr which forms protective layer of chromium (III) oxide.

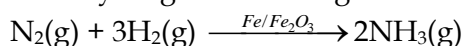
Tin plating: Complex formation and corrosion behaviour.

Tin(II) ions form a complex with carboxylic acids like citric acid (tridentate ligand), by reducing the $\text{Sn}^{2+}(\text{aq})$ concentration, the $\text{Sn}(\text{s})/\text{Sn}^{2+}(\text{aq})$ half-cell potential is then made more negative than that of iron. Hence the protective thin layer of tin is sacrificially corroded, at the expense of the iron.

2.4.5 Use of iron and its ions

Heterogeneous catalysis

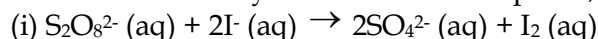
An iron/iron (III) oxide mixture is used as a catalyst in the Haber synthesis of ammonia from hydrogen and nitrogen.



The catalyst and the reactants are in different phases and the reaction above illustrates heterogeneous catalysis. Reactants are adsorbed onto the surface of the solid catalyst in appropriate orientation to facilitate reaction. The product is desorbed from the surface of the catalyst

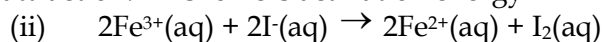
Homogeneous catalysis

Iron (II)/iron (III) ion catalyse the oxidation of iodide ions by peroxodisulphate ions. The reactants and catalysts are in the same phase; homogeneous catalysis.

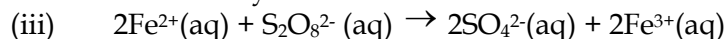


The uncatalysed reaction involves the collision of two repelling negative ions hence

activation energy is high. The collision of an Fe^{3+} ion and an I^{-} ion involves positive-negative attraction. This lowers activation energy



Followed by

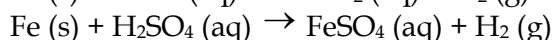
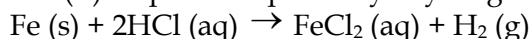


The iron (III) ion is regenerated in the cycle.

2.4.6 Iron (II) and Iron (III) chemistry

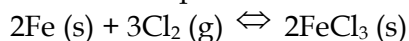
The most common oxidation states of iron in its compounds are +2 and +3.

Iron readily dissolves in dilute hydrochloric or sulphuric acid to form iron (II) chloride and iron(II) sulphate respectively. Hydrogen gas is evolved and it is a redox reaction.

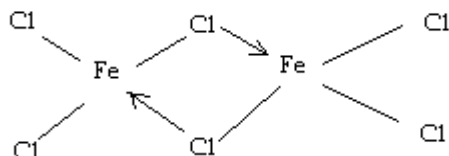


The pale green salts $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ can be made by careful evaporation and crystallisation of the solution. However, they are readily oxidised by dissolved oxygen to form iron(III) compounds.

If chlorine is passed over heated iron, brown anhydrous iron (III) chloride is formed



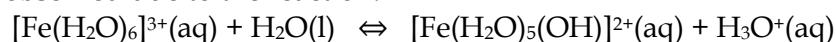
Iron(III) chloride is a brown covalently bonded, relatively volatile chloride. It exists in the solid form as a dimer Fe_2Cl_6 , one of the chlorines forming a dative co-ordinate bond with the other iron atom.



Some reactions of iron (II) and iron (III) ions:

The hexaaquairon(II) ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ is pale green.

The 'pure' hexaaquairon (III) ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ is pale purple but yellow-light brown is observed due to the reaction:

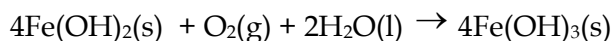


The alkalis sodium hydroxide or ammonia, produce the respective hydrated hydroxide precipitates. There is no further reaction with excess of either.



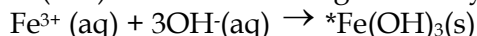
Iron (II) compounds can be readily oxidised to iron (III) compounds by the oxygen in air.

