LECTURE NOTES

ON

1FY2-03/ 2FY2-03 - ENGINEERING CHEMISTRY

B. Tech. I & II Semester

(Common for all Branches)

Director

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Education, Ministry of HRD, Govt of India & Affiliated to Rajasthan Technical University. Kota, Rajasthan)

ENGINEERING CHEMISTRY
(NOTES)
(Common for all Branches)

FOREWORD

We are indeed very happy to present engineering chemistry lecture notes for B.Tech. Aeronautical Engineering and B.Tech. Mechatronics Engineering (Semester-1 & 2) Bikaner Technical University, Rajasthan.

Chemistry is the branch of science that deals with the study of matter, its composition, physical and chemical properties and applications.

It is important for engineers to have knowledge of chemistry as those may face problems in fields as diverse as design and development of new materials.

Chemistry is the backbone in designing and understanding the nature of various engineering materials. Many advances in engineering and technology produce a huge chemical demand.

These Lecture Notes in engineering chemistry is prepared for the students studying in B.Tech. Aeronautical Engineering and B.Tech. Mechatronics Engineering (Semester- 1 & 2) Bikaner Technical University, Rajasthan. This Lecture Notes are written in simple and easily understandable manner.

The Department of Engineering Chemistry of School of Aeronautics is very much grateful to the Director, School of Aeronautics for his deep involvement and encouragement in preparing this syllabus wise learning material.

Further suggestions for improvement are welcome.

SYLLABUS

1FY2-03/ 2FY2-03: Engineering Chemistry
Common to all branches of UG Engineering & Technology

Credit: 4 **Max. Marks: 200 (IA: 40, ETE: 160)**
3L+1T+0P **End Term Exam: 3 Hours**

UNIT NO	CONTENT	HOURS
1	**MODULE 1:** **WATER:** Common impurities, hardness, determination of hardness by complexometric (EDTA method), Degree of hardness, Units of hardness Municipal water supply: Requisite of drinking water, Purification of water; sedimentation, filtration, disinfection, break point chlorination. Boiler troubles: Scale and Sludge formation, Internal treatment methods, Priming and Foaming, Boiler corrosion and Caustic Embrittlement Water softening; Lime-Soda process, Zeolite (Permutit) process, Demineralization process. Numerical problems based on Hardness, EDTA, Lime-Soda and Zeolite process. **MODULE 2:** **CORROSION AND ITS CONTROL:** Definition and significance of corrosion, Mechanism of chemical (dry) and electrochemical (wet) corrosion, galvanic corrosion, concentration corrosion and pitting corrosion. Protection from corrosion; protective coatings-galvanization and tinning, cathodic protection, sacrificial anode and modifications in design.	14

2	**MODULE 3:** **ENGINEERING MATERIALS:** Portland Cement; Definition, Manufacturing by Rotary kiln. Chemistry of setting and hardening of cement. Role of Gypsum. Glass: Definition, Manufacturing by tank furnace, significance of annealing, Types and properties of soft glass, hard glass, borosilicate glass, glass wool, safety glass Lubricants: Classification, Mechanism, Properties; Viscosity and viscosity index, flash and fire point, cloud and pour point, Emulsification and steam Emulsification number. **MODULE 4:** **ORGANIC REACTION MECHANISM AND INTRODUCTION OF DRUGS:** Organic reaction mechanism: Substitution; SN1, SN2, Elecrophilic aromatic substitution in benzene, free radical halogenations of alkanes, Elimination; elimination in alkyl halides, dehydration of alcohols, Addition: electrophilic and free radical addition in alkenes, nucleophilic addition in aldehyde and ketones, Rearrangement; Carbocation and free radical rearrangements Drugs: Introduction, Synthesis, properties and uses of Aspirin, Paracetamol.	16
3	**MODULE 5:** **ORGANIC FUELS:** Solid fuels: Coal, Classification of Coal, Proximate and Ultimate analyses of coal and its significance, Gross and Net Calorific value, Determination of Calorific value of coal by Bomb Calorimeter. Metallurgical coke, Carbonization processes; Otto-Hoffmann by- product oven method. Liquid fuels : Advantages of liquid fuels, Mining, Refining and Composition of petroleum, Cracking, Synthetic petrol, Reforming, Knocking, Octane number, Anti-knocking agents, Cetane number Gaseous fuels; Advantages, manufacturing, composition and Calorific value of coal gas and oil gas, Determination of calorific value of gaseous fuels by Junker's calorimeter Numerical problems based on determination of calorific value (bomb calorimeter/Junkers calorimeter/Dulongs formula, proximate analysis & ultimate and combustion of fuel.	10
TOTAL HOURS		**40**

SUMMARY

UNITS	PARTICULARS	HRS
1	Module- 1 ,2	14
2	Module – 3,4	16
3	Module - 5	10
TOTAL HOURS		**40**

UNIT – I

MODULE-1

WATER

TOPICS:-

- Common impurities, hardness, determination of hardness by complexometric (EDTA method), Degree of hardness, Units of hardness.
- Municipal water supply: Requisite of drinking water, Purification of water; sedimentation, filtration, disinfection, breakpoint chlorination.
- Boiler troubles: Scale and Sludge formation, Internal treatment methods,
- Priming and Foaming, Boiler corrosion and Caustic Embrittlement
- Water Softening; Lime-Soda process, Zeolite (Permutit) process, Demineralization process.
- Numerical problems based on Hardness, EDTA, Lime-Soda and Zeolite process.

UNIT- I

MODULE - 1

WATER

INTRODUCTION

Water is the most essential compound for all living matter on the earth. It plays an important role in human living, industrial and agricultural purposes. So there is no life in the earth without water.

Sources of water

The two important sources of water are (1) surface water and (2) underground water.

Surface water

The water available on the earth's surface is called as surface water.

Surface water includes rainwater, river water, lake water and seawater.

Underground water

Underground water includes water present between the rocks in the earth crust, spring water, well water etc.

Reason for Depletion of underground water

The decrease in the quantum of underground water is depletion of water. Depletion of water is mainly caused by, modernization; industrialization and population growth Global warming causing excess evaporation of surface water.

Deforestation Decrease in rainfall caused by seasonal changes and Effluents from the industries spoiling the ground water source.

To meet out this depletion of ground water sources, it is essential to find alternate plans using water management techniques to recharge the ground water sources. One of the techniques adopted is rainwater harvesting.

Types of impurities present in water

There are three types of impurities present in water. They are

- Suspended and colloidal impurities.
- Dissolved salts.
- Micro-organisms.

Types of water:

There are two types of water.

They are (i) Soft water and (ii) Hard water.

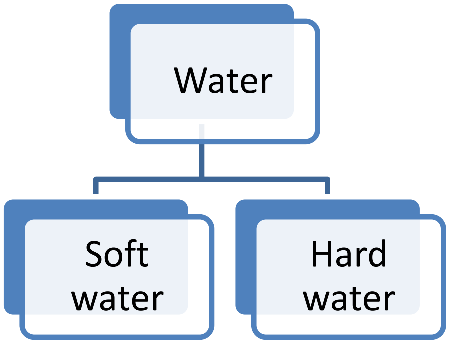


Figure-1.1. Types of water

Soft water readily gives lather with soap.

Hard water does not give lather with soap.

Hardness of water

There are two types of hardness in water. They are:

- **Temporary Hardness: (Carbonate hardness)**

It is due to the presence of calcium bicarbonate [$Ca(HCO_3)_2$] and magnesium bicarbonate [$Mg(HCO_3)_2$].

Temporary Hardness can be removed by boiling.

- **Permanent Hardness: (Non-Carbonate hardness)**

It is due to the presence of chloride and sulphate salts of calcium and Magnesium. ($CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$).Hence it is called as permanent hard water.

Methods of expressing the Hardness

The hardness of water can be expressed by any one of the following two methods.

Method 1: Units for measuring hardness is mg/litre of $CaCO_3$ equivalent

It is the number of mg $CaCO_3$ is present in one litre of water or mg/lit, or part per million of $CaCO_3$.

It is the number of parts by weight of $CaCO_3$ present in million parts of water or ppm.

Method 2: 1mg / litre = 1 ppm

Usually, the hardness of water is expressed in terms of calcium carbonate equivalents.

The formula used to convert the mass of hardness producing salt to the mass of $CaCO_3$ equivalent is given below.

$$\text{Calcium Carbonate Equivalents} = \left.\right\} \frac{\text{Mass of salt x Molecular mass of } CaCO_3}{\text{Molecular mass of salt}}$$

To prove the relation between mg/litre and ppm

Suppose Y mg of $CaCO_3$ is present in 1000g water or if Y mg of $CaCO_3$ is present in 10^3 g water.

Therefore in 10^6g water → Y × 1000g of $CaCO_3$ is present.

Hence hardness of water is = Y ppm. Therefore, 1 mg / litre = 1 ppm. Hence it is proved.

Even though $CaCO_3$ is not a hardness producing salt and is insoluble in water, it is used as the standard to express the hardness of water. Since the hardness producing salts are present in traces, mass of $CaCO_3$ equivalent to hardness producing salt is calculated to express the hardness of a water sample.

The formula used to convert the mass of hardness producing salt to mass of $CaCO_3$ is given as follows.

Multiplication factor for converting into equivalents of salt of $CaCO_3$

$$\text{Multiplication factor(M.F)} = \frac{\text{Mol.weight of CaCO3}}{2 \times \text{chemical equivalent of hardness producing substance}}$$

Example: To find the multiplication Factor of $Mg(HCO_3)_2$

Step-1: Molar mass of $Mg(HCO_3)_2 = 146$

Chemical equivalent of $Mg(HCO_3)_2 = 73$

Step-2: Molar mass of $CaCO_3 = 100$

Step-3: Multiplication factor = $\frac{100}{2\times 73}$

Now we can calculate hardness of $Mg(HCO_3)_2$ in the terms of CaCo₃ equivalent.

Suppose x quantity of $Mg(HCO_3)_2 = x.\frac{100}{146}$ amount of $CaCO_3$

Thus, the factor of $\frac{100}{146}$ is multiplication factor of $Mg(HCO_3)_2$

Hardness producing salt	Molecular Mass
$CaSO_4$	136
$MgSO_4$	120
$CaCl_2$	111
$MgCl_2$	95
$Ca(HCO_3)_2$	162
$Mg(HCO_3)_2$	146

Table 1.1 Molecular Mass of Hardness producing Salts dissolves in water

A water sample contains 48 mg of $MgSO_4$ per 200ml of water. Calculate the hardness in terms of $CaCO_3$ equivalent in mg/litre of $CaCO_3$.

One molecular mass of $MgSO_4$ = one molecular mass of $CaCO_3$

i.e. 120 mass of Mg SO_4 = 100 mass of $CaCO_3$

Therefore mass of 48mg of $MgSO_4$ = $\frac{48\times100}{120} = 40 mg\ of\ CaCO_3$

Mass of $CaCO_3$ present in 200 ml of water = 40mg Therefore,

Mass of $CaCO_3$ present in 1000ml of water = 200mg

Hardness of water = 200mg/litre of $CaCO_3$

Disadvantages of a hard water sample

- Hard water cannot be used for drinking, as it does not quench thirst.
- It cannot be used for cooking purposes.
- It cannot be used for bathing and washing purposes as it does not give lather with soap.
- Hard water cannot be used in laboratories as it gives unwanted chemical reactions.
- Hard water cannot be used in boilers in steam rising.
- It cannot be used in sugar and paper industries.
- Hard water cannot be used in textile and leather industries.

ESTIMATION OF HARDNESS OF WATER -EDTA METHOD

EDTA method is used to determine the hardness of a sample of water. EDTA refers to Ethylene-diamine tetra acetic acid. This method is also called Modern method.

PRINCIPLE:

This is a volumetric method based on the principle of formation of complexes. Ethylene diamine tetra acetic acid (E.D.T.A.) forms colorless complexes with Ca^{2+} and Mg^{2+} ions present in water. Similarly Eriochrome Black-T, another dye, also forms wine red coloured complexes with Ca^{2+} and Mg^{2+} ions. Pure Eriochrome Black-T is blue in colour. At the pH range of 9 to 10, the Eriochrome complexes are less stable when compared to E.D.T.A. complexes. Thus when E.D.T.A. solution is added to Eriochrome-Ca^{2+} or Mg^{2+} complexes it displaces pure Eriochrome to form E.D.T.A-Ca^{2+} or Mg^{2+} complexes. Thus at the end point E.D.T.A. frees the total Eriochrome Black-T to change the colour of the solution from wine red to steel blue.

Eriochrome - Ca^{2+} + E.D.T.A → E.D.T.A-Ca^{2+} + Eriochrome Black-T

Wine Red **Steel Blue**

PROCEDURE:

The burette is filled with the standard E.D.T.A. solution. A 50-ml pipette is washed with distilled water and rinsed with the sample of hard- water. Exactly 50 ml of hard-water is pipetted out into a conical flask and 5 ml of NH_4Cl - NH_4OH buffer solution is added. A pinch of Eriochrome Black-T indicator is added. The colour of the conical flask solution changes into wine red. The water sample is titrated against the E.D.T.A. Solution taken in the burette. The colour changes from wine red to steel blue. This is the end point of the titration. The burette reading is noted. Titrations are repeated until two consecutive values agree. From the volume of E.D.T.A. the hardness of the sample of water is calculated.

Note: In the estimation of hardness of water, a standard already established formula is used. This gives a standard data relating the mass of $CaCO_3$ and volume of 0.01M EDTA solution. The formula is

1ml of 0.01M EDTA solution ≡ 1mg of $CaCO_3$

HARD WATER Vs EDTA

Sl. No.	Volume of Hard water	Burette Reading		Volume of EDTA (ml)	Indicator
		Initial	Final		
1	20	0			Eriochrome Black-T
2	20	0			
3	20	0			

Table 1.2. Hard water Vs EDTA

CALCULATION:

Let V ml be the volume of E.D.T.A. Hard water.

1 ml of 0.01 M E.D.T.A. = 1 mg of $CaCO_3$

Therefore V ml of 0.01 M E.D.T.A. = V mg of $CaCO_3$

50 ml of Hard water contains = V mg of $CaCO_3$

Therefore Weight of CaCO3 present in 1000 ml of Hard water

$$\frac{V\times 1000}{50} mg$$

= 20 V mg

HARDNESS OF WATER = 20 V mg /litre of $CaCO_3$

(**Note**: In the estimation of hardness, 0.01M EDTA solution is prepared by dissolving 3.72 g of Disodium salt of EDTA in 1000 ml of distilled water.

NH_3 - NH_4Cl buffer solution is prepared by dissolving 67.5 g of ammonium chloride (AR) in 200ml of water and by adding 570ml of Liquor ammonia (AR) with specific gravity 0.92 and the total volume is made up to one litre.)

Worked out Example:

Example-1

A sample of 100 ml of hard water consumes 25 ml of 0.01M EDTA solution. Calculate the hardness of the sample of water.

Formula

1ml of 0.01M EDTA solution ≡ 1mg of $CaCO_3$

Therefore, 25ml of 0.01M EDTA solution ≡ 25 mg of $CaCO_3$

By titration, 25ml of 0.01M EDTA solution ≡100 ml of hard water

Therefore

Mass of $CaCO_3$ present in 100 ml of hard water = 25 mg

Therefore Mass of $CaCO_3$ present in 1000ml of hard water = 250mg

Hence hardness of water = 250mg/litre of $CaCO_3$

To give in ppm

Mass of $CaCO_3$ present in 100 ml of hard water = 25 mg

Mass of $CaCO_3$ present in 100g of hard water = 25×10^{-3}g

Therefore Mass of $CaCO_3$ present in 10^6g of hard water = 250g

Hence hardness of water = 250 ppm of $CaCO_3$ or 250mg/L

Example-2

A sample of 100 ml of water consumed 12.5 ml of 0.01 M EDTA solution. In another titration 100 ml of the same sample, after boiling for half an hour consumed 8.2 ml of the same EDTA solution. Calculate the carbonate and non-carbonate hardness of the sample of water.

(**NOTE:** In the given problem, volume of EDTA consumed in the first titration is equivalent to total hardness of water which includes both carbonate and non-carbonate hardness. But the volume of EDTA consumed by the water after boiling is equivalent to non-carbonate hardness as carbonate hardness in water can be removed by boiling water.)

Total hardness

1ml of 0.01M EDTA solution ≡ 1mg of $CaCO_3$

Therefore,

12.5ml of 0.01M EDTA solution ≡ 12.5 mg of $CaCO_3$

By titration,

12.5ml of 0.01M EDTA solution ≡100 ml of hard water

Therefore

Mass of $CaCO_3$ present in 100 ml of hard water = 12.5 mg

Therefore mass of $CaCO_3$ present in 1000ml of Hard water =125mg

Hence Total hardness of water = 125 mg/litre of $CaCO_3$ Non-carbonate Hardness

1ml of 0.01M EDTA solution ≡ 1mg of $CaCO_3$

Therefore,

8.2ml of 0.01M EDTA solution ≡ 8.2 mg of $CaCO_3$

By titration,

8.2ml of 0.01M EDTA solution ≡100 ml of hard water

Therefore

Mass of $CaCO_3$ present in 100 ml of hard water = 8.2 mg Therefore

Mass of $CaCO_3$ present in 1000ml of hard water = 82 mg Hence

Non-carbonate hardness of water =82 mg/litre of $CaCO_3$ Therefore

Carbonate Hardness = Total hardness – Non-carbonate hardness

= (125 – 82) = 43 mg/litre of $CaCO_3$

SOFTENING OF HARD WATER

The method of converting the hard water into soft water is called softening of hard water. Two important methods of softening the hard water are

1. Ion- Exchange method
2. Reverse Osmosis method.

Ion Exchange method

(Demineralization Method or de-ionization method)

In this method the hard water is first passed through an acidic resin having replaceable hydrogen ion (RH_2) to remove the cations [Ca^{2+}, Mg^{2+}] and then it is passed through a basic resin [$R'(OH)_2$] having replaceable hydroxyl ion to remove the anion. Thus both types of ions are totally removed.

Acid resin is represented by RH_2. Base resin is represented by $R'(OH)_2$.

Softening Process

When the hard water sample is passed through the acid resin, calcium and magnesium ions are removed.

$2RH + Ca^{2+} \rightarrow R_2Ca \quad + \quad 2H^+$

Acidic resin

$2RH + Mg^{2+} \rightarrow R2Mg \quad + \quad 2H^+$

Acidic resin

When this water is passed through the base resin, chloride, bicarbonate and sulphate ions are removed.

$R'OH \ + Cl^{--} \rightarrow R'Cl \quad + \ OH^-$
$2R'OH \ + SO_4^{2-} \rightarrow R'_2SO_4 \quad + \ 2\ OH^-$

Basic resin

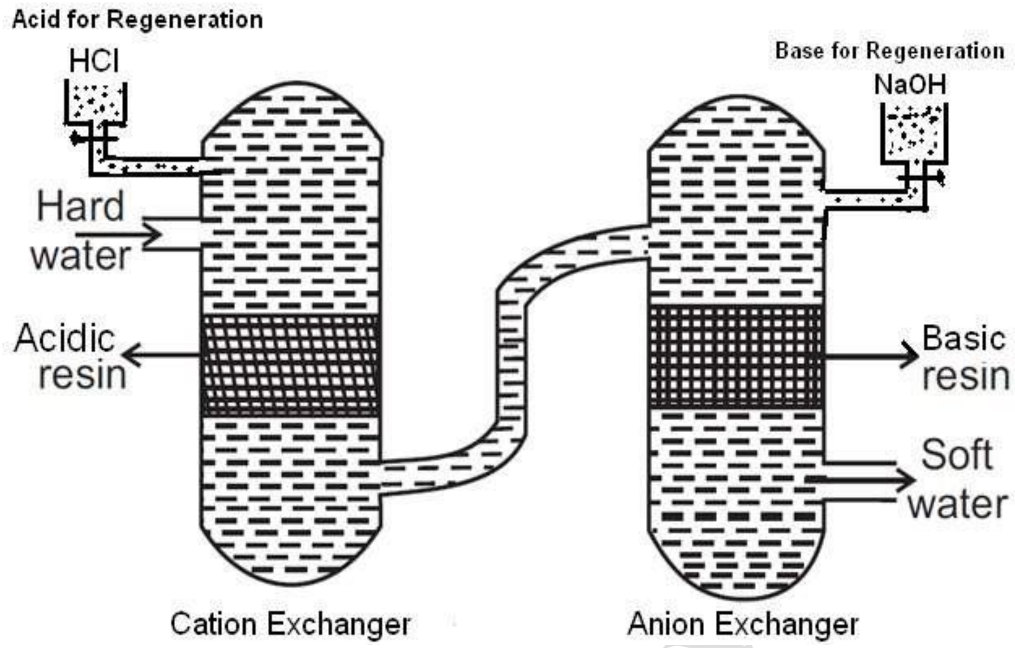


Figure 1.2. Ion Exchange Process

Thus both types of ions are removed from water. The H^+ and OH^- ions combine together to form water.