Iron (II) hydroxide forms a 'dirty green' ppt., which on exposure to air rapidly turns brown on oxidation to iron(III) hydroxide by dissolved molecular oxygen.



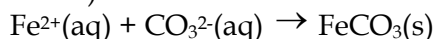
Fe oxidised from (+2) \rightarrow (+3), O reduced (0) \rightarrow (-2)

$\text{Fe}(\text{OH})_3$ can also be thought of as hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (x is variable)

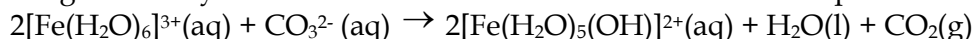


Iron (III) hydroxide is orange-brown.

Aqueous sodium carbonate is weakly alkaline and gives the hydroxide ppts. but excess reagent has no further effect. The iron (II) ion gives the carbonate and the hydroxide too (see above).



which slowly changes to $\text{Fe}(\text{OH})_2$, which in turn is readily oxidised to $\text{Fe}(\text{OH})_3$. The iron(III) ion gives the hydroxide and carbon dioxide because the hexa-aqua ion is acidic.



and this process of proton donation continues until the $[\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3](\text{s})$ precipitate is formed

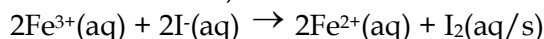
No $\text{Fe}_2(\text{CO}_3)_3$ is formed because of this acid-base reaction. The acidity of the hydrated iron(III) ion makes it react with the carbonate ion. Note Al^{3+} and Cr^{3+} ions behave in the same way.

Reducing action of aqueous iron (II) ions: These two reactions can be used to quantitatively estimate Fe^{2+} ions.

- (i) with potassium manganate(VII), KMnO_4
- (ii) with potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$

Oxidising action of iron (III) ions:

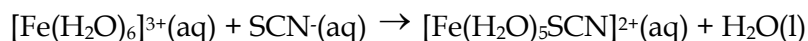
With iodide ions, dark brown solution of iodine (or black solid) formed with iron(II) ions.



2.4.7 Simple test for aqueous iron (III) ions:

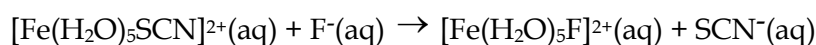
Add a few drops of ammonium/potassium thiocyanate solution ($\text{NH}_4\text{SCN}/\text{KSCN}$).

A blood red cationic complex is formed in a ligand exchange reaction, one ligand is displaced by another.



The reaction is NOT given by hexa-aqua iron (II) ions.

If fluoride ions (e.g. via $\text{KF}(\text{aq})$) are added the red colour disappears immediately because a ligand displacement reaction occurs forming the fluoro-complex ion.



The fluoride ligand bonds more strongly than the thiocyanate ion.

Cobalt

2.5.1 Biochemical importance

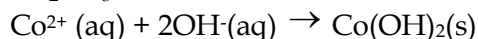
Cobalt is the metal ion in the complex making up vitamin B_{12} . It is quite complex and plays a key role in the normal functioning of the brain and nervous system as well as also in the formation of blood.

Cobalt is alloyed with chromium and tungsten to make a metal hard enough, even at red heat, to be used for high speed cutting tools and valves for internal combustion engines.

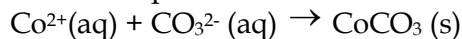
2.5.2 Cobalt Chemistry

Cobalt forms the stable pink hexaaquacobalt (II) ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

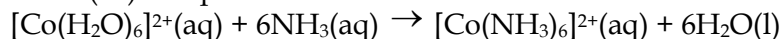
The alkalis sodium hydroxide and ammonia, produce the hydrated cobalt (II) hydroxide blue ppt. which turns pink on standing. There is no further reaction with excess of NaOH or Na_2CO_3 .



Alkaline aqueous sodium carbonate solutions produces a precipitate of cobalt(II) carbonate.