H^+ + OH → H_2O

The quality of water obtained by this method is equivalent to distilled water.

Regeneration of Acidic Resin and Basic Resin:

After a long use, the acidic resin can be regenerated by washing it with strong solution of Hydrochloric acid.

R_2Ca + 2HCl → 2RH + $CaCl_2$

The basic resin after a long use can be regenerated by washing it with a strong solution of NaOH.

R'Cl + NaOH → R'OH + NaCl

R'_2SO_4 + 2NaOH → 2R'OH + Na_2SO_4

Advantages

- In this method, both types of hardness are removed.
- The quality of water obtained is equivalent to distilled water.
- There is no wastage of water.

MUNICIPAL WATER SUPPLY

WATER FOR DRINKING PURPOSE (Potable water)

- Water used for drinking should be Colourless and odourless
- Free from colloidal and suspended impurities and
- Free from microorganisms and bacteria.

The three stages involved in purifying a water sample for drinking purpose are

1. Sedimentation
2. Filtration
3. Sterilization

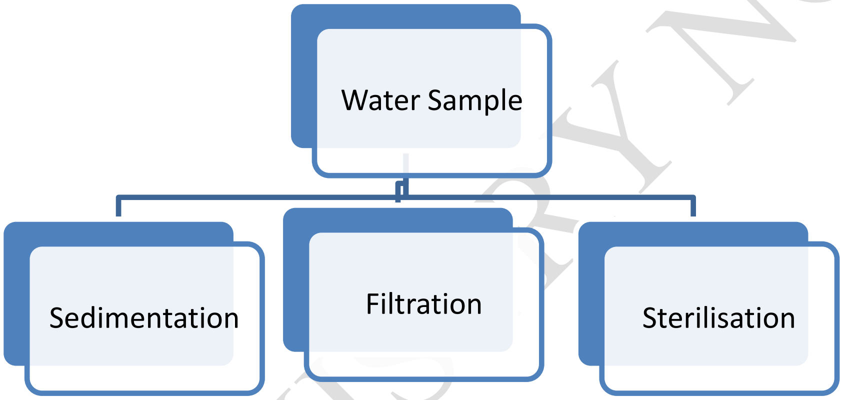


Figure 1.3. Stages involved in purifying water sample.

SEDIMENTATION

Water from river or lake is taken in the big tank called sedimentation tank. Here the insoluble matter settles down at the bottom of the tank as sediments. In this tank, the colloidal impurities are converted into precipitate by adding Alum. The clear water from the top layer is sent to the next tank called Filtration tank.

FILTRATION TANK

In filtration tank, the suspended impurities and the microorganisms are removed. In all types of filtration, the filter bed used is constructed as follows.

The filter bed consists of a layer of fine sand followed by the layer of coarse sand, which is then followed, by a layer of gravel. There is a drain at the bottom to remove the filtered water. The layer of fine sand acts as the filtering unit and the other two beds support the fine sand layer. Generally filtration is done due to the gravitational force. The filtered water is then taken to the sterilization tank.

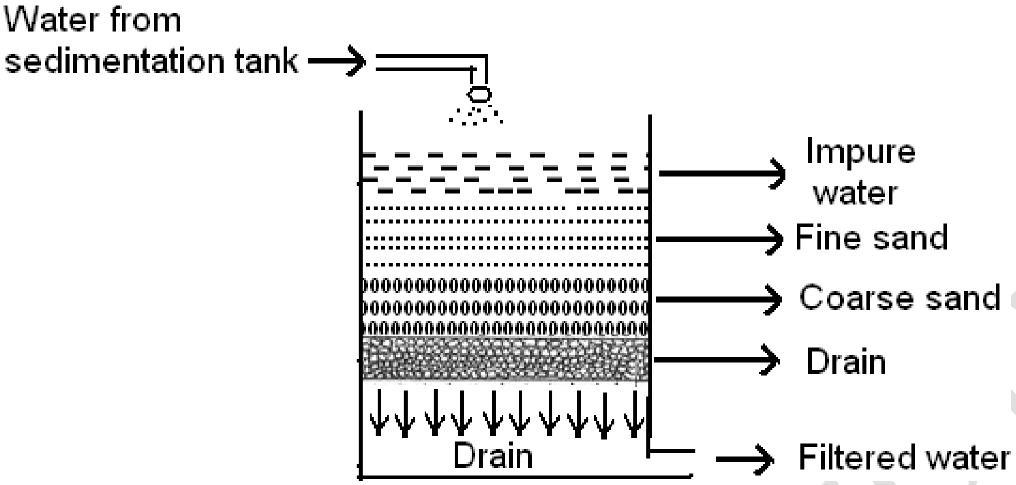


Figure 1.4. Filtration Tank

(**Note:** In drinking water supply schemes, generally gravity filters are used. However, in industrial areas where large amount of drinking water is required in short period, pressure filters are used in which water is sent through filter beds using external pressure. In gravity filtration, there are two types namely slow sand filtration and rapid sand filtration. The difference between these two methods is mainly in the recovery of filter beds used.)

STERILIZATION

Sterilization is the process of killing the bacteria. It is done by Chlorination.

Chlorination

Chlorination is addition of chlorine. Chlorine is added to water in the acidic pH range of 6.5 to 7. When chlorine is added to water, it forms HCl and HOCl. The hypochlorous acid molecule enters into the living cells of bacteria and kills them.

$H_2O + Cl_2 \rightarrow HCl + HOCl$ (Hypochlorous acid)

Other sterilizing agents used apart from chlorine are chloramines, bleaching powder etc. The advantage of using chloramines is that it does not evaporate out easily and can be carried over to a longer distance along with the water.

Ultra-violet rays can also be used for sterilizing purpose.

BOILER FEED WATER

Water is used in boilers, steam engines etc., to raise steam. When a sample of hard water is used in boiler to prepare steam, the following problems will occur.

- Scale formation
- Corrosion of boiler metal
- Caustic Embrittlement and
- Priming and foaming.

Boiler Scale Formation:

When hard water is used in boilers to get steam, the impurities that are present in the hard water will settle down on the sides of the boiler. This residue in due course will adhere to the boiler vessel surface in the form of a sludge or scale. This is called as boiler scale. The following calcium salts are responsible for the formation of boiler scale $CaSO_4$, $CaCO_3$, $Ca(OH)_2$, $Mg(OH)_2$ etc.

Disadvantages of hard water in Boilers

The salt deposit formed is a poor conductor of heat. Therefore fuel is wasted in raising the temperature of the boiler.

Due to the increase in the temperature, the plates may melt. This may lead to explosion of boiler.

At higher temperature, more oxygen may be absorbed by the boiler metal, which causes corrosion of boiler metal.

The sudden spalling of the boiler scale exposes the hot metal suddenly to super-heated steam, which causes corrosion of boiler.

Methods employed to prevent scale formation are,

1. Internal conditioning method
2. External conditioning method.

Internal conditioning methods involve addition of complexing agents like Calgon to boiler feed water. Another method of internal conditioning is Phosphate conditioning. In this method, sodium phosphate is added to boiler feed water which forms non-sticky Calcium and Magnesium Phosphate Which can be removed by blow down operation**.**

External conditioning methods water is purified either by Zeolite process or by ion-exchange method before being fed into boilers.

Corrosion of Boiler metal:

Water containing the following impurities is responsible for the corrosion of boiler metal. The impurities such as dissolved oxygen, dissolved Carbon dioxide, mineral acids, dissolved salts of calcium and magnesium, organic matter etc. are responsible for the corrosion of the boilers.

The dissolved matter undergoes hydrolysis and forms acids. The acid slowly attacks the inner part of the boiler.

The dissolved oxygen attacks iron at high temperature. The CO_2 and H_2O form carbonic acid (H_2CO_3), which slowly attacks the metal.

Prevention of Boiler Corrosion:

- By using proper water treatment procedures.
- By degasification to remove the dissolved gases like oxygen, CO_2 etc.,
- The dissolved CO_2 can be removed by the addition of limewater.
- Adding calculated amount of base could neutralize the mineral acids.

Caustic Embrittlement:

Sometimes cracks appear inside the boiler parts, particularly at the places, which are under stress. Metal becomes brittle at these places. It is due to the high concentration of caustic soda (NaOH) and a little amount of silica in water. This is called as caustic Embrittlement.

Caustic soda is formed by the hydrolysis of Na_2CO_3.

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$

Removal of Na_2CO_3 present in water can prevent caustic Embrittlement.

This can be done by the following methods.

- By adding sulphuric acid.
- By adding $CaSO_4$ and $CaCl_2$ to boiler water
- By adding Na_2SO_4.
- By adding trisodium phosphate. etc.

Foaming and Priming

Foaming:

Foaming is nothing but the formation of foam. Bubbles of water will enter the surface of water inside the boilers and results in the formation of foam. Foam comes out of the boiler along with the steam. Hence the steam becomes wet and the heat content of the steam is reduced considerably. This type of wet steam spoils the machine parts where it is used. The main cause for foaming is the presence of dissolved salts in water. Hence soft water should be used in boilers to avoid foaming.

Priming:

Priming is violent and rapid boiling of water inside the boiler. Due to priming, the water particles mix up with the steam when it comes out of the boiler. Like foaming, priming also reduces the heat content of the steam and reduces the efficiency of the steam.

Main reasons for Priming:

Defective design of the boiler. Presence of large quantities of dissolved salts, oily matter, alkaline and suspended matter.

Control

Priming can be controlled by proper design of the boiler

By uniformly heating the water in the boiler.

By using a better sample of water.

WATER SOFTENING:

LIME SODA:

Soda lime is a process used in water treatment to remove Hardness from water. This process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime (CaO) and soda (Na2CO3) to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are easily calculated from the analysis of the water and stoichiometry of the reactions. The lime-soda uses lime, Ca (OH)2 and soda ash, Na2CO3, to precipitate hardness from solution.

Carbon dioxide and carbonate hardness (calcium and Magnesium bicarbonate) are complexed by lime. In this process Calcium and Magnesium ions are precipitated by the addition of lime (Ca(OH)2) and soda ash (Na2CO3).

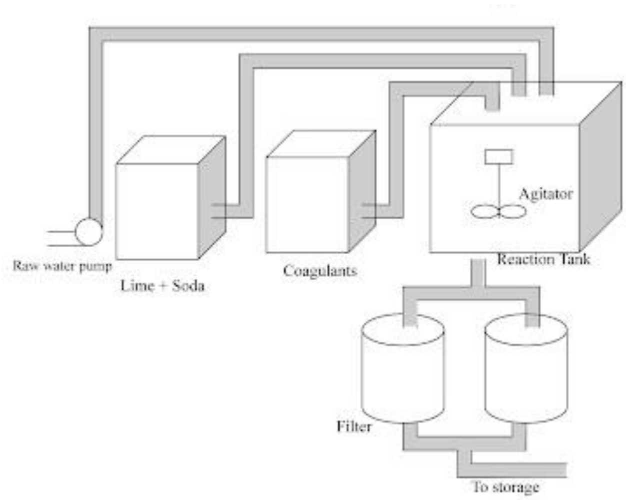


Figure 1.5. Lime Soda Process

Following are the reactions that take place in this process:

As slacked lime is added to water, it will react with any carbon dioxide present as follows:
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$....(1)

The lime will react with carbonate hardness as follows:

$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$.....(2)

$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 \downarrow + 2H_2O$.....(3)

The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

$Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$.....(4)

Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:
$Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$.....(5)

Lime addition removes only magnesium hardness and calcium carbonate hardness. In equation 5 magnesium is precipitated, however, an equivalent amount of calcium is added. The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5. Soda ash is added to remove calcium non-carbonate hardness
$Na_2CO_4 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3\downarrow$..... (6)

To precipitate $CaCO_3$ requires a pH of about 9.5; and to precipitate $Mg(OH)_2$ requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.

The amount of lime required: lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l)

The amount of soda ash required: soda ash (meq/l) = non-carbonate hardness (meq/l)

After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate. Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$

$CO_2 + Mg(OH)_2 \rightarrow MgCO_3 + H_2O$

Further recarbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:

$CO_2 + CaCO_3 + H_2O \rightarrow Ca(HCO_3)_2$

It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

Limitation of Soda Lime Process:

Lime soda softening cannot produce a water at completely free of hardness because of the solubility (little) of $CaCO_3$ and $Mg(OH)_2$.

Thus the minimum calcium hardness can be achieved is about 30 mg/L as $CaCO_3$, and the magnesium hardness is about 10 mg/L as $CaCO_3$.

We normally tolerate a final total hardness on the order of 75 to 120 mg/L as $CaCO_3$, but the magnesium content should not exceed 40 mg/L as $CaCO_3$ (because a greater hardness of magnesium forms scales on heat exchange elements)

ZEOLITE PROCESS :

Zeolites are naturally occurring sodium aluminum silicates having different amounts of water of crystallization. They are represented as $Na_2O.Al_2O_3.xSiO_2.yH_2O$ where x and y varies from 2 to 10 and 2 t 6 respectively. They are produced synthetically as well. They have the property of exchanging their Na ions for hardness causing ions like Ca++ and Mg++

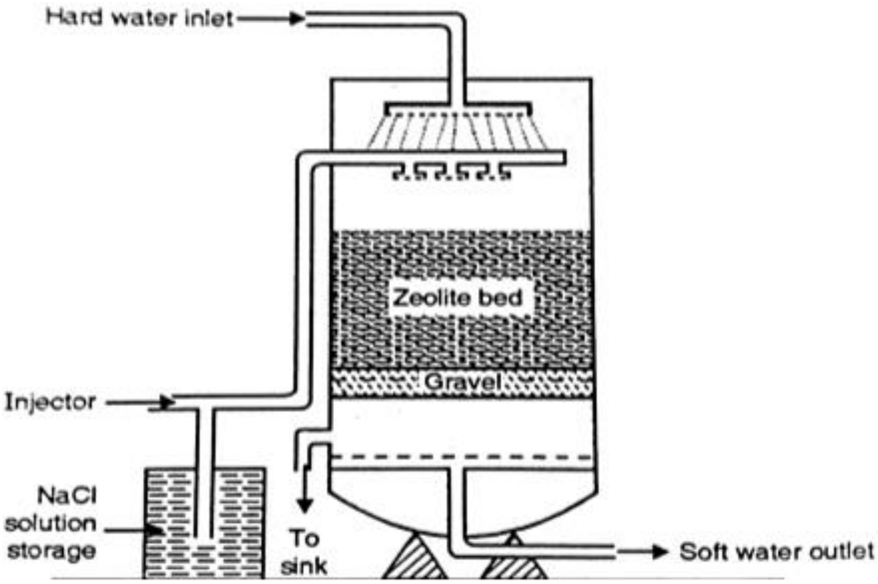


Figure 1.6. Zeolite Process

The reactions taking place the softening process are as follows-

$Ca(HCO_3)_2 + Na_2Ze$ → $CaZe + 2NaHCO_3$

$MgSO_4 + Na_2Ze$ → $MgZe + Na_2SO_4$

$CaCl_2 + Na_2Ze$ → $CaZe + 2NaCl$

Where Ze represents Zeolite.

The Ze mineral gets exhausted when all the Na+ are replaced by Ca^{+} and Mg^{++}ions. Now Ze can be regenerated by passing Nacl solution,

$CaZe + 2NaCl$ → $CaCl_2 + Na_2Ze$

$MgZe + 2NaCl$ → $MgCl_2 + Na_2Ze$

The regenerated Ze can now be used for replacing Ca^{++} and Mg^{++} from hard water. Zeolite softening is carried out in large cylindrical tank as shown, holding Ze material on a perforated platform. The tank has two inlets for feeding raw water and passing saturated NaCl solution. There are two outlets for softened water and removing $CaCl_2$, $mgcl_2$, $CaCl_2$, $mgcl_2$, the wash water formed during the regeneration.

Limitations-

- Raw material must be free from turbidity and suspended impurities.
- Highly acidic water is not suitable as it affects mineral.
- Zeolites of iron and manganese cannot be easily regenerated by passing NaCl solution. Hence iron and manganese impurities in the water to be treated must be minimum.

Advantages-

- Water of about less than 15 ppm is obtained.
- The process automatically adjusts for different hardness of incoming water.
- The equipment is compact and requires less space.
- It requires less skill in maintenance as well as operation.

Calculation of Hardness of Water by Zeolite Process:-

The amount id NaCl used for regeneration of exhausted Zeolite and the hardness of water may be calculated using following formula

$$\text{Hardness of water (Mg/L)} = \frac{50\times W\times V_2\times 10^3}{58.5\times V_1}$$

Where:

W = Amount of NaCl present per litre in gms

V_2= Total volume of NaCl used for regeneration in litre

V_1 = Total volume of water softened in litres.

QUESTIONS FOR REVISION

PART – A

1. Define hard and soft waters?
2. List the salts that cause Carbonate and non-carbonate hardness in a water sample?
3. What is ppm?
4. What is sedimentation?
5. What is sterilization of water?
6. Explain the reaction that takes place when chlorine is added to water?
7. What are boiler scales?
8. What is caustic Embrittlement?
9. What is priming?
10. What is foaming?
11. Give any one problem caused by boiler scale?

PART – B

1. List the problems caused by hard water?

PART-C

1. Explain Ion Exchange method of softening a hard water sample?
2. What is regeneration of Ion-exchange plant? How is it carried out?
3. Explain EDTA method of estimating hardness of a sample of water?
4. Describe the method used in water supply schemes to get potable water?
5. What are boiler scales? List the problems caused by boiler scale. How to overcome this problem?
6. Explain caustic Embrittlement, priming and foaming in boilers during the production of steam?

UNIT- 1

(MODULE -2)

CORROSION AND ITS CONTROL

TOPICS:-

- Definition and significance of corrosion, Mechanism of chemical (dry) and electrochemical (wet) corrosion, galvanic corrosion, concentration corrosion and pitting corrosion.
- Protection from corrosion; protective coatings-galvanization and tinning, cathodic protection, sacrificial anode and modifications in design.

UNIT- 1

(MODULE -2)

CORROSION AND ITS CONTROL

INTRODUCTION

Corrosion

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

The process of decay metal by environmental attack is known as corrosion.

Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

Example- Iron undergoes corrosion to form reddish brown colour rust [$Fe_2O_3 . 3H_2O$].

Copper undergoes corrosion to form a green film of basic carbonate [$CuCO_3 + Cu(OH)_2$]

Causes of corrosion

The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.

During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.

Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores).

When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

Effects of corrosion

Wastage of metal in the form of its compounds. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

Theories of corrosion

Dry corrosion or Chemical corrosion

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:-

(1.) Oxidation corrosion

(2.) Corrosion due to other gases

(3.) Liquid metal corrosion

Oxidation Corrosion

This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).

$M \rightarrow M^{2+} + 2e-$ (Oxidation)

$O_2 + 2e \rightarrow 2O^{2-}$ (Reduction)

$M + O_2 \rightarrow M^{2+} + 2O^{2-}$ (Metal oxide)

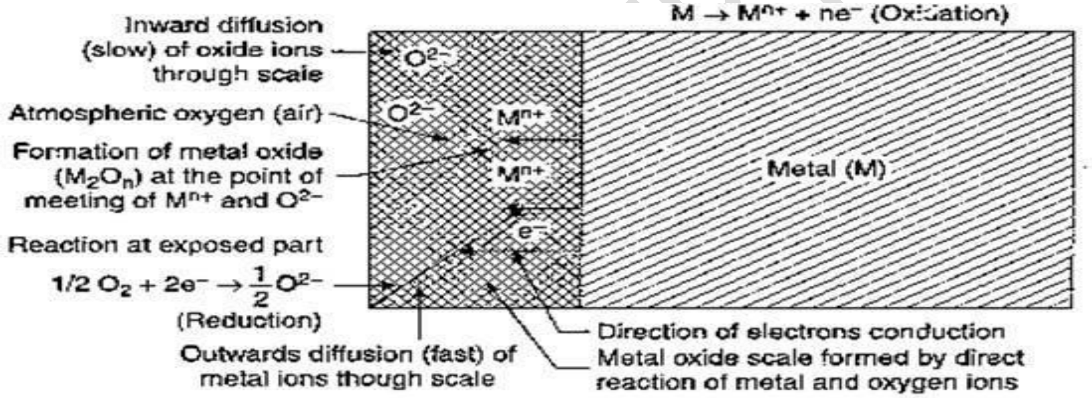


Figure 2.1 . Oxidation Corrosion

Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

If the metal oxide is stable, it behaves has a protective layer which prevents further Corrosion.

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation corrosion is not possible.

Example- Ag, Au and Pt do not undergo oxidation corrosion.

If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrodes the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.

Example- Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

Corrosion due to other gases

This type of corrosion is due to gases like SO_2, CO_2, Cl_2, H_2S, F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bed worth rule.

If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent; non-porous does not allow the penetration of corrosive gases.

$Ag + Cl_2 \rightarrow \quad 2AgCl$ (protective film)

If the volume of the corrosion film formed is less than the underlying metal, it forms

Pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Example- In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale. Fe (steel) + H_2S FeS (porous)

Liquid metal corrosion

This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal

Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet corrosion or electrochemical corrosion

This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.

At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

$M \rightarrow M^{n+} + ne^-$

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Evolution of hydrogen

This type of corrosion occurs in acidic medium.

Example- Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with Liberation of electrons.

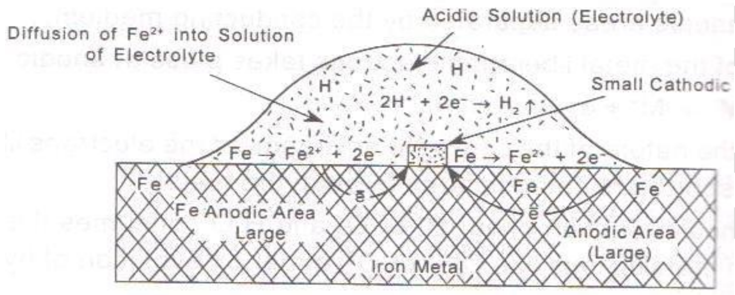


Figure 2. 2 Hydrogen evolution corrosion Anode: $Fe \rightarrow Fe_2+ + 2e-$ (Oxidation)

The electrons released flow through the metal from anode to cathode, whereas H+ ions of acidic solution are eliminated as hydrogen gas.

Cathode: $2H^+ + 2e \rightarrow H_2$ (Reduction)

The overall reaction is: $Fe + 2H+ \rightarrow Fe_{2+} + H_2$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

Absorption of oxygen

For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large. The released electrons flow from anode to cathode through iron metal.

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

Cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (Reduction)

Overall reaction: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2OH^-$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

The product called yellow rust corresponds to $Fe_2O_3 . 3H_2O$.

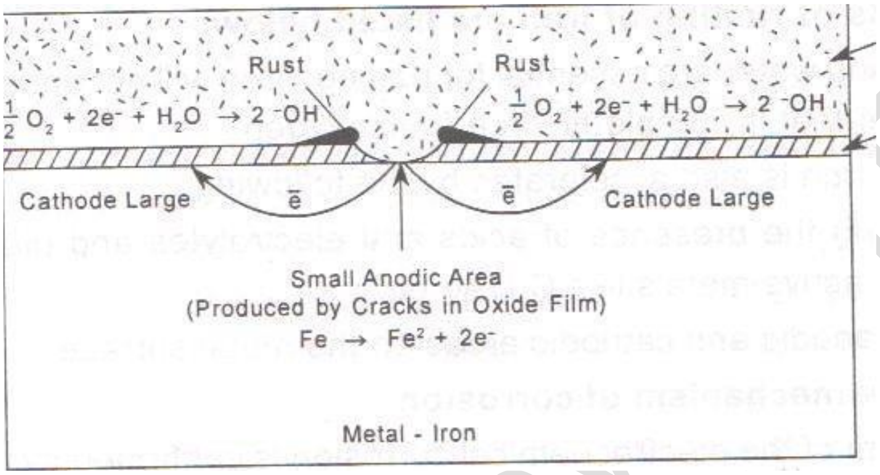


Figure 2.3. Oxygen absorption corrosion

Types of corrosion

1. Waterline corrosion or Concentration cell corrosion

This type of corrosion occurs due to electrochemical attack of the metal surface exposed to electrolyte of varying concentrations or varying aeration.

This type of corrosion is due to

1. Difference in concentration of metal ions.
2. Difference in the exposure to air/oxygen (Differential aeration corrosion)
3. Difference in temperature.

Differential aeration corrosion is the most common type of concentration cell corrosion. When a metal is exposed to different air concentrations, it has been found that poorly oxygenated of the metal becomes anodic and well oxygenated part becomes cathodic.

The potential difference is created which causes the flow of electrons from anode (metallic part immersed in Nacl solution) to cathode (exposed to atmosphere).

Example- Zn rod immersed deep in Nacl solution, Anode Zn rod above Nacl solution, Cathode.

The anodic area of zinc metal gets corroded in a corrosive environment due to oxidation process.

$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation) anode

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (reduction) cathode.

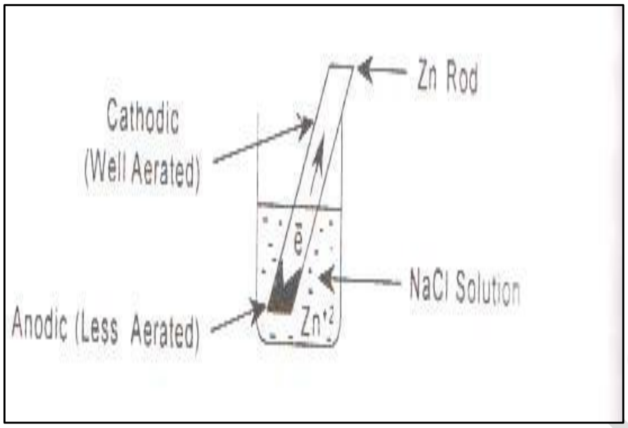


Figure 2.4. Differential Aeration Corrosion

2. Crevice corrosion:

Crevice corrosion refers to corrosion occurring in confined spaces to which the access of the working fluid from the environment these spaces are generally called crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Crevice corrosion usually occurs in gaps a few micrometers wide, and is not found in grooves or slots in which circulation of the corrodent is possible. Crevice corrosion is a very similar mechanism to corrosion. Crevice corrosion can be viewed as a less severe form of localized corrosion when compared with pitting. The depth of penetration and the rate of propagation in pitting corrosion are significantly greater than in crevice corrosion.

Factors effecting corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

Factors due to nature of metal

Purity of the metal: Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

Electrode potentials: metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (Examples - Zn, Mg, Al etc.).

Position of metal in galvanic series: Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.

The rate of corrosion depends on the difference in their position in galvanic series. Greater the difference more will be the extent of corrosion at anode.

Example- The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Examples- Bolt & nuts, screw & washer).

Relative areas of anodic and cathodic cells: the relative areas o of corrosion is influenced by cathodic to anodic cells. If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the electrons are liberated at anode which is consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.

Hydrogen over voltage: when a cathode reaction is hydrogen evolution type, the metal with Lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.

Physical state of metal: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

Nature of surface film: If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Example. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

Factors due to nature corrosive environment

Temperature: The rate of corrosion reactions increases with increase in temperature.

Humidity in air: The moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

Presence of impurities: Atmosphere is contaminated with gases like CO_2, SO_2, H_2S; fumes of H_2SO_4, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion.

P^H value: pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

Amount of oxygen in atmosphere: As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

Corrosion control methods:

I. Cathodic protection

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

1. Sacrificial anode method
2. Impressed current method

Sacrificial anode method

In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.

The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Example- A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Example- The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode. Zinc is used as sacrificial anode in good electrolytes like see water. Magnesium is used in high resistivity electrodes, like soil, due to its more negative potential and it can provide highest current output.

Example- The formation of rusty water is prevented by insertion of magnesium sheet or rod into domestic water boilers or tanks.

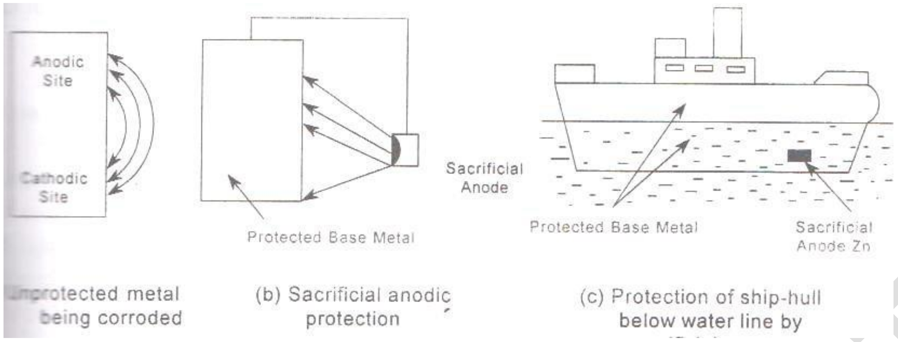


Figure 2.5 . Sacrificial anode method: ship hull and underground water pipeline

Impressed current method

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The impressed current is taken from a battery or rectifier on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.

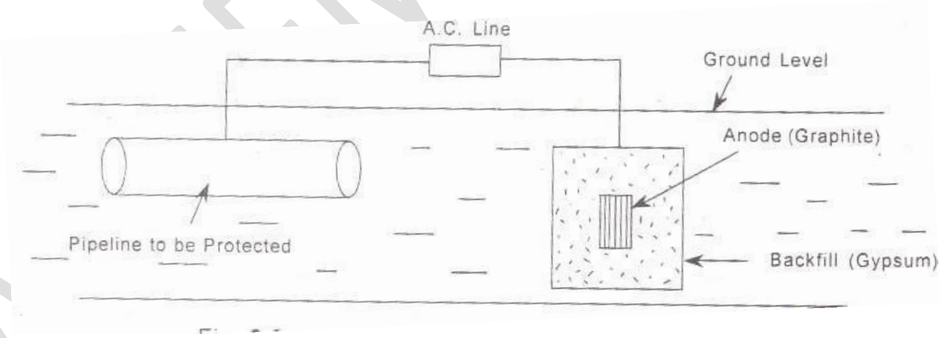


Figure 2.6. Impressed current method

Advantages

1. Applicable in high resistivity environments.
2. Effective in protecting on coated and poorly coated structure.

Disadvantages

1. Required external power resulting in monthly power costs.
2. Over protection can cause coating damage.

Metallic coating

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

a. Anodic coating

The metal used for the surface coating is more anodic than the base metal which is to be protected.

For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.

The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

b. Cathodic coating

Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.

Cathodic coating protects the base metal only when the coating is uniform and free from pores.

The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings

Hot dipping

Hot dipping process is applicable to the metals having higher melting point than the coating metal.

It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.

The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Example- Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are galvanizing and tinning.

Galvanizing

Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.

It is the anodic protection offered by the zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90˚C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried.

Then steel article is dipped in the bath containing molten zinc which is at 425-450˚C. To prevent it from oxide formation, the surface of bath is covered with ammonium chloride flux**.** When the iron sheet is taken out it is coated with a thin layer of zinc.

To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450^{o}C followed by cooling

Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

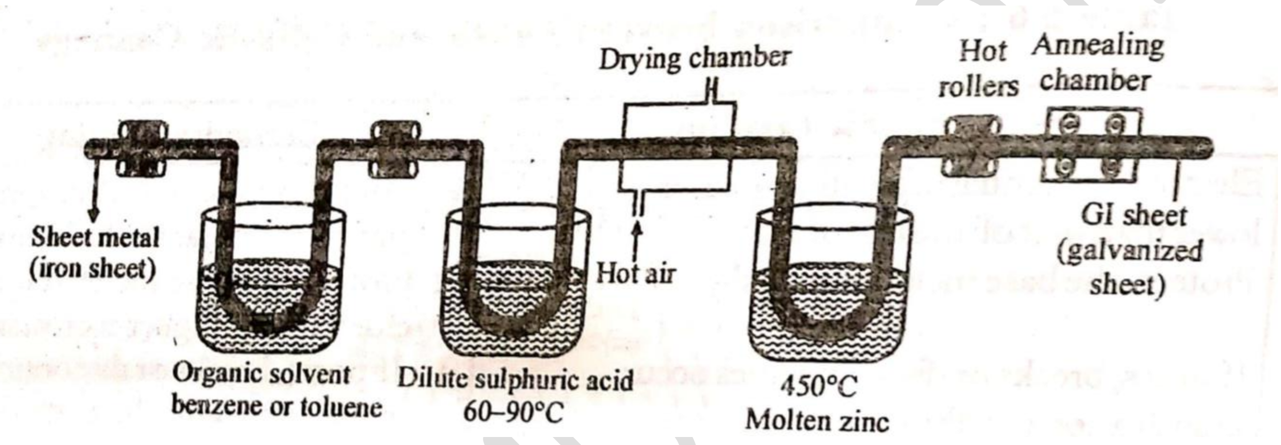


Figure 2.7. Galvanization of Steel Sheet

Tinning – Cathodic Metal Coating

The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.

Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.

A cleaned iron sheet is passed through a bath $ZnCl_2$ molten flux followed by molten tin and finally through a suitable vegetable oil. The $ZnCl_2$ flux helps the molten metal to adhere to the base metallic surface.

Palm oil protects the tin coated surface against oxidation. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.

Application

Copper sheet coated with tin are used for making utensils. Edible oil, butter are preserved in tinning cans.

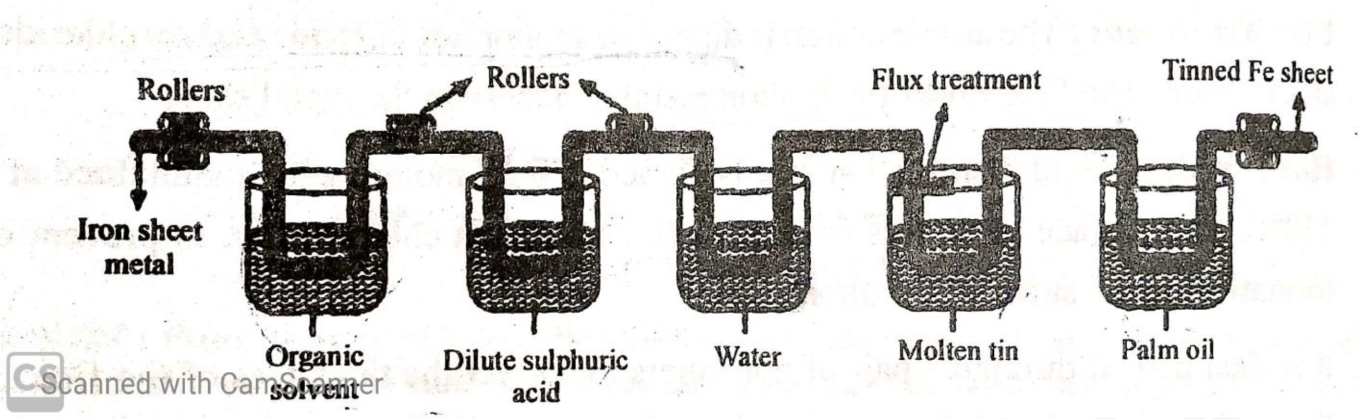


Figure 2.8. Tinning of steel sheet

Electroplating

Electroplating is the process of coating metals and protects them from corrosion, wear and chemical attack.

Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals and alloys.

The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.

The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.

When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.

Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

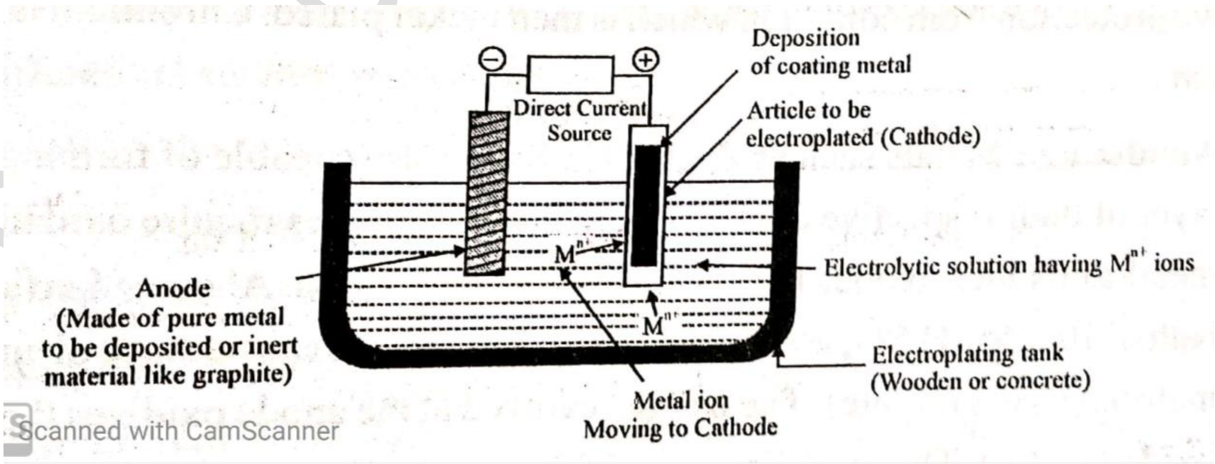


Figure 2.9. Electroplating

Surface coatings

The application of surface coating is the common method to protect the surface of the metal from the corroding environment. These surface coatings exhibit chemical inertness to corrosive environment, adhesive properties and impermeable.

Organic surface coatings

Organic surface coatings are applied over the metallic surfaces to prevent from the corrosion.

Properties of Organic surface coatings

1. Chemical inertness to the corrosive environment
2. Good surface adhesion
3. Impermeability to water gases and salts Example. Paints
4. Paint is a mechanical dispersion mixture of several constituents in a vehicle oil or drying oil.

The following are the constituents of paints and their functions.

Constituent Functions Examples

Pigment

1. It is a major constituent of the paint.
2. Provides desired colour to the paint
3. It protects the paint by reflecting harmful U.V radiation.
4. Gives strength and increases weather resistance of the film
5. white lead, ZnO
6. Red lead,
7. Ferric oxide
8. Vehicle oil/ Drying oil
9. It forms the film forming constituent of the paint.
10. It acts as medium for the dispersion of various constituents.
11. It gives durability, adhesion and water proofness to the paint.
12. Sunflower oil, Mustard oil, Soya bean oil

Thinners

Reduces the viscosity and increases the elasticity of the paint.

Paint film

Enhances the dissolving the additives in vehicle medium. Eg- Turpentine, Kerosene, Naphtha

Driers

Driers are oxygen carrying catalysts. They accelerate the drying of the paint film through oxidation, polymerization and condensation. Tunstates and naphthalenes of Pb, Zn and Co.

Extenders/ Fillers

Low refractive indices materials. They reduce the cost and cracking nature of the paint film.

$BaSO_4$, gypsum,

Plasticizers

They provide elasticity to the film and minimize cracking.

Tributylphosphate,

triphenylphosphate

Anti skinning agents

They prevent the gelling nature the paint film.

Polyhydroxy phenols

Modification in design to prevent corrosion

There are a few key design rules that can be followed to help prevent corrosion:

1. Adjust Wall Thickness.
2. Ensure that there's Adequate Drainage.
3. Minimize Bi-Metallic Corrosion Cells.
4. Avoid Differential Aeration Cells.
5. Minimize Temperature Gradients.
6. Minimize Stress Gradients.
7. Separate Environments.

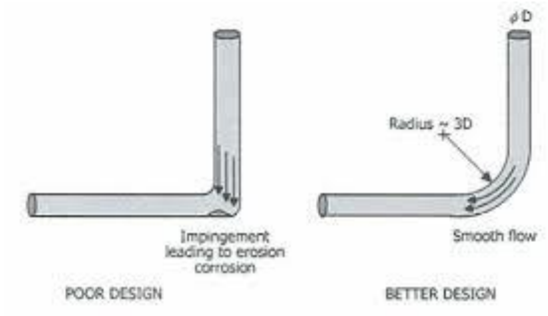


Figure 2.10. Prevention of Corrosion by avoiding sharp corner and stress

QUESTIONS FOR REVISION

PART – A

1. What is corrosion?
2. What is dry corrosion?
3. What is wet Corrosion?
4. What type of corrosion takes place in a metal when anode is small `and cathode is large? Why.

PART- B

1. Write a note on galvanic cell formation theory.
2. Write a note on differential aeration theory.
3. What are the factors influencing the rate of corrosion?

PART-C

1. Explain the mechanism of galvanic corrosion.
2. Explain the differential aeration theory with suitable examples.

TEST YOUR UNDERSTANDING

a. Why corrosion often takes place under metal washers.
b. Welded joints are better than riveted joints. Why?

UNIT- II

(MODULE -3)

ENGINEERING MATERIALS

TOPICS:

- Portland cement; Definition, Manufacturing by Rotary kiln. Chemistry of setting and hardening of cement. Role of Gypsum.
- Glass: Definition, Manufacturing by tank furnace, significance of annealing, Types and properties of soft glass, hard glass, borosilicate glass, glass wool, safety glass.
- Lubricants: Classification, Mechanism, Properties; Viscosity and
- Viscosity index, flash and fire point, cloud and pour point. Emulsification and steam emulsion number.

UNIT-II

(MODULE -3)

ENGINEERING MATERIALS

CEMENT

INTRODUCTION

Cement is a building material. It is applied in the form of a soft paste with sand and water and later its sets into a hard mass. It is a mixture of calcareous material and argillaceous material. It is a mixture of silicates of calcium and aluminum.

Portland cement

A paste of cement with water on setting and hardening gave a hard mass whose colour and hardness were similar to those of stones from Portland in England. Thus, it derived the name Portland cement. Portland cement is a mixture of silicates of calcium and aluminum.