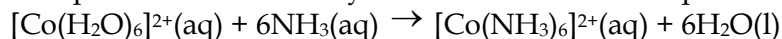
When excess ammonia is added to a cobalt (II) salt solution, the hexaamine complex is formed but this is unstable in the presence of dissolved oxygen and is oxidised to the cobalt(III) complex.



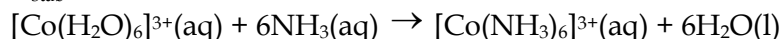
Pink hexaaquacobalt (II) ion /brown hexaamminecobalt(II) ion.

The uncharged ligand molecules ammonia NH_3 and water H_2O are similar in size and ligand exchange occurs without change in co-ordination number.

Comparison of the stability of the hexaamine complexes

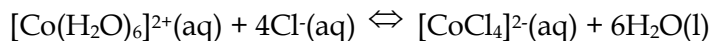


$$K_{\text{stab}} = 7.7 \times 10^4 \text{ mol}^{-6} \text{ dm}^{18}$$



$$K_{\text{stab}} = 4.5 \times 10^{33} \text{ mol}^{-6} \text{ dm}^{18}$$

The more highly charged $\text{Co}^{3+}(\text{aq})$ ion complexes more strongly than the $\text{Co}^{2+}(\text{aq})$ ion i.e. forms a more stable complex



This particular ligand substitution/exchange reaction involves several changes:

- the larger chloride ion ligand leads to a change in co-ordination number from 6 to 4,
- the complex ion shape changes from octahedral to tetrahedral
- the colour of the complex changes from pink to blue,
- the complex changes from a cationic to an anionic ion.
- There is no oxidation state change at all.

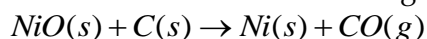
Effect of changing conditions on equilibrium:

- dilution shifts the position of equilibrium to the left, more pink,
- increasing the chloride ion concentration shifts the position of equilibrium to the right, more blue.
- increasing the solution temperature shifts the position of equilibrium to the right, more blue or if prepared at higher temperature, with just enough chloride to turn the solution blue, on cooling it becomes pink.
- this shows that left to right is endothermic and right to left is exothermic.

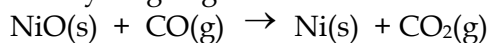
2.6 Nickel

2.6.1 Production of nickel

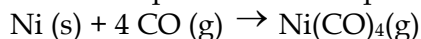
Ores include millerite, NiS, pentlandite (a mixture of iron and nickel sulphides) and garnierite, $(\text{Ni},\text{Mg})\text{SiO}_3 \cdot x\text{H}_2\text{O}$. The ores are converted to nickel (II) oxide. The nickel (II) oxide is reduced to nickel using carbon.



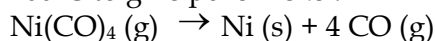
Pure nickel (99.99%) can be obtained by reacting NiO with a mixture of carbon monoxide and hydrogen gas at 350°C.



The nickel produced is not pure. It is heated at 60°C in carbon monoxide.



The product $\text{Ni}(\text{CO})_4$ distills leaving impurities behind. It is then decomposed by heating to 200°C to give pure nickel.



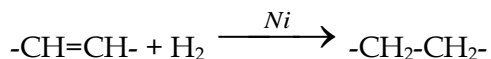
2.6.2 Alloys of nickel

Nickel has many uses; 'silver' coinage metals and money; used for chemical reactors - both are alloys with copper and are chemically inert.

2.6.3 Hydrogenation of unsaturated hydrocarbons

Nickel is an important hydrogenation catalyst in converting unsaturated vegetable oils to saturated fats like margarine.

unsaturated oil + hydrogen \rightarrow low melting solid more saturated fat
 Oils are unsaturated, ie they have some double bonds: $-\text{CH}=\text{CH}-$
 Saturation can be achieved with the use of nickel as a heterogeneous catalyst



2.7 Copper

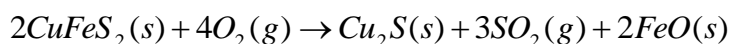
2.7.1 Copper is an important metal in many alloys e.g. brass (with zinc), bronze (with tin) and coinage metals (with nickel). Some uses of the alloys of copper are given in the table below