Major constituents of cement

1. Dicalcium silicates($2CaO.SiO_2$)-28%[C_2S]
2. Tricalcium silicates($3CaO.SiO_2$)-46%[C_3S]
3. Tricalcium aluminates($3CaO.Al_2O_3$)-10%[C_3A]
4. Tetra calcium aluminoferrite($4CaO.Al_2O_3.Fe_2O_3$)-9%[C_4AF]
5. Small quantities of CaO and MgO-7%

Manufacture of cement by wet process Raw materials required:

1. Calcareous materials – These materials supply lime Examples: Limestone, chalk, marble
2. Argillaeous materials – These materials supply silica.

Example: Clay, Powdered coal (fuel), Gypsum

Process:

The cement is manufactured by wet process as follows:-

1. The limestone is crushed and powdered well.
2. The clay is intimately mixed with water in wash mill.
3. The powdered limestone and wet clay are mixed and made into a paste in a grinding mill. This paste is known as slurry. The slurry contains 30 to 40% water.
4. The slurry is fed into the top of the rotary kiln. The rotary kiln is made of steel plates lined with fire bricks.

5. The kiln is heated by burning powdered coal which is injected at the lower end by an air blast.
6. In the upper part of the kiln (drying zone) where the temperature is 400°C, the slurry loses all its water.
7. When the charge enters the middle portion of the kiln (calcinations zone) where the temperature is about 900 – 1000°C, limestone decomposes to form CaO and CO_2.
8. Then the charge enters lower portion of the kiln (burning zone) where the temperature is about 1400°C.
9. Lime adds clay combines to form calcium silicates and aluminates called clinker.
10. The hot clinker is cooled and then grinded with 3 – 4% gypsum in a grinding mill. Gypsum retards the setting of cement. In the absence of gypsum, cement sets rapidly.
11. The cement coming out of the grinding mills is stored in concrete storage tanks and then packed in bags.

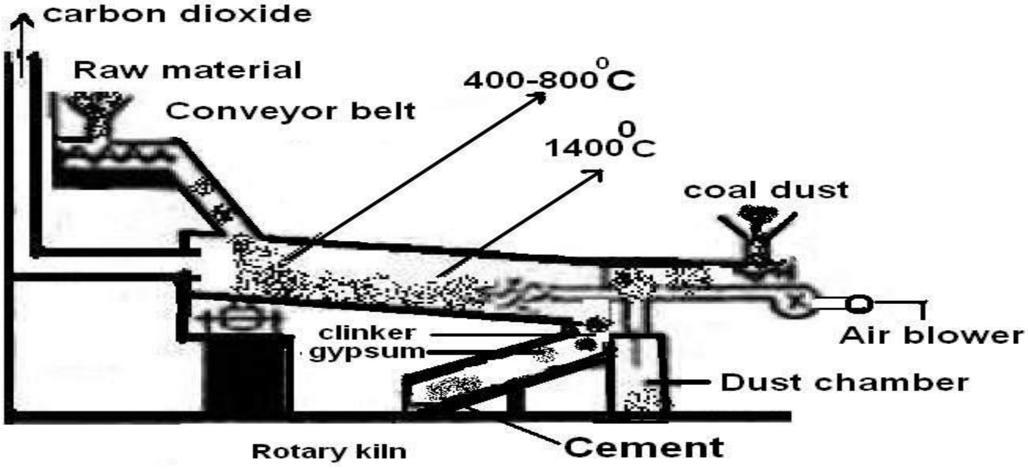


Figure 3.1. Rotary Kiln

Setting of cement:

When water is added to cement, sudden setting of cement occurs (flash set). The hardening of cement by the addition of water is known as setting of cement.

The setting and hardening of cement are mainly due to hydration and hydrolysis reactions of the different constituents present in cement.

The Dicalcium silicate (C_2S), Tricalcium silicate (C_3S), Tricalcium aluminate (C_3A) and tetra calcium aluminoferrite (C_4AF) present in cement undergoes hydration.

The process of solidification comprises of :-

i. Initial setting ii. Final Setting and hardening

Initial Setting: when cement is mixed with water, the cement paste becomes quite rigid with in a short time which is known as Initial setting. This is due to dehydration of C_3A (few days) and gel formation of (C_4AF).

i. $3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3 . 6H_2O + 880$ kJ/Kg

$C_3A + 6H_2O \rightarrow C_3A.6H_2O + 880$ KJ/kg

Tricalcium aluminate → Hydrated tricalcium aluminate (crystals)

The tricalcium aluminoferrite **(**C_4AF) then reacts with water forming both gels and crystalline compounds.

C_3A is responsible for initial set or flash set. Its early strength is good but ultimate strength is quite low.

ii. $4CaO. Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow 3CaO.Al_2O_3 . 6H_2O + CaO. Fe_2O_3 .H_2O + 420$KJ/kg

(Crystals) (gel)

Dicalcium Silicate C_2S also contributes to initial setting by forming Tobermonite gel (which process very high surface area and adhesive property) on hydrolysis.

iii. $2[2\ CaO.SiO_2] + 4H_2O \rightarrow 3CaO.SiO_2.3H_2O + Ca(OH)_2 + 250$ KJ/kg

Dicalcium silicate Tobermonite Gel Crystals

Role of Gypsum:

After initial setting the paste becomes stiff. However, the gypsum ($CaSO_4.2H_2O$) added to cement return to dissolution of tricalcium aluminate (C_3A) by forming in soluble calcium sulphoaluminate.

$3CaO.Al_2O_3 + xCaSO_4.2H_2O \rightarrow 3CaO.Al_2O_3 . xCaSO_4.2H_2O$

Tricalcium sulphoaluminate

Final setting and hardening:

Final setting and hardening of cement is mainly due to deformation of Tobermonite gel($3CaO.SiO_2.3H_2O$) + crystalation of ($Ca(OH)_2$) and hydration of ($3CaO.Al_2O_3$).

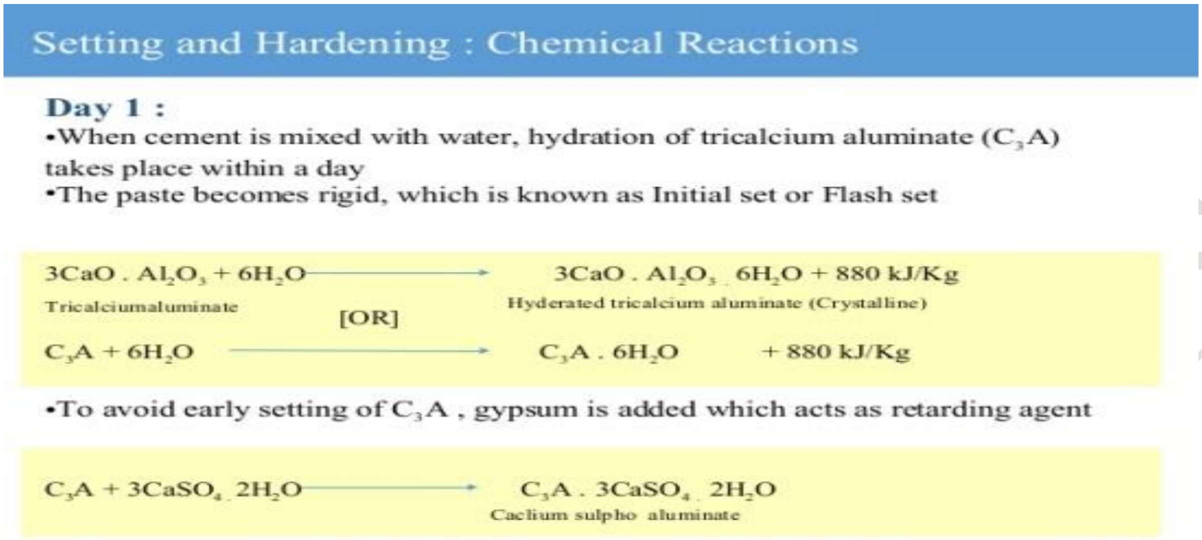
$2[3CaO.SiO_2] + 6H_2O \rightarrow 3CaO.SiO_2.3H_2O + 3Ca(OH)_2 + 500$ KJ/kg

The strength and hardness of the set mass increase or hydrolysis and crystallization process continues for 7-28 days.

(The process of setting and hardening of cement is depicted in serial order figure 2,3 and 4).

The hydration of cement is an exothermic crystal reaction and the volume of cement increases in hydration. The heat is evolved during the first seven days of hardening. The compound responsible for the evolution of heat in descending order ($C_3A > C_3S > C_4AF > C_2S$).

The evolved used in setting of cement.



Setting and Hardening : Chemical Reactions

Day 1 :

- When cement is mixed with water, hydration of tricalcium aluminate (C_3A) takes place within a day
- The paste becomes rigid, which is known as Initial set or Flash set

$$3CaO \,.\, Al_2O_3 + 6H_2O \longrightarrow 3CaO \,.\, Al_2O_3 \,.\, 6H_2O + 880\ kJ/Kg$$

Tricalciumaluminate

Hyderated tricalcium aluminate (Crystalline)

[OR]

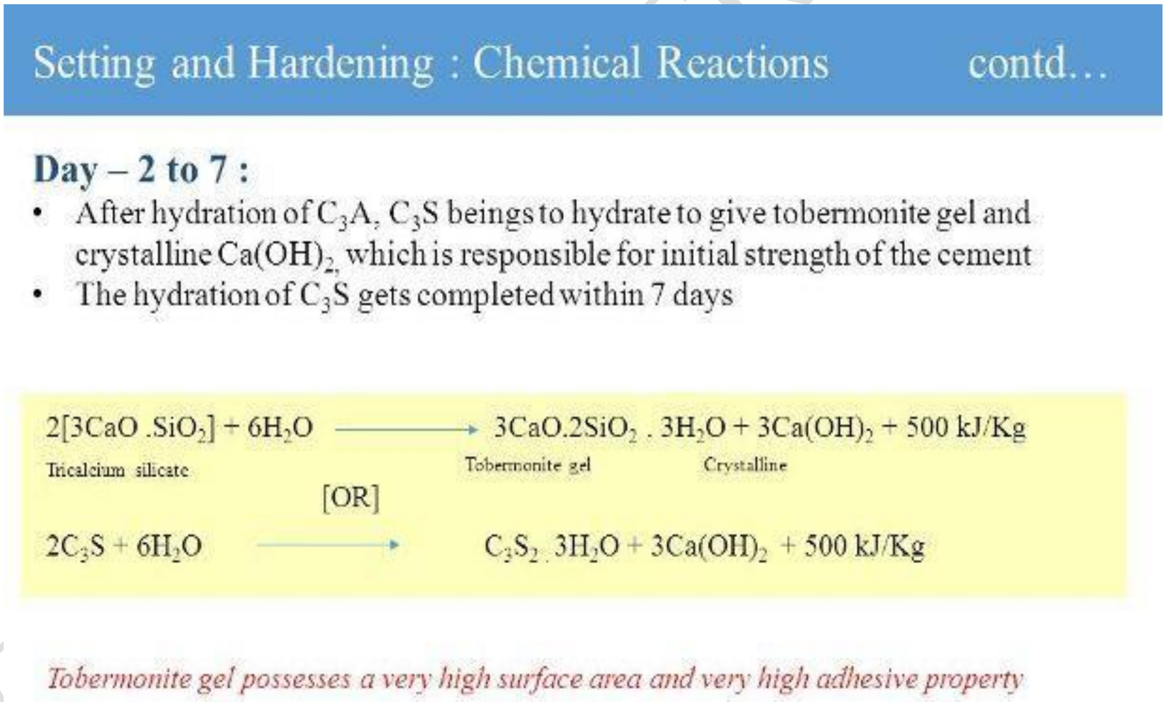
$$C_3A + 6H_2O \longrightarrow C_3A \,.\, 6H_2O + 880\ kJ/Kg$$

- To avoid early setting of C_3A , gypsum is added which acts as retarding agent

$$C_3A + 3CaSO_4 \,.\, 2H_2O \longrightarrow C_3A \,.\, 3CaSO_4 \,.\, 2H_2O$$

Caclium sulpho aluminate

Figure 3.2. Setting and Hardening of Cement (Day 1)



Setting and Hardening : Chemical Reactions contd…

Day – 2 to 7 :

- After hydration of C_3A, C_3S beings to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$, which is responsible for initial strength of the cement
- The hydration of C_3S gets completed within 7 days

$$2[3CaO \,.SiO_2] + 6H_2O \longrightarrow 3CaO.2SiO_2 \,.\, 3H_2O + 3Ca(OH)_2 + 500\ kJ/Kg$$

Tricalcium silicate

Tobermonite gel

Crystalline

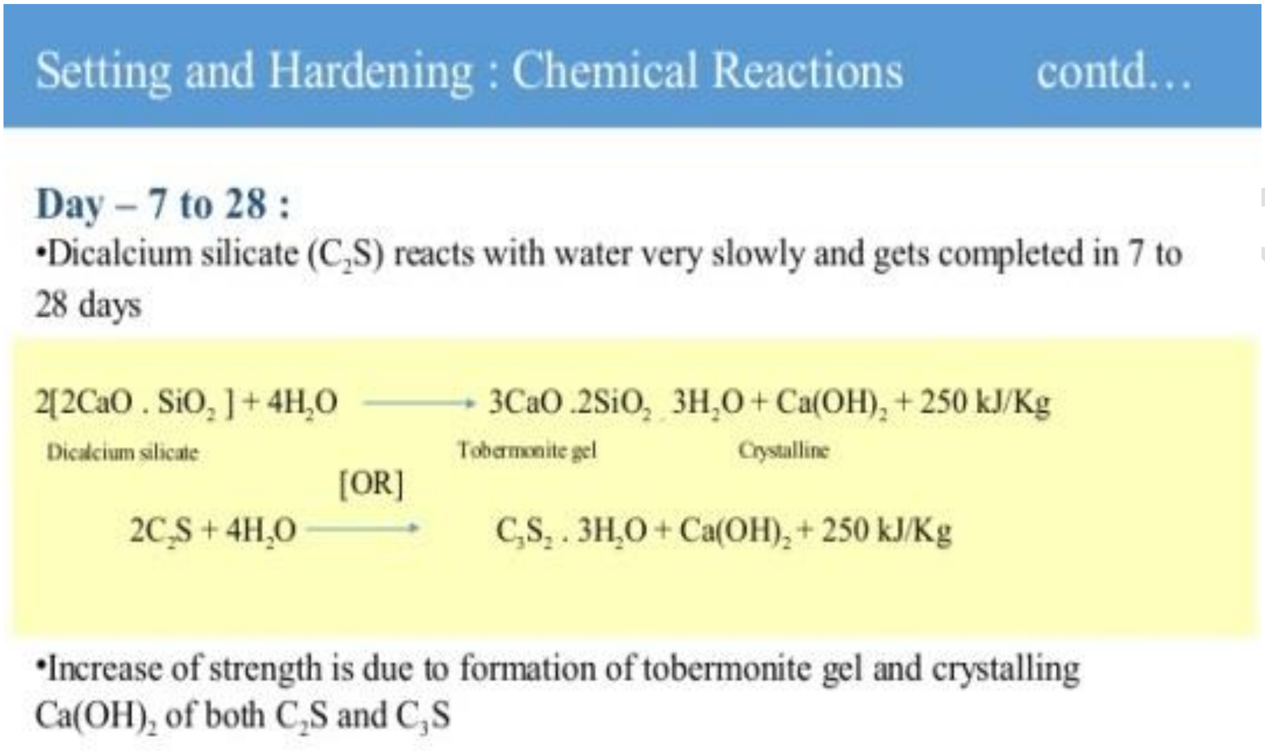
[OR]

$$2C_3S + 6H_2O \longrightarrow C_3S_2 \,.\, 3H_2O + 3Ca(OH)_2 + 500\ kJ/Kg$$

Tobermonite gel possesses a very high surface area and very high adhesive property

Figure 3.3. Setting and Hardening of Cement (Day 2 - 7)

Note : The initial set stage occurs when cement paste attains a certain stiffness which can be marked by use of a standard needed which may penetrate a certain depth of a mixture prepared in a standard manner. Physical changes occurring in setting and hardening of cement is depicted in next figure 4 and 5



Setting and Hardening : Chemical Reactions contd…

Day – 7 to 28 :

- Dicalcium silicate (C_2S) reacts with water very slowly and gets completed in 7 to 28 days

$$\underset{\text{Dicalcium silicate}}{2[2CaO\ .\ SiO_2\ ]} + 4H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO\ .2SiO_2\ .\ 3H_2O} + \underset{\text{Crystalline}}{Ca(OH)_2} + 250\ kJ/Kg$$

[OR]

$$2C_2S + 4H_2O \longrightarrow C_3S_2\ .\ 3H_2O + Ca(OH)_2 + 250\ kJ/Kg$$

- Increase of strength is due to formation of tobermonite gel and crystalling $Ca(OH)_2$ of both C_2S and C_3S

Figure 3.4. Setting and Hardening of Cement (Day 7-28)

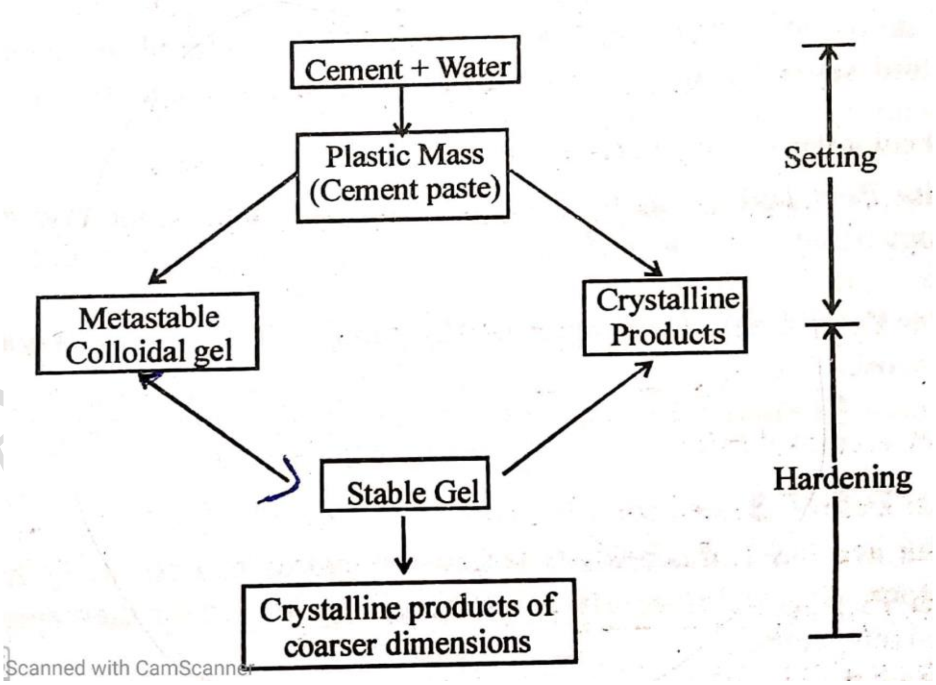


Figure 3.5. Process of Setting and Hardening of cement

QUESTIONS FOR REVISION

PART – A

1. What is cement?
2. What is Portland cement?
3. Why is gypsum added during the manufacture of cement?

PART – B

1. What are the raw materials required for the manufacture of Portland cement?
2. Write a note on setting of cement.

PART – C

1. Explain the manufacture of Portland cement by wet process.

TEST YOUR UNDERSTANDING

a. What are the various types of cement?
b. How the quality of cement is tested?

GLASS

INTRODUCTION

Glass is an engineering material. It may be defined as an amorphous, rigid, brittle, hard, transparent super cooled liquid. It is resistant to heat. It is a transparent mixture of silicates of potassium or sodium. It is produced by the fusion of certain basic oxides and acidic oxides, with sand and other materials.

Chemically, glass may be define as fused mixture of silicates of alkali and alkaline earth compounds and other glass constituents like CaO, MgO, SnO_2 , barium oxide and lead oxide.

Glass is completely vitrified solid solution which has no definite composition. However, it may be represented as $xR_2O.yMO.6SiO_2$ where, x and y are whole number, R monovalent alkali metal atom and M is a bivalent metal atom.

Composition of Glass:

The composition of some common verities of glass is as follows.

1. Soda lime glass Na_2O. CaO.$6Sio_2$.
2. Potash lime Glass: $K_2O.CaO.6Sio_2$.
3. Potash lead glass: $K_2O.PbO.6Sio_2$.

Raw material required for the manufacture of glass:

The raw materials for the manufacture of ordinary glass are of two kinds.

1. **Acidic oxides:** sand (Sio_2). Boron oxides (B_2O_3).
2. **Basic oxides:** Sodium-oxides (Na_2O),potassium oxides (K_2O),calcium oxides (Ca_2O),Lead Oxide (PbO),Zinc Oxide (ZnO),Magnesium Oxide (MgO) and Aluminum Oxide (Al_2O_3).

Manufacture of Glass:

1. Raw materials are:
2. Sand
3. Sodium carbonate
4. Calcium carbonate

Mixing:

The raw materials are powdered well and they are mixed homogeneously. With this some of the broken glass powders are also added to get an intimate mixture known as" Batch". Raw materials sand Na_2CO_3 and lime stone are ground to powder and mix with cullets. The cullet is used in the mixture to lower the melting point of the mixture.

Fusion:

The batch is then transferred to the tank or pot furnace. This batch is heated to 1400-1500°C. At this temperature the substances present in the batch react together forming a mixture of silicates. This mixture of silicates is known as glass.

On continued heating, the entire amount of CO_2 escapes out and viscous fused mass is obtained called molten mass. Completion of fusion is checked by taking out test samples on an iron hook from time to time. When charge becomes transparent and free from bubbles and gases, the resulting fuse mass is known as plane. Heating is stopped.

Batch Reactions:

a. **Below 600˚C**

   Moisture, chlorides of Na,K,Fe, Sn, sodium Sulphate and small amount of oxides of As,Sb,Pb,B are evaporated .

b. **At 700-900˚C**

   Silica(SiO_2) reacts with soda ash Na_2CO_3 to form sodium silicate and CO_2 escape

Fining:

The molten glass is kept at the highest temperature for some time to remove gas bubbles. This is called fining.Na_2CO_3 is often added to lower the viscosity of the molten glass. The impurities rise to the top as scum and it is removed. Cullet, oxidizing agents, reducing agents and other materials are also added to the molten glass according to the requirements.

Tank Furnace:

This furnace resembles the reverberatory furnace adopted for puddling of the wrought-iron. Fig. 14-2 shows the section of a tank furnace adopted for the melting of glass. It is constructed with reinforced masonry. The roof is given special shape to deflect the flames of heated gas.

The ports are provided for the entry of preheated producer gas. The doors are provided for charging and for taking out the molten glass. A bridge separates the tank into two unequal compartments.

The batch is heated in large compartment and it contains somewhat impure glass. It flows through opening of bridge into small compartment. The gall or floating impurities are collected at the top of large compartment. The refractory lining is provided to the interior surface of tank.

The tank is filled with raw materials. The furnace is heated by allowing producer gas through ports. The charging of raw materials and taking out of molten mass are simultaneous. This is a continuous process and it is adopted to melt large quantities of glass at a time.

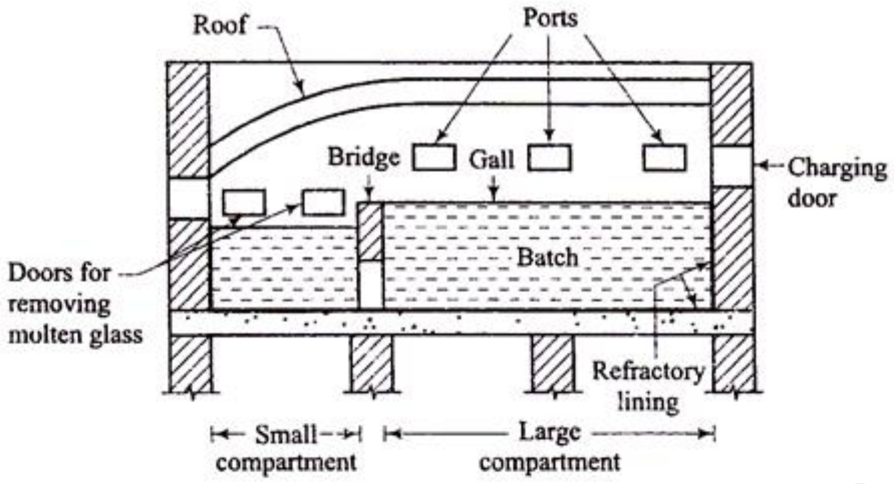


Figure 3.6. Tank Furnace

Fabrication:

Coloring material may be added to the molten glass to get desired coloured glass.

Molten glass is then moulded or fabricated into articles of desired shape by blowing, moulding, or pressing.

Coloring Materials

Cobalt oxides - Blue
Cuprous salt - Red
Chromium oxide- Green
Ferric iron - yellow
Potassium dichromate- Green

Annealing of Glass:

The method of slow cooling of glass is called annealing. If the manufactured hot glass articles are cooled suddenly, it will easily break. To avoid this glass is cooled very slowly by passing them through several hot chambers. The temperature of the hot chamber is in the decreasing order gradually. This process of slow cooling of glass is called as annealing. The manufacturing glass being a bad conductor of heat and if glass material is cool rapidly, upper layer will cool down first, living the inner portion in a straight and stress and strain as glass is bad conductor of heat. Due to this unequal expansion of glass materials are much like to crack to pieces. They cannot with stand chill of temperature or shock. To avoid such problems, annealing is done. The temperature range of cooling is from hot glass to cool glass.

(Hot glass) 1000˚C → 900˚C → 800˚C → 700˚C → 600˚C → 500˚C →400˚C→300˚C→200˚C. (cool glass)

Different Types of glasses:

a. **Photo chromatic glass**:

Photo chromic lenses are lenses that darken on exposure to specific types of light, most commonly ultraviolet radiation. Once the light source is removed, the lenses will gradually return to their clear state. Photo chromic lenses may be made of glass, polycarbonate, or another plastic. Traditional photo chromic eyeglasses are generally alkali Boro-alumino -silicates with 0.01 to 0.1 percent silver halide and a small amount of copper. Upon absorption of light, the silver ion reduces to metallic silver, which nucleates to form colloids about 120 angstroms in size. This is small enough to keep the glass transparent, but the colloids are dense enough to make the glass look gray or black.

Figure 3.7. Photo chromatic glass

b. **Windshield glass**

A framed pane of usually curved glass or other transparent shielding located in front of the occupants of a vehicle to protect them from the wind. A shield placed to protect an object from the wind.

Modern windshields are generally made of laminated safety glass, a type of treated glass, which consists of two (typically) curved sheets of glass with a plastic layer laminated between them for safety, and are bonded into the window frame. Motorbike windshields are often made of high-impact acrylic plastic.

Laminated glass is produced by permanently bonding two pieces of glass together with a tough Glass plastic interlayer (polyvinyl butyral, PVB) under heat and pressure. Once bonded together, the glass and which acts as a single unit and generally appears very similar to standard clear glass. The inter layer is virtually invisible when viewed in transmission with glass on either side.

The benefit of laminated glass is that if broken, glass fragments will adhere to the PVB interlayer rather than falling free, thereby reducing the risk of physical injury and property damage. PVB also has properties that effectively filter over 99% of UV. It also reduces transmission of sound. Hence the windshield glass in cars is a safety device just like seatbelts & airbags.

Laminated glass is commonly used in automobiles (for windshields), airports, museums, sound studios, schools, greenhouses. Windshields protect the vehicle's occupants from wind and flying debris such as dust, insects, and rocks, and provide an aerodynamically formed window towards the front.

Figure 3.8. Windshield glass

- **c. Optical glass: (Crown glass)**

Optical glass is a type of optical glass used in lenses and other optical components. It has relatively low refractive index (≈1.52) and low dispersion Crown glass is produced from alkali-lime (RCH) silicates containing approximately 10% potassium oxide and is one of the earliest low dispersion glasses.

Figure 3.9. Optical Glass or Crown Glass

Optical glass is mainly produced in a continuous melting process. Optical glasses acquire their properties through their chemical composition, melting process, and finishing methods. There are two common optical glasses: flint glass and crown glass. The difference between the two lies in their index of refraction;

Our range of optical glasses includes:
Arsenic-free N-glasses, precision molding and High transmission glasses.

MAJOR GLASS TYPES AND THEIR USES

Glass Type	Properties	Limitations	Uses
Soda lime	Inexpensive; easy to melt and shape; most widely used glass	Poor durability; not chemically resistant; poor thermal shock resistance	Windows; bottles; light bulbs; jars
Lead glass (often 20–30% Pb oxide)	High density; brilliant; very easy to melt, shape, cut, and engrave	Poor durability; easily scratched	Fine crystal radiation windows; TV tube parts
Borosilicate (usually 5–13% B_2O_3)	High density; brilliant; very easy to melt, shape, cut, and engrave	Poor durability; easily scratched	Fine crystal radiation windows; TV tube parts
	Very good thermal shock resistance and chemical durability; easy to	Not suitable for long-term high temperature use melt and shape	Lab ware; kitchenware; special light bulbs; glass pipe; sealed beam headlights
Aluminosilicate (usually 5–10% Al_2O_3)	Excellent thermal resistance; durability	More difficult to melt and shape than borosilicate	Top-of-stove cookware; high quality fiberglass
High silica (Vycor 96.5%; fused quartz 100%)	Outstanding thermal resistance	Difficult to make; very expensive	Spacecraft windows; lab ware; fiber optics

Table 3.1.Major Glass types and their uses.

Glass wool and its uses :

Glass wool is made from silica sand to which recycled glass (cullet) and fluxing agents are added. The material is melted to 1100°C in an electric furnace and then conditioned in a gas fired fore hearth. The fiber is formed by centrifugation through drilled circular baskets, where after, binding products and elements specific to the usage are added. No CFC`s or HCFC`s are produced in the production process. The fibers are gathered in a mat form in a collection chamber and then conveyed to an oven where it is cured under controlled conditions to the required thickness and density. Once complete the product is then packaged in roll or batt form.

Use of glass wool insulation

- Glass wool products are non-combustible and positioned for operating temperatures up to 300°C.
- It is made of 80% recyclable materials
- Is poses no health hazards
- It is lightweight and easy to install
- Glass wool will not promote mould growth or vermin infestation
- It is non corrosive to metal

Applications of Glass Wool insulation

Glass wool insulation products are manufactured to be applied in multiple areas of buildings. Glass wool is most commonly known for insulation in ceilings of residential buildings, but we also offer products for the following applications:

- Cavity wall and dry wall insulation
- HVAC and Air-conditioning system insulations
- Pipe insulation
- Over purl in roof insulation in commercial buildings
- Suspended ceilings
- Industrial roof insulation
- Higher temperature insulations
- High performance sound proofing

Figure 3.10. Roll of Glass Wool

QUESTIONS FOR REVISION

PART- A

1. Define glass?
2. What is meant by Annealing glass?
3. What is chemical difference between soft and hard glass?
4. What is glass transition temperature?
5. What is optical glass?

PART- B

1. Write a note on windshield glass
2. Write a note on photo chromatic glass.
3. When windshield glass of a bus/car broken due to accident, it shatters into harmless fragments. How?
4. Today windshield in cars is a safety device just like seatbelts & airbags. How?
5. What are cullets? Why they are added during manufacturing of ordinary glass?

PART- C

1. How is ordinary glass manufactured?
2. What is annealing of glass? Whyis it necessary?
3. Write any three varieties of glass?
4. Describe tank process of melting of mixture for glass?
5. What do you mean by glass wool? How it is prepared, write its uses and application?

LUBRICANTS

INTRODUCTION:

Lubricants:

Any substance introduced between the two moving and sliding surfaces with a view to reduce frictional resistance to know as lubricant.

A lubricant is a substance, usually organic, introduced to reduce friction between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move. It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the surfaces. The property of reducing friction is known as lubricity.

In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats in use in frying pans, in baking to prevent food sticking), bio applications on humans (e.g. lubricants for artificial joints), ultrasound examination, medical examination. It is mainly used to reduce friction and to contribute to a better and efficient functioning of a mechanism.

Properties :

A good lubricant generally possesses the following characteristics:

- A high boiling point and low freezing point (in order to stay liquid within a wide range of temperature)
- A high viscosity index
- Thermal stability
- Hydraulic stability
- Demulsibility
- Corrosion prevention
- A high resistance to oxidation

There are two types of Properties of Lubricants:

a. Formulation and b. Additives.

a. Formulation

Typically lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as Hydrogenated polyolefin's , esters, silicones, fluorocarbons and many others are sometimes used as base oils Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc Non-liquid lubricants include powders (dry graphite, PTFE, molybdenum disulphide, tungsten disulphide, etc.), PTFE(**Polytetrafluoroethylene**) tape used in plumbing, air cushion and others. Dry lubricants such as graphite, molybdenum disulphide and tungsten disulphide also offer lubrication at temperatures (up to 350 °C) higher than liquid and oil-based lubricants are able to operate. Limited interest has been shown in low friction properties of compacted oxide glaze layers formed at several hundred degrees Celsius in metallic sliding systems, however, practical use is still many years away due to their physically unstable nature.

b. Additives

A large number of additives are used to impart performance characteristics to the lubricants. Modern automotive lubricants contain as many as ten additives, comprising up to 20% of the lubricant, the main families of additives are:

- Pour point depressants are compounds that prevent crystallization of waxes. Long chain alkyl benzenes adhere to small crystallites of wax, preventing crystal growth.
- Anti-foaming agents are typically silicone compounds which increase surface tension in order to discourage foam formation.
- Viscosity index improvers (VIIs) are compounds that allow lubricants to remain viscous at higher temperatures. Typical VIIs are polyacrylates and butadiene.
- Antioxidants suppress the rate of oxidative degradation of the hydrocarbon molecules within the lubricant. At low temperatures, free radical inhibitors such as hindered phenols are used, e.g. butylated hydroxytoluene. At temperatures >90 °C, where the metals catalyze the oxidation process, dithiophosphates are more useful. In the latter application the additives are called metal deactivators.
- Detergents ensure the cleanliness of engine components by preventing the formation of deposits on contact surfaces at high temperatures.
- Corrosion inhibitors (rust inhibitors) are usually alkaline materials, such as alkylsulfonate salts, that absorb acids that would corrode metal parts.
- Anti-wear additives form protective 'tribofilms' on metal parts, suppressing wear. They come in two classes depending on the strength with which they bind to the surface. Popular examples include phosphate esters and zinc dithiophosphates.
- Extreme pressure (anti-scuffing) additives form protective films on sliding metal parts. These agents are often sulfur compounds, such as dithiophosphates.
- Friction modifiers reduce friction and wear, particularly in the boundary lubrication regime where surfaces come into direct contact.

Types of lubricants depending on composition

a. **Paraffinic**

Paraffin wax is a soft colorless solid derived from petroleum, coal or shale oil that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms

b. **Naphthalene**

Naphthenic base oil possesses low pour point, high solvency, low wax, and low aromatic content. Naphthenic base oil is employed in various end-use applications such as printing inks, adhesive & sealants, gear oils, oil extender polymers, process oil, metal working, and battery separators

Semi-solid Lubricant or Greases:

- **Semi-fluid lubricants (greases)**

Semi-fluid lubricants (greases) are produced by emulsifying oils or fats with metallic soap and water at 400-600°F (204-316°C). Typical mineral oil base grease is Vaseline Grease properties are determined by a type of oil (mineral, synthetic, vegetable, animal fat), type of soap (lithium, sodium, calcium, etc. salts of long-chained fatty acids) and additives (extra pressure, corrosion protection, anti-oxidation, etc.).

Semi-fluid lubricants (greases) are used in variety applications where fluid oil is not applicable and where thick lubrication film is required: lubrication of roller bearings in railway car wheels, rolling mill bearings, steam turbines, spindles, jet engine bearings and other various machinery bearings.

- **Solid lubricants**

Solid lubricants possess lamellar structure preventing direct contact between the sliding surfaces even at high loads. Graphite and molybdenum disulfide particles are common Solid lubricants. Boron nitride, tungsten disulfide and Polytetrafluoroethylene (PTFE) are other solid lubricants. Solid lubricants are mainly used as Additives to oils and greases. Solid lubricants are also used in form of dry powder or as constituents of coatings.

Lubrication Mechanisms:

Three mechanisms have been proposed to explain the action of lubricants they are

Thin film (or) Boundary Lubrication:

In this type of lubrication a thin film of lubricant is absorbed on the surface and held by vandarwaals forces. When the lubricant is not viscous enough to generate a film of sufficient thickness for the separation of surfaces under heavy loads, friction is reduced by thin film lubrication. Thin film lubrication is applied when the speed is very low, the loading heavy, the oil has low viscosity.

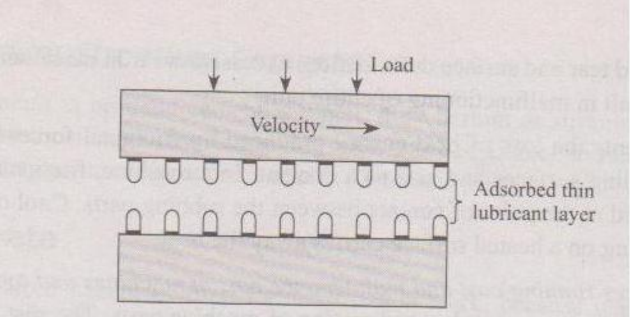


Figure 3.11.. Boundary film lubrication

In this type of lubrication a thin film of lubricant is absorbed on the surface and held by vandarwaals forces. When the lubricant is not viscous enough to generate a film of sufficient thickness for the separation of surfaces under heavy loads, friction is reduced by thin film lubrication. Thin film lubrication is applied when the speed is very low, the loading heavy, the oil has low viscosity.

Some peaks may have higher thickness than the film of lubricant which results in wearing and tearing. Hence the chemical or physical forces on some metal surfaces would avoid the direct contact of metals and absorb a thin layer of lubricating oil. The co-efficient of friction is reduced due to oiling.

Fluid Film (or) Hydrodynamic Lubrication:

This type of lubrication is also known as thick film lubrication. It is carried out with the help of liquid lubricants. In fluid film lubrication the two sliding surfaces are separated by a thick film of about 1000A° which is applied to prevent direct surface to surface contact. Wearing and tearing of metals is minimized.

In a ball bearing the irregularities of the shaft and bearing surfaces are covered by a thick film of lubricants and don't not allow. The content of metallic surfaces with each other as shown in the figure. The resistance to moment is only due to resistance of the lubricant. Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, scientific equipments.

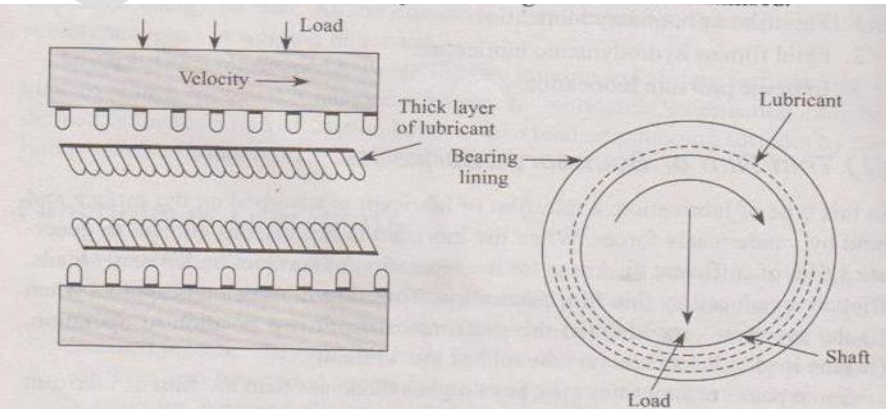


Figure 3.12. Fluid film lubrication

Extreme Pressure Lubrication:

It involves chemical action on the part of lubricant. Under heavy load and high speed conditions, high local temperature is generated. The liquid film may not stick, it may decompose and vaporizes. Hence special additives called extreme pressure additive are blended with lubricating oil to form more durable film to with stand high temperature and pressure.

Chlorinated esters, sulpharised oils and tricrysyl phosphates are used as extreme pressure additives. These additives combined with the metallic surfaces with high temperature to form metallic chlorides.

Properties of Lubricants:

Cloud and Pour Points

Cloud Point: The temperature at which the impurities being to separate from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point.

Pour Point: The temperature at which the oil ceases to flow and pour is called pour point.

Flash point: The flash point of a volatile material is the lowest temperature at which vapors of the material will ignite, given an ignition source.

Fire point: The fire point of a fuel is the lowest temperature at which the vapor of that fuel will continue to burn for at least 5 seconds after ignition by an open flame.

Viscosity:

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of lubricating oil. The lower viscosity greater the flow ability. If temperature increases viscosity of the lubricating oil decreases and pressure increases viscosity of lubricating oil increases.

Viscosity Index:

The rate at which the viscosity of oil changes with temperature is measured by an empirical number known as the viscosity index. A relatively small change in viscosity with temperature is indicated by high viscosity index. Where as a low viscosity index shows a relatively large change in viscosity with temperature.

Viscosity Index or Effect of temperature on Viscosity

Viscosity of lubrication of fluid is inversely proportional to temperature

This is due to decrease in inter molecular attraction a good lubricating oil should show minimum variation in viscosity with temperature change, so that it can be used continuously under varying conditions of temperature. Lubricating oil with low viscosity index is considered as of poor quality.

QUESTIONS FOR REVSION

PART – A

1. What is a lubricant?
2. How are lubricants classified?
3. Mention the uses of graphite.
4. Mention the uses of molybdenum sulphide.

PART – B

1. How are lubricants classified? Give examples.
2. Write a note on semi-solid lubricant.

PART – C

1. List the essential characteristics of lubricants.
2. Write a note on solid lubricants.
3. Write a note on liquid lubricants.