Alloy	Composition	Use
Brass	Cu and Zn	Catridges, radiator cores, lamp holders
Bronze	Cu and Sn	Bearings, clips, electrical connectors

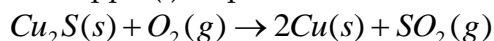
2.7.2 Production of copper

Copper is extracted from the ore copper pyrites CuFeS_2 . The pyrites are crushed to smaller pieces. This is followed by concentration of the ore by froth floatation.

The ore is roasted in limited supply of air. The iron in the pyrites is converted to iron(II) oxide.

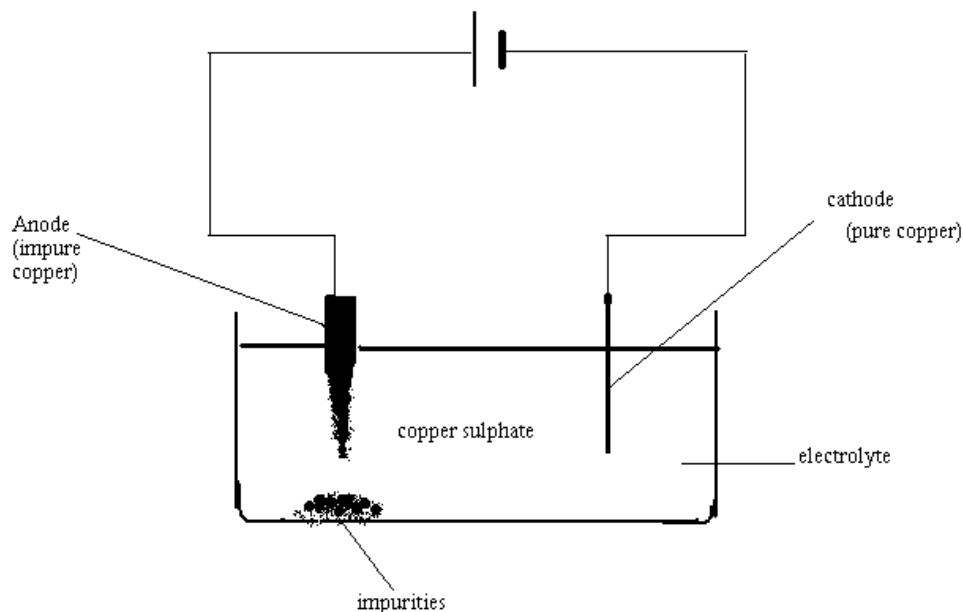


The copper(I) sulphide Cu_2S is reduced to copper by heating in air

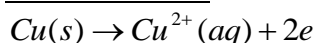


2.7.3 Electro-refining of copper

The copper produced by reduction is not pure and it is purified using an electrochemical method. Thick slabs of impure copper are used as the anodes in electrolysis of copper sulphate solution. The cathodes consist of thin strips of pure copper.

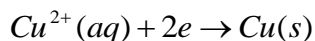


Anode reaction



Copper atoms from the anode go into solution. The anode becomes thin with time. Noble metal impurities such as silver, gold and platinum in the anode do not react and fall to the bottom of the tank as sludge. The metals are recovered from the sludge.

Cathode reaction

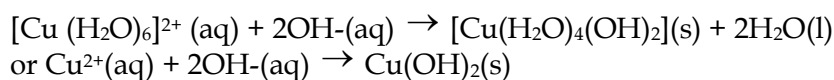


Copper ions from the electrolyte accept electrons forming copper atoms. The cathode grows thick. Pure 99.95% copper is deposited on the cathode.

2.7.4 Copper (II) chemistry

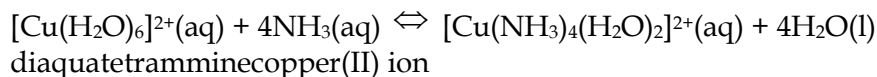
Reaction with aqueous ammonia or sodium hydroxide

The blue hexaaquacopper (II) ion solution, a gelatinous blue precipitate of the hydroxide is formed.