TEST YOUR UNDERSTANDING

a. What types of lubricants are used for transformers?

b. Why does graphite act as a good lubricant on the surface of the motion?

UNIT – II

(MODULE – 4)

ORGANIC REACTION MECHANISM AND INTRODUCTION OF DRUGS

TOPICS:

- Organic reaction mechanism: Substitution; SN1, SN2, Elecrophilic aromatic substitution in benzene, free radical halogenations of alkanes, Elimination; elimination in alkyl halides, dehydration of alcohols,
- Addition: electrophilic and free radical addition in alkenes, nucleophilic addition in aldehyde and ketones,
- Rearrangement; Carbocation and free radical rearrangements
- Drugs : Introduction, Synthesis, properties and uses of Aspirin, Paracetamol

UNIT – II

(MODULE – 4)

ORGANIC REACTION MECHANISM AND INTRODUCTION OF DRUGS

INTRODUCTION

Organic Reaction:

Organic reactions are chemical reactions involving organic compounds. The basic organic chemistry reaction types are addition reactions, elimination reactions, substitution reactions, pericyclic reactions, rearrangement reactions, photochemical reactions and redox reactions. In organic synthesis, organic reactions are used in the construction of new organic molecules. The production of many man-made chemicals such as drugs, plastics, food additives, fabrics depend on organic reactions.

Types of Organic Reactions:

There are mainly five types of organic reactions:

1. Substitution reaction
2. Elimination reaction
3. Addition reaction
4. Radical reactions
5. Oxidation-Reduction Reactions.

Substitution Reactions

In a substitution reaction, one atom or a group of atoms is substituted by another atom or a group of atoms to form a new substance.

Let us take an example of a C-Cl bond, in which the carbon atom has a partial positive charge due to the presence of highly electronegative chlorine atom. In a nucleophilic substitution reaction, the nucleophile must have a pair of electrons and also should have a high affinity for the electropositive species as compared to the substituent which was originally present.

Elimination reaction

There are some reactions which involve the elimination or removal of the adjacent atoms. After these multiple bonds are formed and there is a release of small molecules as products.

One of the examples of elimination reaction is the conversion of ethyl chloride to ethylene.

$CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + HCl$

In the above reaction, the eliminated molecule is HCl, which is formed by the combination of H^+ from the carbon atom which is on the left side and Cl– from the carbon atom which is on the right side.

On the basis of mechanism elimination reaction may be α - elimination and β- elimination.

Addition reactions

Addition reaction is nothing but just the opposite of elimination reaction. In an addition reaction, the components A and B are added to the carbon-carbon multiple bonds and this is called addition reaction. In the reaction given below when HCl is added to ethylene, it will give us ethylene chloride.

$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$

Radical reactions

Many of the organic reactions involve radicals. Addition of a halogen to a saturated hydrocarbon involves free radical mechanism. There are three stages involved in a radical reaction i.e. initiation, propagation, and termination. Initially when the weak bond is broken initiation of the reaction takes place with the formation of free radicals. After that when the halogen is added to the hydrocarbon a radical is produced and finally, it gives alkyl halide.

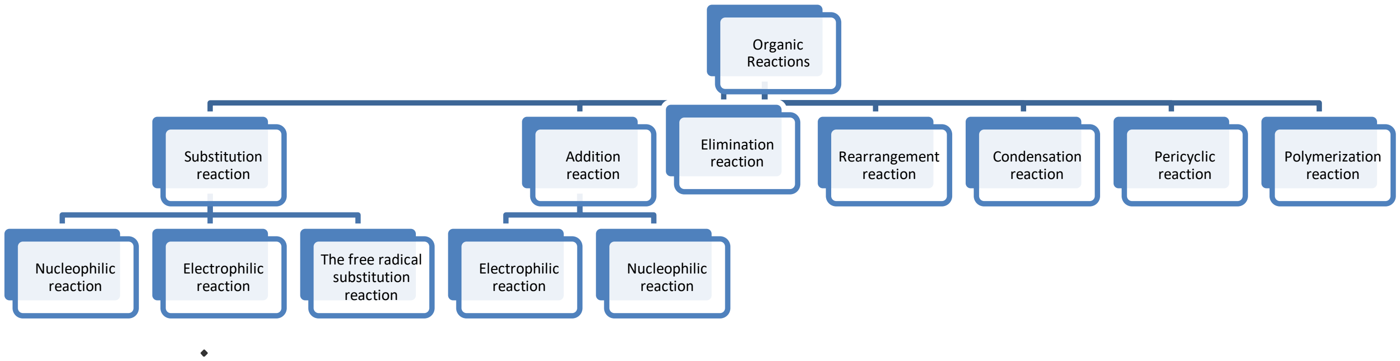


Figure 4.1. Types of Organic Reactions

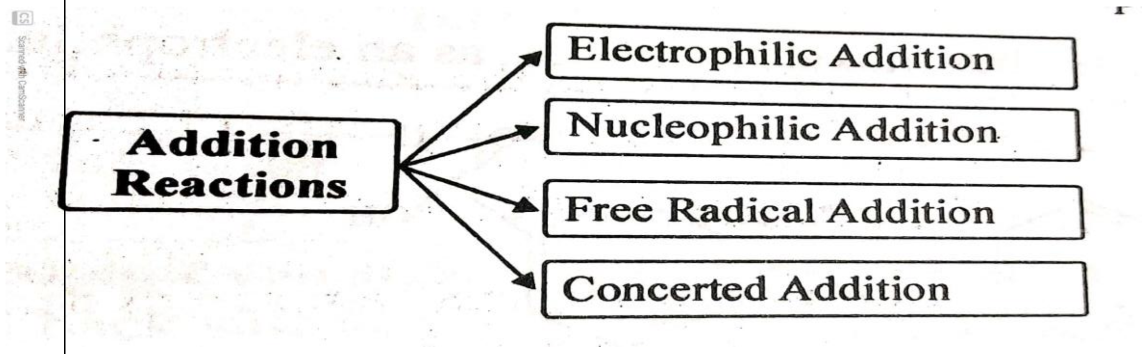


Figure 4. 1 (a) Types of Addition Reaction

SUBSTITUTION REACTIONS:

These reactions involves to displacement of an atom or a group by another atom or group

$$RCH_2CH_2X \quad + \quad y^- \xrightarrow{\text{Substitution reaction}} RCH_2CH_2Y \quad + \quad X^-$$

Substrate attacking reagent product leaving group

Substitution reaction takes place at:

a. sp^3 hybridized carbon(alkane,heloalkane, alcohol)
b. sp^2 hybridized carbon (benzene)

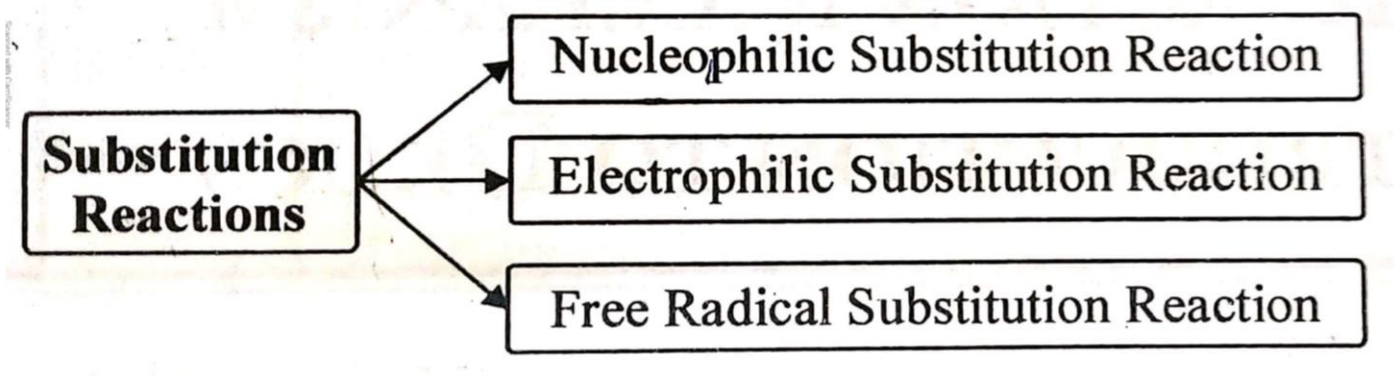


Figure 4.2. Types of Substitution Reaction

Nucleophilic substitution

Nucleophilic substitution is a fundamental class of reactions in which an electron rich nucleophile selectively bonds with or attacks the positive or partially positive charge of an atom or a group of atoms to replace a so-called leaving group.

Nucleophilic substitution reactions are commonplace in organic chemistry, and they can be broadly categorized as taking place at a saturated aliphatic carbon or at (less often) an aromatic or other unsaturated carbon centre.

There are two main mechanisms at work, both of them competing with each other. The two main mechanisms are the S_N1 reaction and the S_N2 reaction. *S* stands for chemical substitution, *N* stands for nucleophilic, and the number represents the kinetic order of the react

S_N2 reaction:

S_N2 reaction, the addition of the nucleophile and the elimination of leaving group take place simultaneously (i.e. concerted reaction). S_N2 occurs where the central carbon atom is easily accessible to the nucleophile ion.

In S_N2 reactions, there are a few conditions that affect the rate of the reaction. First of all, the 2 in S_N2 implies that there are two concentrations of substances that affect the rate of reaction: substrate and nucleophile. The rate equation for this reaction would be Rate=k[Sub][Nuc]. For a S_N2 reaction, an aprotic solvent is best, such as acetone, DMF, or DMSO. Aprotic solvents do not add protons (H+) ions into solution; if protons were present in S_N2 reactions,

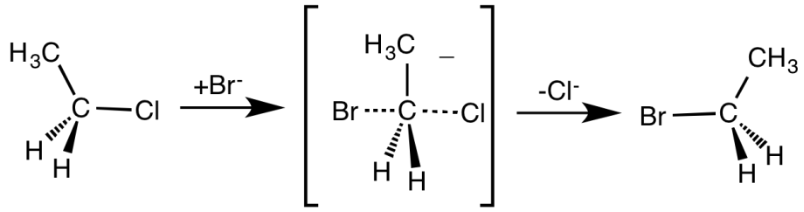


Figure 4.3. S_N2 Mechanism

Halogenation is a good example of a substitution reaction. When chlorine gas (Cl-Cl) is irradiated, some of the molecules are divided into two chlorine radicals (Cl.) whose free electrons are highly nucleophilic. One of them break into a weak C-H covalent bond and takes the liberated proton to form the electrically neutral H-Cl. The other radical changes to covalent bond with the CH3· to form CH3Cl (methyl chloride).

Rate of S_N2 reaction

The rate of such reaction depends on the concentration of alkaline halide (substrate) as well as the base. (Nucleophile)

Rate α $[RX]\ [OH^-]$

Kinetic studies of this reaction reveals that rate of such reaction depends upon alkyl halide as well as the hydroxide ion.

Rate ∝ $[CH_3Br][OH^-]$

If the concentration any of its double then rate of reaction is also doubled.

Energy Profile of S_N2 reaction

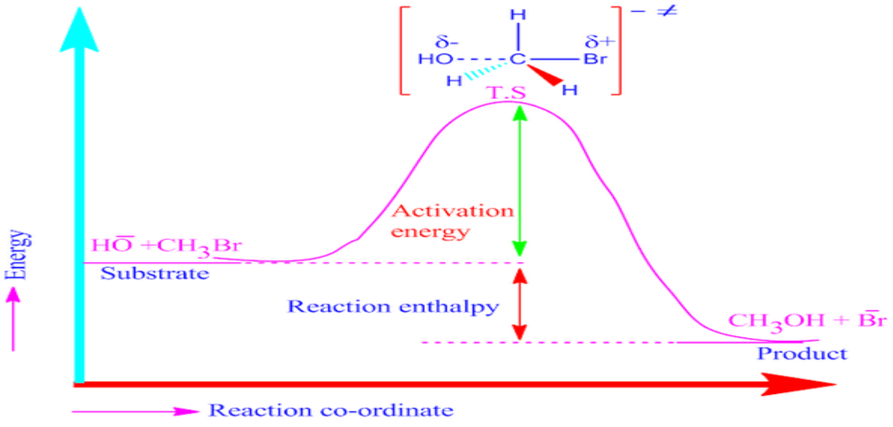


Figure 4.4. Energy Profile of S_N2 reaction

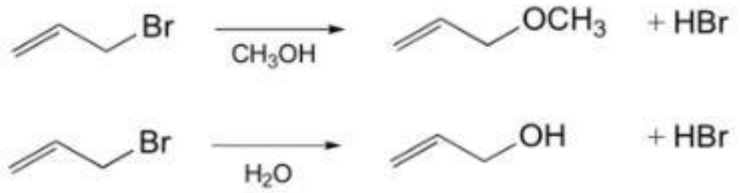
S_N 1 reaction:

S_N1 reaction mechanism follows a step by step process wherein first, the carbocation is formed from the removal of the leaving group. Then the carbocation is attacked by the nucleophile. Finally, the deprotonation of the protonated nucleophile takes place to give the required product. The rate determining step of this reaction depends purely on the electrophilicity of the leaving group and is not impacted at all by the nucleophile.

What is an S_N1 Reaction?

The S_N1 reaction is a nucleophilic substitution reaction where the rate determining step is unimolecular. It is a type of organic substitution reaction. S_N1 stands for substitution nucleophilic unimolecular. Thus, the rate equation (which states that the S_N1 reaction is dependent on the electrophile but not on the nucleophile) holds in situations where the amount of the nucleophile is far greater than the amount of the carbocation intermediate.

This reaction involves the formation of a carbocation intermediate. It is generally seen in the reactions of tertiary or secondary alkyl halides with secondary or tertiary alcohols under strongly acidic or strongly basic conditions. The S_N1 reaction is often referred to as the dissociative mechanism in inorganic chemistry. Given below are some examples of an S_N1 type of nucleophilic substitution reaction.



Effect of Solvent

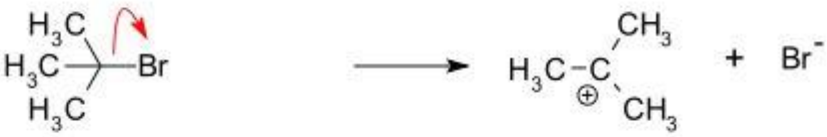
- A solvent that can facilitate the formation of the carbocation intermediate will speed up the rate determining step of the S_N1 reaction.
- The preferred solvents for this type of reaction are both polar and protic.
- The polar nature of the solvent helps to stabilize ionic intermediates whereas the protic nature of the solvent helps solvate the leaving group.
- Examples of solvents used in S_N1 reactions include water and alcohols. These solvents also act as nucleophiles.

S_N1 Reaction Mechanism

Taking the hydrolysis of tertiary butyl bromide as an example, the mechanism of the S_N1 reaction can be understood via the following steps.

Step 1

- The carbon-bromine bond is a polar covalent bond. The cleavage of this bond allows the removal of the leaving group (bromide ion).
- When the bromide ion leaves the tertiary butyl bromide, a carbocation intermediate is formed.
- As mentioned earlier, this is the rate determining step of the S_N1 mechanism.
- It is important to note that the breaking of the carbon-bromine bond is endothermic.



Tert-butyl bromide

3°carbocatine

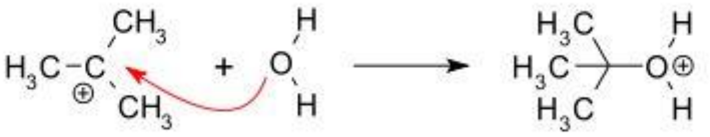
The rate of above reaction depends only on the concentration of Tert-butyl bromide

Rate = k[$(CH_3)_3$ C Br)

It is first order reaction mechanism

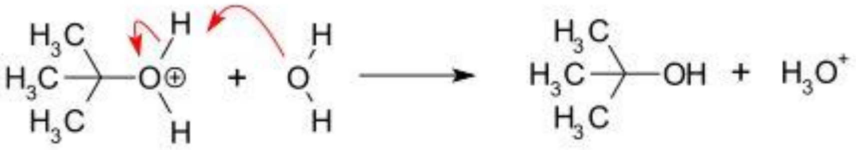
Step 2

- In the second step of the SN1 reaction mechanism, the carbocation is attacked by the nucleophile.
- Since water is used as a solvent, an oxonium ion intermediate is formed.
- Since the solvent is of a neutral nature, a third step where deprotonation occurs is necessary.



Step 3

- The positive charge on the carbocation was shifted to the oxygen in the previous step.
- The water solvent now acts as a base and deprotonates the oxonium ion to yield the required alcohol along with a hydronium ion as the product.
- Step 2 and Step 3 of this reaction are fast.



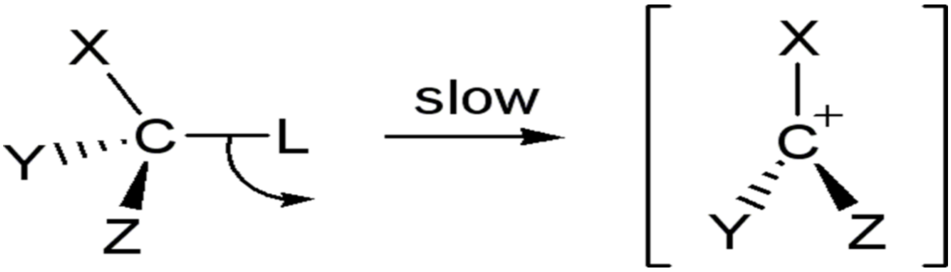
SN1 reactions

SN1 reactions are unimolecular: the rate of this reaction depends only on the concentration of one reactant.

SN1 reactions happen in two steps:

1. The leaving group leaves, and the substrate forms a carbocation intermediate.
2. The nucleophile attacks the carbocation, forming the product.

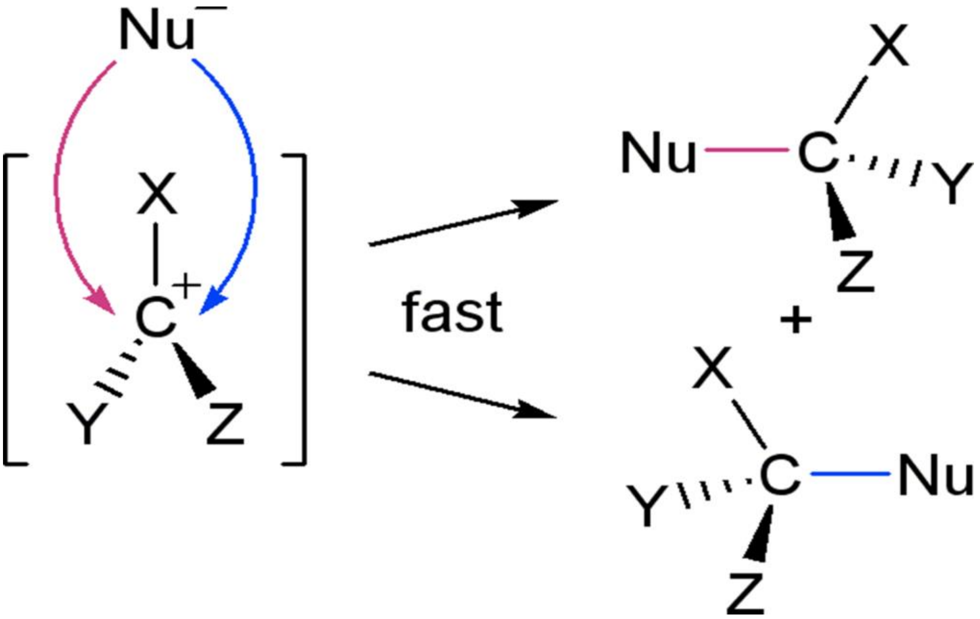
The Slow Step:



First step of the SN1 reaction: The leaving group leaves, and the substrate carbon now only has three substituents, taking on a positive charge. This is called a carbocation. ●Carbocations are most stable when there are more atoms to distribute this positive charge. ●Carbocation stability: 3º > 2º >> 1º ●

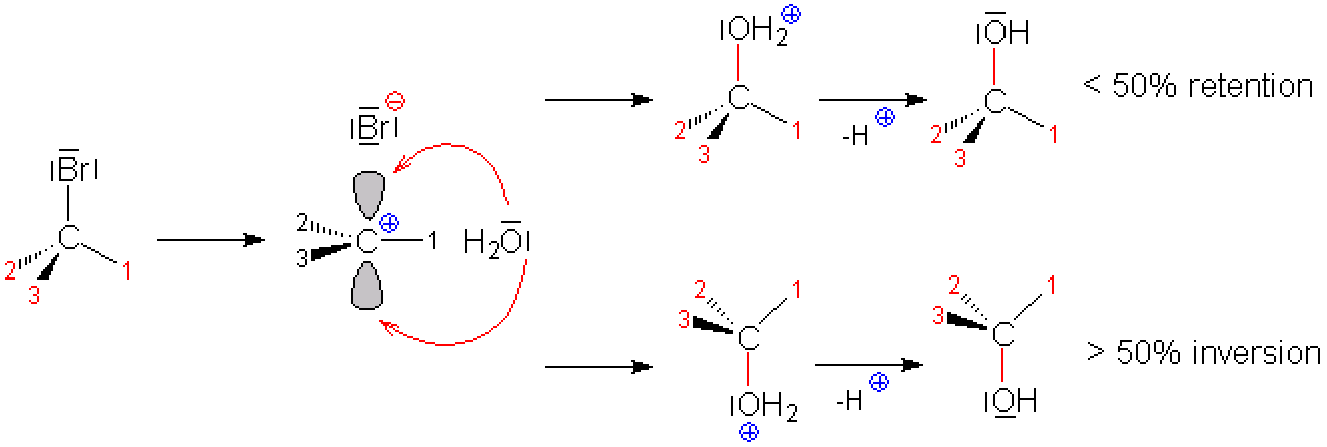
The Fast Step:

Second step of the SN1 reaction: The nucleophile attacks the carbocation intermediate, bringing its electron pair to resolve the positive charge. ●The substrate loses any stereo specificity during the carbocation into



Stereochemistry of SN1 Reactions

Due to the carbocation's trigonal planar shape, its two enantiotopic sides are susceptible to attack by the nucleophile with the same probability. However, practically speaking, only an incomplete racemization occurs frequently enough. Then, a small excess of the inversion product is detected



Geometrical Shape carbokataine

Energy profile of S_N1 reactions:

A potential energy diagram for an S_N1 reaction shows that the carbocation intermediate can be visualized as a kind of "mountain valley" in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.

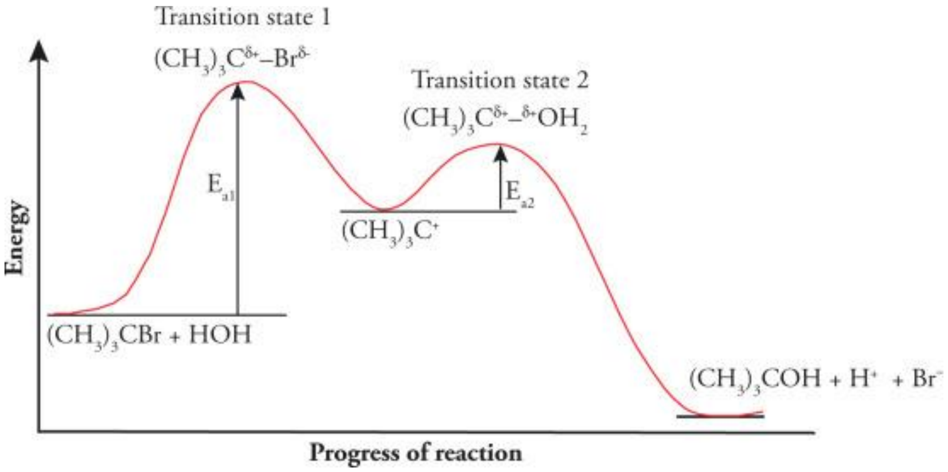


Figure 4. 5 Energy Profile for S_N1 reactions

Difference between SN1 and SN2

The major difference involved between these two types of reactions is to study the different properties of the departure group that helps us in finding out the pathway of the group. Understanding the major differences between these two will give us the key differences between one and the other. For a full list of differences between the two, check out the tabular column below:

Difference between SN1 and SN2	
SN1	**SN2**
The rate of reaction is unimolecular.	The rate of reaction is bimolecular
It is a two step mechanism	It is only a one step mechanism
Carbocation is formed as an intermediate part of the reaction.	No carbocation is formed during the reaction.
There is no partial bond formed with the carbon during this reaction.	Carbon forms a partial bond with the nucleophile and the leaving group.
There are many steps in this reaction which start with the removal of the group while attacking the nucleophile.	The process takes place in only one cycle, with a single intermediate stage.

Uses of Nucleophilic substitution reaction:

Nucleophilic substitution reactions are an important class of reactions that allow the inter conversion of functional groups. For alcohols, the range of substitution reactions possible can be increased by utilizing the tosylates (R-OTs), an alternative method of converting the -OH to a better leaving group.

Electrophilic substitution reactions

Electrophiles are involved in electrophilic substitution reactions, mainly in electrophilic aromatic substitutions reaction.

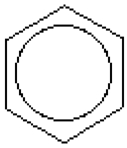
In this example below, the benzene ring's electron resonance arrangement is attacked by an electrophile E+. The resonating bond is destroyed and a carbocation resonating structure form. Finally, a proton is removed out and a new aromatic compound is made.

Examples of Electrophiles are hydronium ion (H_3O^+, from Bronsted acids), boron trifluoride (BF_3), aluminum chloride ($AlCl_3$), and the halogen molecules fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

Formation of Electrophiles in Electrophilic substitution reaction in Benzene:

Electrophilic Substitution mechanisms:

- Benzene, C_6H_6 is a planar molecule containing a ring of six carbon atoms each with a hydrogen atom attached.
- There are delocalized electrons above and below the plane of the ring
- The presence of the delocalized electrons makes benzene particularly stable.
- Benzene resists addition reactions because that would involve breaking the demonization and losing that stability.
- Benzene is represented by this symbol, where the circle represents the delocalized electrons and each corner of the hexagon has a carbon atom with a hydrogen attached**.**



Symbol of Benzene

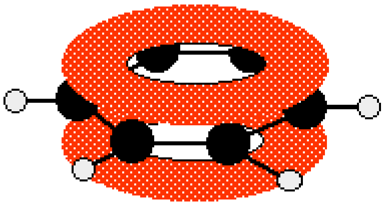
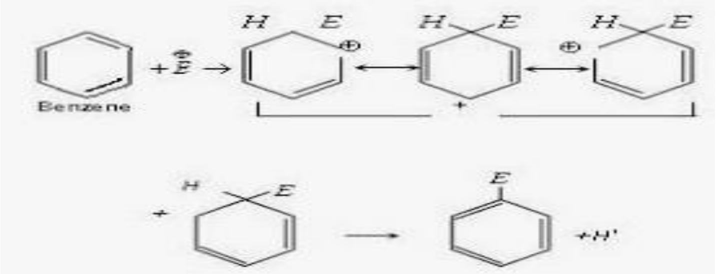


Figure 4.6. Delocalized electrons of benzene



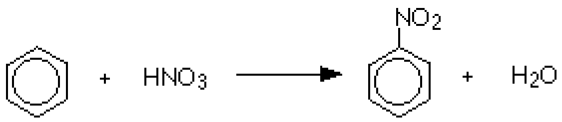
resonance structure of benzene carbocation

The nitration of benzene:

Benzene is treated with a mixture of concentrated nitric and concentrated sulphuric acid at a temperature not exceeding 50˚C. As temperature increases there is a greater chance of getting more than one nitro group , $^+NO_2$, (electrophile) substituted on to the ring.

Nitrobenzene is formed.

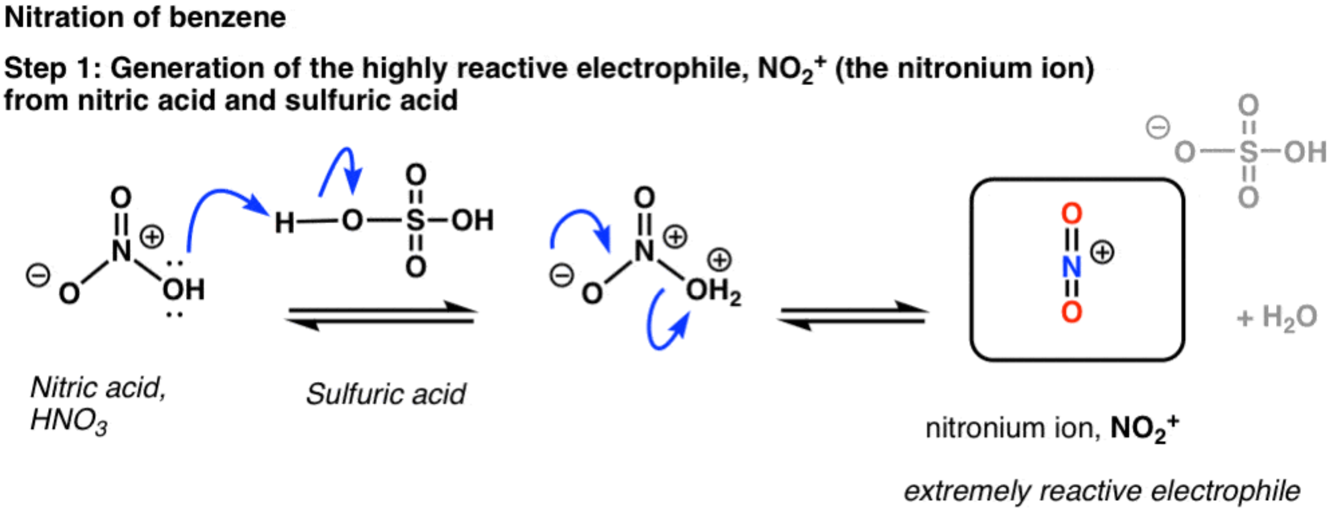
$$HNO_3 + 2H_2SO_4 \leftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$



Laboratory preparation of nitro benzene:

Take 10ml of benzene in round bottom flask and add 5 to 6 ml of concentrated nitric and sulphuric acid (1:2 ratio) in the flask. Fit reflex condenser in the flask and heat the flask for 1 hour in water bath. Keeping the temperature 50˚C. Yellow color of nitro benzene will appear in separate layer in the flask. After cooling the flask or fill this mixtures solution in separating funnel. Yellow colour nitrobenzene will separate out.

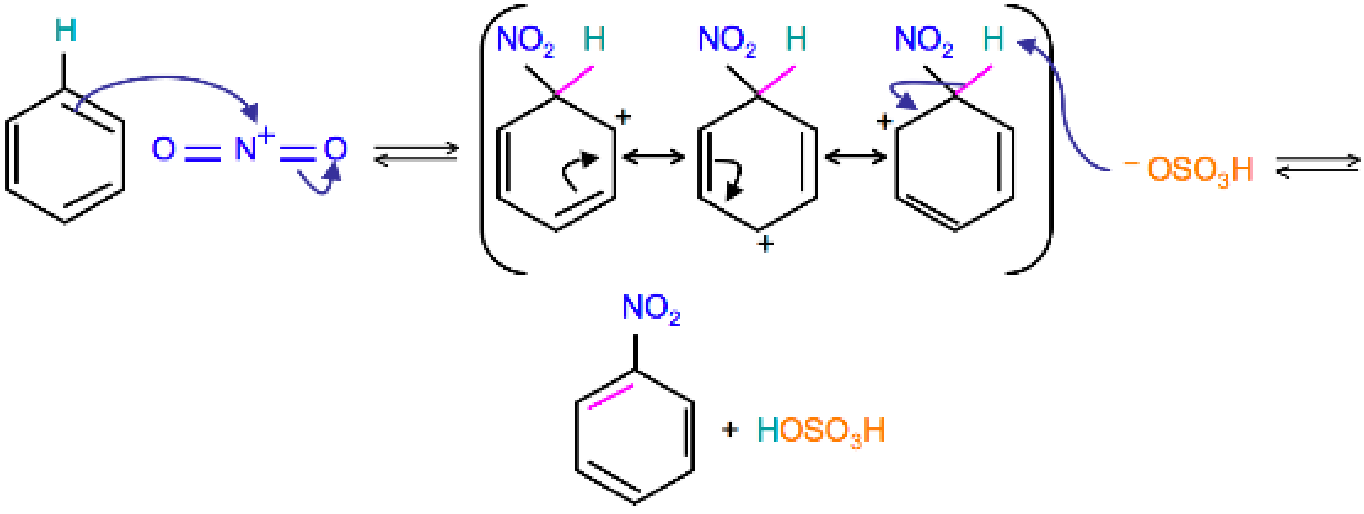
Mechanism of Nitration of Benzene



Nitration of benzene

Step 1: Generation of the highly reactive electrophile, NO_2^+ (the nitronium ion) from nitric acid and sulfuric acid

Step 2 –



Nitro Benzene

The Friedel craft acylation of Benzene

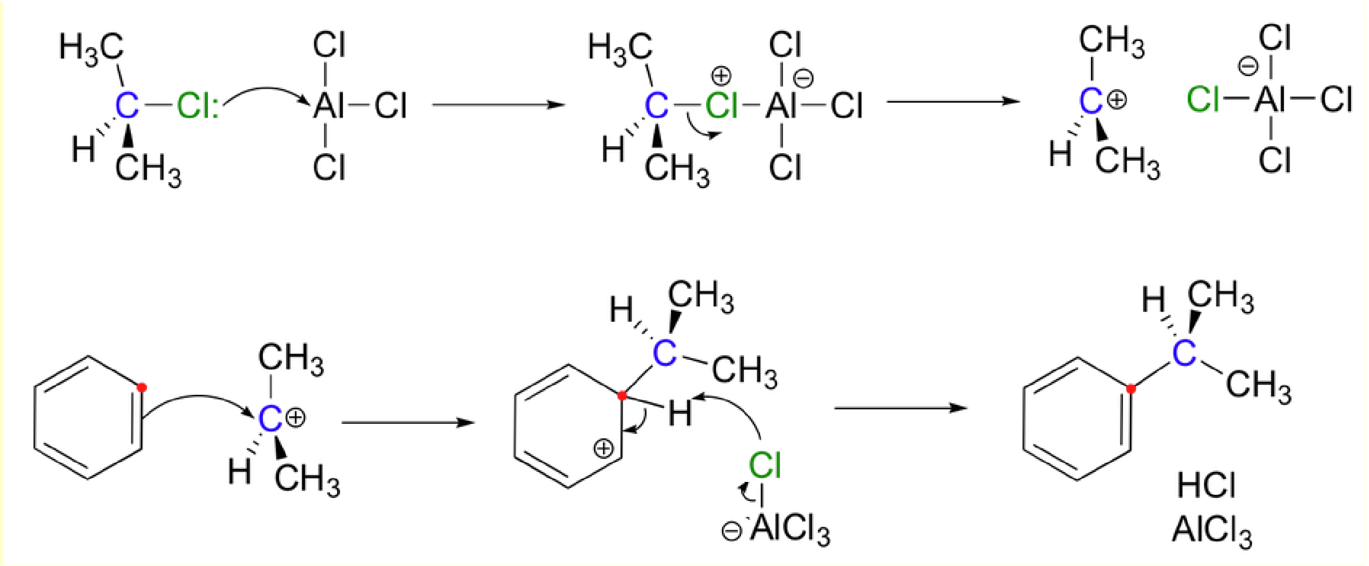
An acyl group is an alkyl group attached to a carbon-oxygen double bond. If "R" represents any alkyl group, then an acyl group has the formula RCO-. Acylation means substituting an acyl group into something - in this case, into a benzene ring.

The most commonly used acyl group is CH_3CO-. This is called the ethanoyl group. In the example which follows we are substituting a CH_3CO- group into the ring, but you could equally well use any other alkyl group instead of the CH_3.

The most reactive substance containing an acyl group is an acyl chloride (also known as an acid chloride). These have the general formula RCOCl.

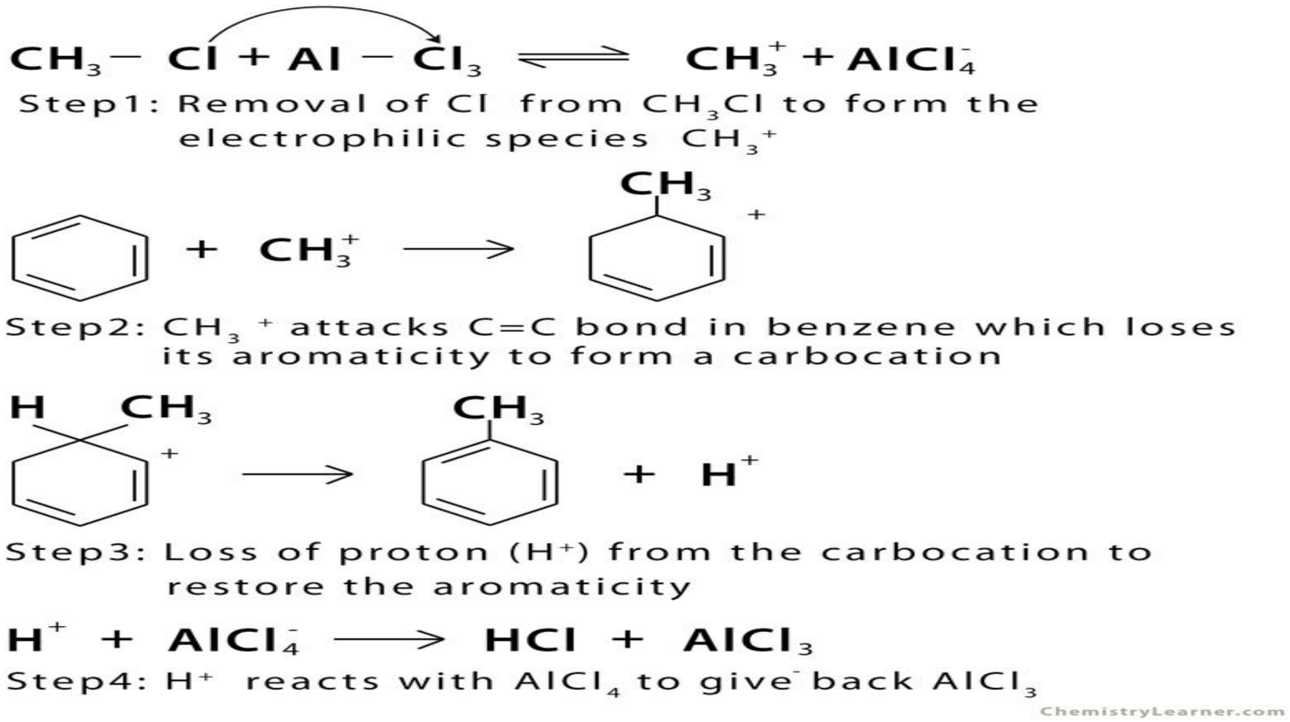
Benzene is treated with a mixture of ethanoyl chloride, CH_3COCl, and aluminium chloride as the catalyst. A ketone called phenylethanone is formed.

$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCL$



Mechanism of Acylation oF benzene

Friedel-Crafts alkylation mechanism



$CH_3-Cl + Al-Cl_3 \rightleftharpoons CH_3^+ + AlCl_4^-$

Step1: Removal of Cl from CH_3Cl to form the electrophilic species CH_3^+

Step2: CH_3^+ attacks C=C bond in benzene which loses its aromaticity to form a carbocation

Step3: Loss of proton (H^+) from the carbocation to restore the aromaticity

$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

Step4: H^+ reacts with $AlCl_4^-$ to give back $AlCl_3$

Elimination reaction

In these reactions, two substituents are thrown out from a molecule in any one or two-step mechanism. The one-step mechanism is called the "E2 reaction", and the two-step mechanism is called the "E1 reaction". The numbers do not have to do anything with the number of steps in the mechanism, however bimolecular and unimolecular the kinetics of the reaction separately. In cases where the molecule is able to form an anion but has a poor leaving group, the third kind of reaction, E1CB, occurs. Eventually, the pyrolysis of xanthate and acetate esters proceeds through an "internal" removal mechanism, known as the Ei mechanism.