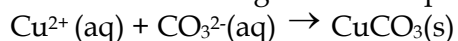


Excess sodium hydroxide has no further effect,

Addition of excess ammonia, results in a deep blue solution.

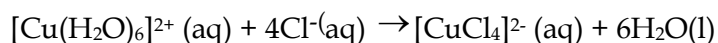


Sodium carbonate gives the turquoise precipitate of copper(II) carbonate,



Reaction with sodium chloride or hydrochloric acid

The pale yellow-brown tetrachlorocuprate (II) complex ion is formed. The actual colour observed is green, that is yellow brown plus the original blue colour of Cu^{2+} ion).

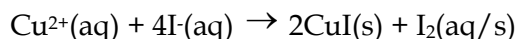


This particular ligand substitution/exchange reaction involves several changes.

- the larger chloride ion ligand leads to a change in co-ordination number from 6 to 4,
- the complex ion shape changes from octahedral to tetrahedral
- the colour of the complex changes from blue to yellow-brown (green due to residual blue),
- the complex changes from a cationic complex ion to an anionic complex ion.
- There is no oxidation state change at all, copper is in the +2 state throughout the reaction.
- If you dissolve copper (II) chloride in water you get a greenish-blue solution as both copper (II) complexes are present in equilibrium.
- By adding water i.e. dilution, it shifts the position of equilibrium to the left, more blue.
- Increasing the chloride ion concentration by adding hydrochloric acid or sodium chloride solution shifts the position of equilibrium to the right, more green ==> yellowish brown.

The reaction between copper (II) salts and iodide salts:

A redox reaction takes place between the copper (II) ion and the colourless potassium iodide ion, the dark colour of iodine formation is seen. A white copper (I) iodide precipitate is also formed but it is masked by the iodine.



2.7.5 Copper (I) Chemistry

Disproportionation reactions:

When solid copper(I) oxide is dissolved in dilute sulphuric acid a pinky-brown precipitate of copper and a blue solution of copper(II) sulphate solution are obtained.

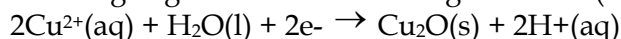


Oxidation number changes: (I) \rightarrow (0) and (II)

$\text{Cu}^+(\text{aq})$ is not stable in aqueous media and spontaneously undergoes a redox change. A chemical change in which a species in one oxidation state undergoes reduction and oxidation is a disproportionation reaction.

Test for aldehydes/ reducing sugars

Copper(I) oxide Cu_2O is formed as a brick red-brown precipitate when an aldehyde or reducing sugar reacts with Fehlings solution (a copper(II) complex with a carboxylic acid).



Summary

	Important oxidation states and colours	Stable oxidation states
vanadium	+2(purple), +3(green), +4(Blue) , +5(pale yellow)	+3 and +5
Chromium	+2(blue), +3(green), +6(yellow) +6(orange in dichromate)	+3 and +6
Manganese	+2(Pale pink) +4(black) +6(dark green), +7(purple)	+2, +4 and +7

Iron	+2(pale green), +3(yellow brown)	+3
Cobalt	+2(pink), +3	+3
Copper	+1, +2 (pale blue)	+2

Examination Type Questions

- Use the Data Booklet to predict the reactions, if any, that occur when acidified solutions containing the following pairs of reagents listed in (i) to (iii) below are mixed.

Calculate the relevant overall E^θ cell values, and state the change in oxidation number in any transition metal during any reaction.

- $MnO_4^-(aq)$ and $Br^-(aq)$
 - $Fe^{3+}(aq)$ and Cl_2
 - VO_2^+ and $Sn^{2+}(aq)$
- Describe and explain what would be observed when aqueous ammonia is added to an aqueous cobalt (II) salt, until in excess and the final mixture is left in air for some time.