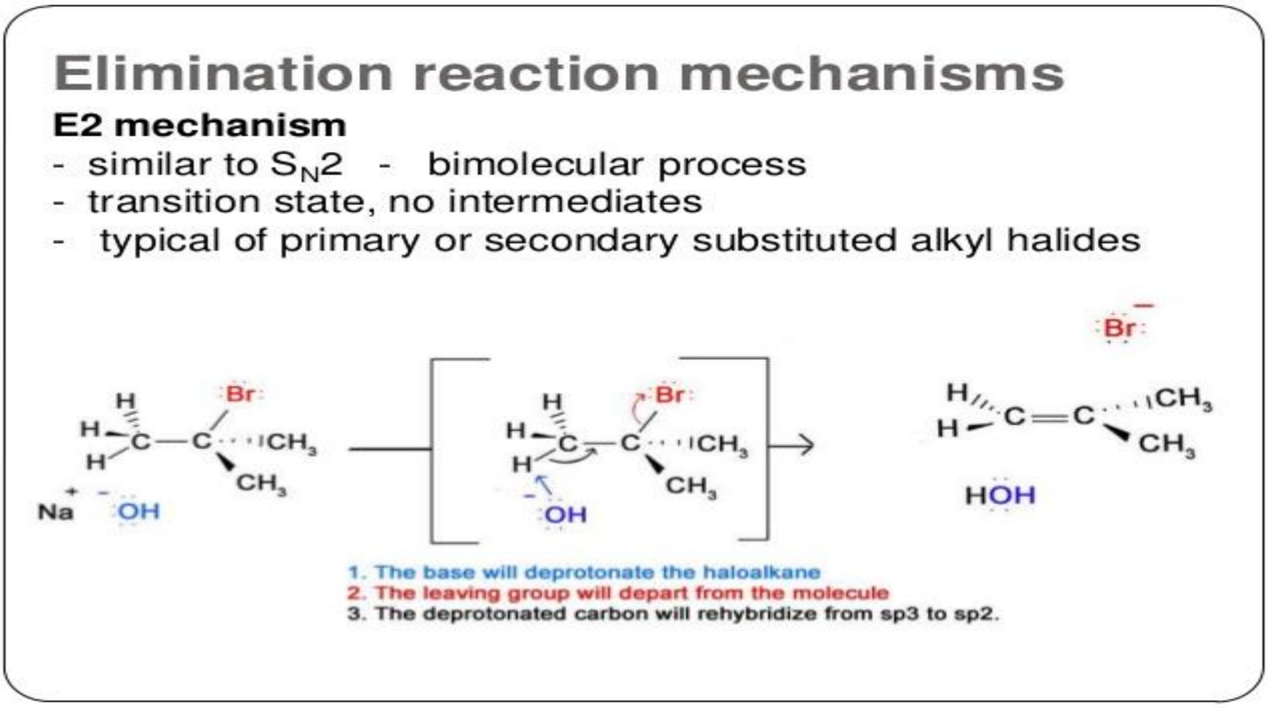
Sir Christopher In gold proposed a model to explain a particular type of chemical reaction during the 1920s: the E2 mechanism. Where E2 stands for bimolecular elimination. The reaction contains a one-step mechanism in which carbon-hydrogen (C-H) and carbon-halogen (C-X) bonds breakdown to procedure a double bond (C=C Pi bond)

E2 is one step elimination process, with a one transition state.

The reaction rate is in second order because it's influenced by both the base (bimolecular) and the alkyl halide.

It is normally undergone by primary substituted alkyl halides but is likely with some secondary alkyl halides and other compounds.

The E2 mechanism results in the expansion of a pi bond, the two leaving groups (often a halogen and hydrogen) need to be in antiperiplanar. An antiperiplanar transition state has a staggered arrangement.



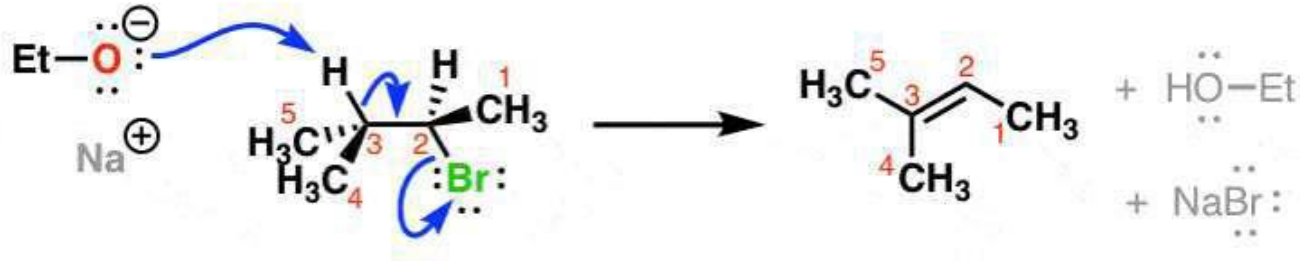
Elimination reaction mechanisms

E2 mechanism

- similar to S_N2 - bimolecular process
- transition state, no intermediates
- typical of primary or secondary substituted alkyl halides

1. The base will deprotonate the haloalkane
2. The leaving group will depart from the molecule
3. The deprotonated carbon will rehybridize from sp3 to sp2.

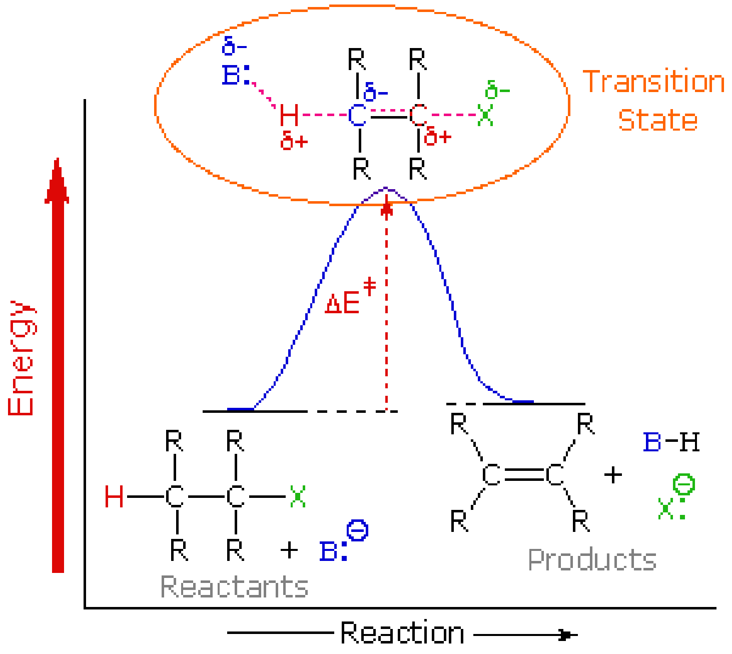
The E_2 Mechanism



One step! Hydrogen removed must be "anti" to the leaving group (dihedral angle 180°)

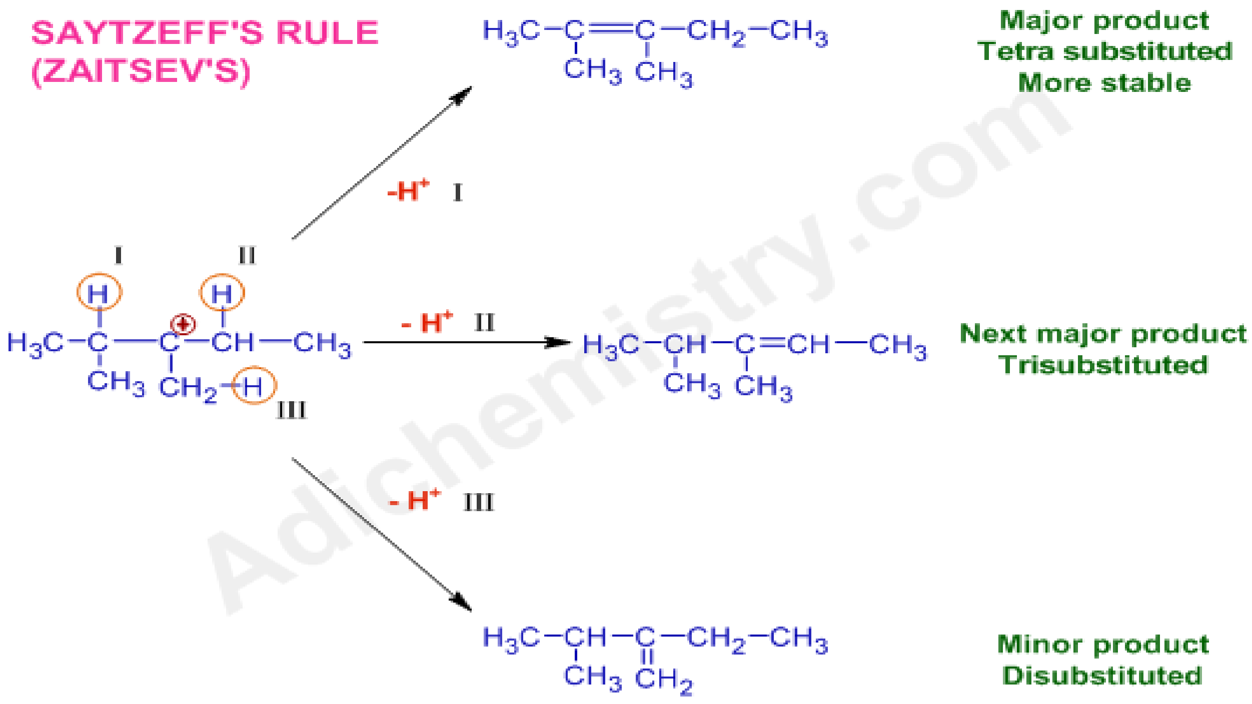
The one-step mechanism is known as the **E2 reaction**, and the two-step mechanism is known as the E2 **reaction**. The numbers refer not to the number of steps in the mechanism, but rather to the **kinetics** of the **reaction**: **E2** is bimolecular (second-order).

Energy Profile of E_2 Reaction:

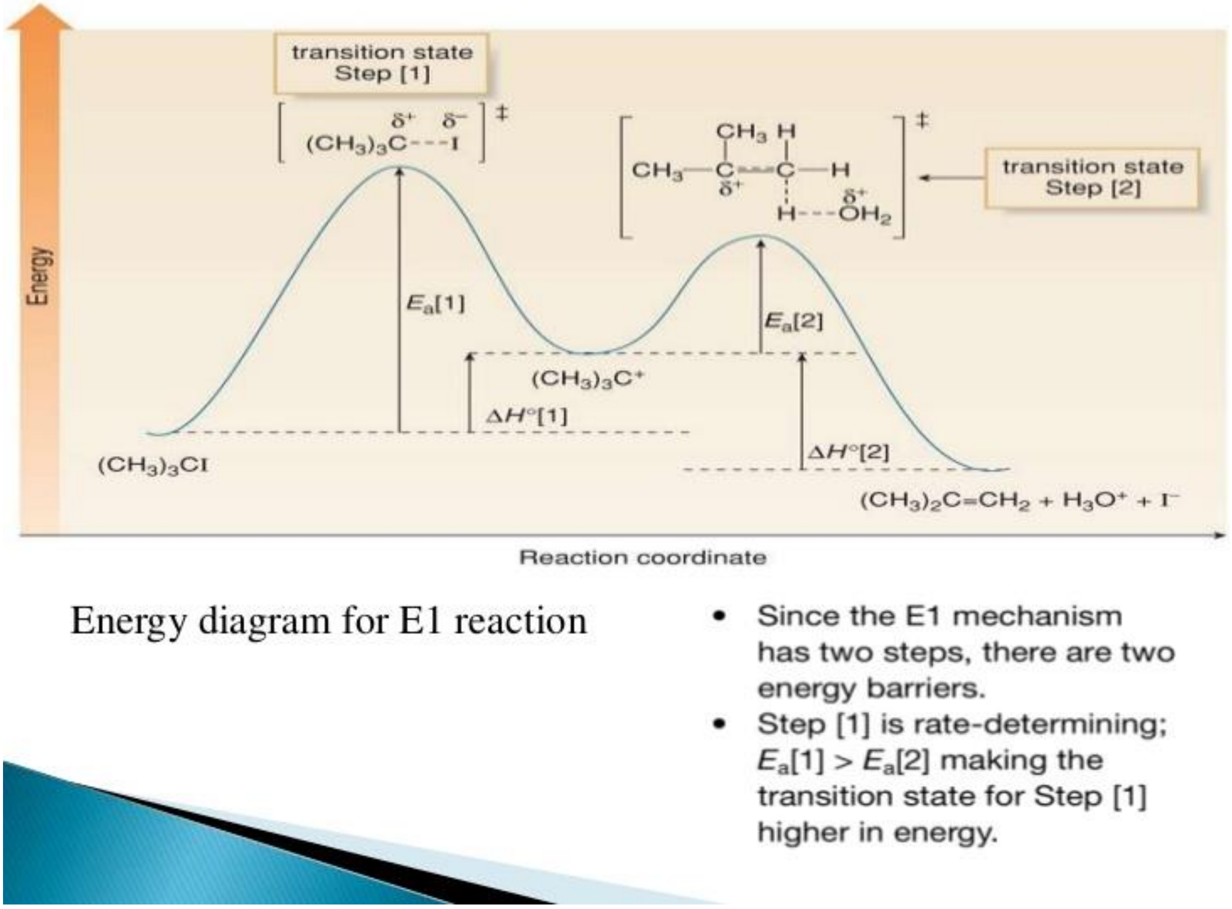


Saytzeff Rule for highly substituted alkane

According to Saytzeff's rule (also known as Zaitsev's rule), during dehydration, more substituted alkene (olefin) is formed as a major product, since greater the substitution of double bond greater is the stability of alkene.



Energy Profile For E_1 Mechanism:



Energy diagram for E1 reaction

- Since the E1 mechanism has two steps, there are two energy barriers.
- Step [1] is rate-determining; $E_a[1] > E_a[2]$ making the transition state for Step [1] higher in energy.

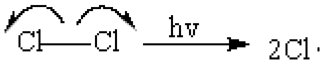
Free Radical halogenation alkanes

Free radical halogenation is a reaction that substitutes a chlorine or a bromine for a hydrogen on an alkanes. This reaction is a photochemical one. That is, it occurs only when performed in the presence of uv light.

Typically, free radical reactions are described in three steps: initiation steps, propagation steps, and termination steps (described below). Note the use of a single headed arrow when describing the movement of a single electron.

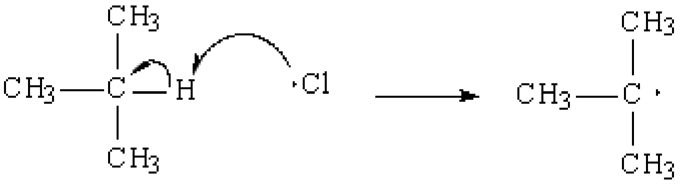
Initiation Step:

The reaction begins with an *initiation step*, which is the separation of the halogen (X_2) into two radicals (atoms with a single unpaired electron) by the addition of uv light. This is called the initiation step because it initiates the reaction.

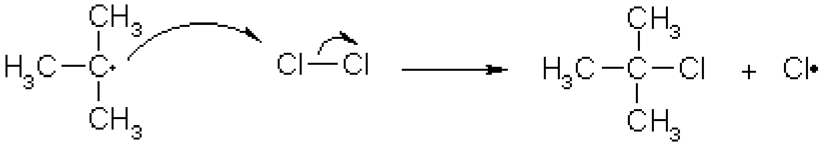


Propagation Steps:

The initiation step, or the formation of the chlorine radicals, is immediately followed by the propogation steps--steps directly involved in the formation of the product. As an example, isobutane (C_4H_{10}) will be used in the chlorination reaction. The first step is the abstraction of the hydrogen atom from the tertiary carbon (a tertiary carbon is a carbon that is attached to *three* other carbon atoms) Note that these are not protons (H+ ions) that are being abstracted, but actual hydrogen atoms since each hydrogen has one electron. This first propagation step forms the tertiary radical.

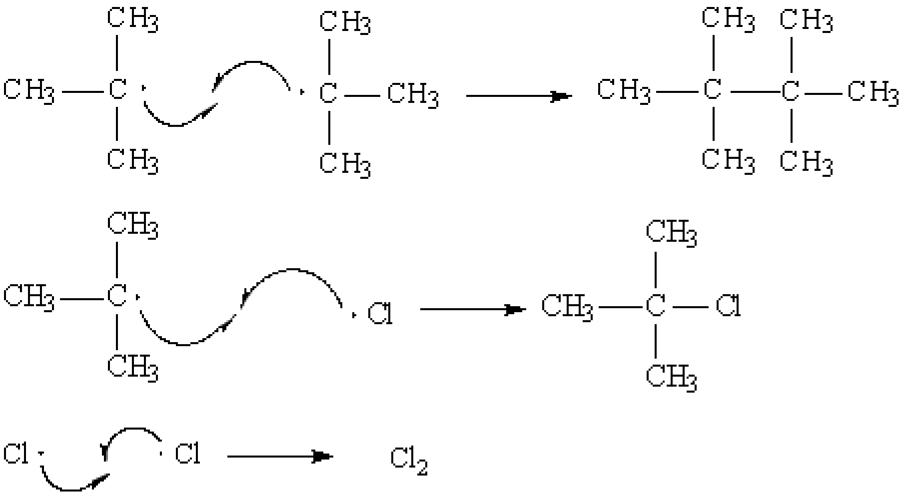


In the last step, the tertiary radical then reacts with another one of the chlorine molecules to form the product. Notice that another chlorine radical is regenerated, so this reaction can, in theory, go on forever as long as there are reagents. This is called a chain reaction.



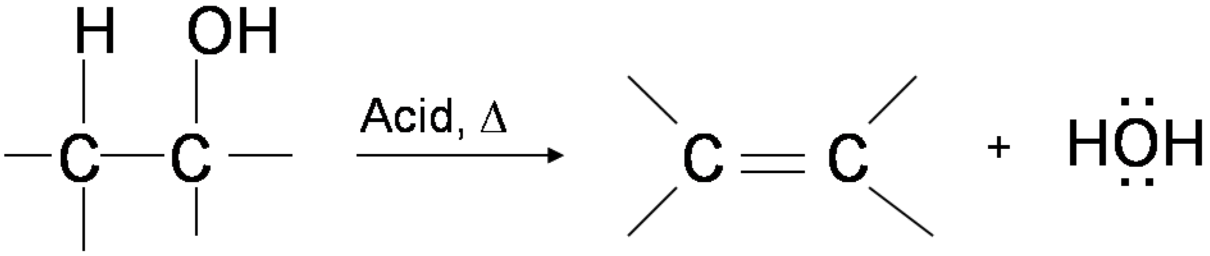
Termination Steps:

Side reactions that can stop the chain reaction are called termination steps. These termination steps involve the destruction of the free-radical intermediates, typically by two of them coming together.



Dehydration of Alcohols

The dehydration reaction of alcohols to generate alkene proceeds by heating the alcohols in the presence of a strong acid, such as sulfuric or phosphoric acid, at high temperatures.



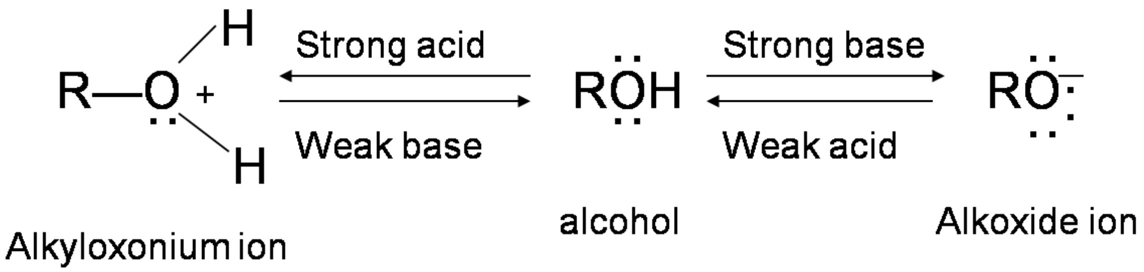
The required range of reaction temperature decreases with increasing substitution of the hydroxy-containing carbon:

- 1° alcohols: 170° - 180°C
- 2° alcohols: 100°– 140 °C
- 3° alcohols: 25°– 80°C

If the reaction is not sufficiently heated, the alcohols do not dehydrate to form alkenes, but react with one another to form ethers (e.g., the Williamson Ether Synthesis).

$$2\ R{-}OH \xrightarrow{\text{Acid, low }\Delta} R{-}O{-}R$$

Alcohols are amphoteric; they can act as both acid and base. The lone pair of electrons on oxygen atom makes the –OH group weakly basic. Oxygen can donate two electrons to an electron-deficient proton. Thus, in the presence of a strong acid, R—OH acts as a base and protonates into the very acidic alkyloxonium ion +OH2 (The pKa value of a tertiary protonated alcohol can go as low as -3.8). This basic characteristic of alcohol is essential for its dehydration reaction with an acid to form alkenes.



Mechanism for the Dehydration of Alcohol into Alkene

Different types of alcohols may dehydrate through a slightly different mechanism pathway. However, the general idea behind each dehydration reaction is that the –OH group in the alcohol donates two electrons to H^+ from the acid reagent, forming an alkyloxonium ion. This ion acts as a very good leaving group which leaves to form a carbocation. The deprotonated acid (the base) then reacts with the hydrogen adjacent to the carbocation and form a double bond.

Primary alcohols undergo bimolecular elimination (E2 mechanism) while secondary and tertiary alcohols undergo unimolecular elimination (E1 mechanism). The relative reactivity of alcohols in dehydration reactions is ranked as follows:

Methanol < primary < secondary < tertiary

Primary alcohols dehydrate through the E2 mechanism. The hydroxyl oxygen donates two electrons to a proton from sulfuric acid (H_2SO_4), forming an alkyloxonium ion. Then the conjugate base, HSO_4^-, reacts with one of the adjacent (beta) hydrogen atoms while the alkyloxonium ion leaves in a concerted process, forming a double bond.

E_1 mechanism of dehydration of alcohol

Mechanism for the Dehydration of Alcohol into Alkene. This ion acts as a very good leaving group which leaves to form a carbocation. The deprotonated acid (the base) then reacts with the hydrogen adjacent to the carbocation and form a double bond. ... Secondary and tertiary alcohols dehydrate through the E1 mechanism.

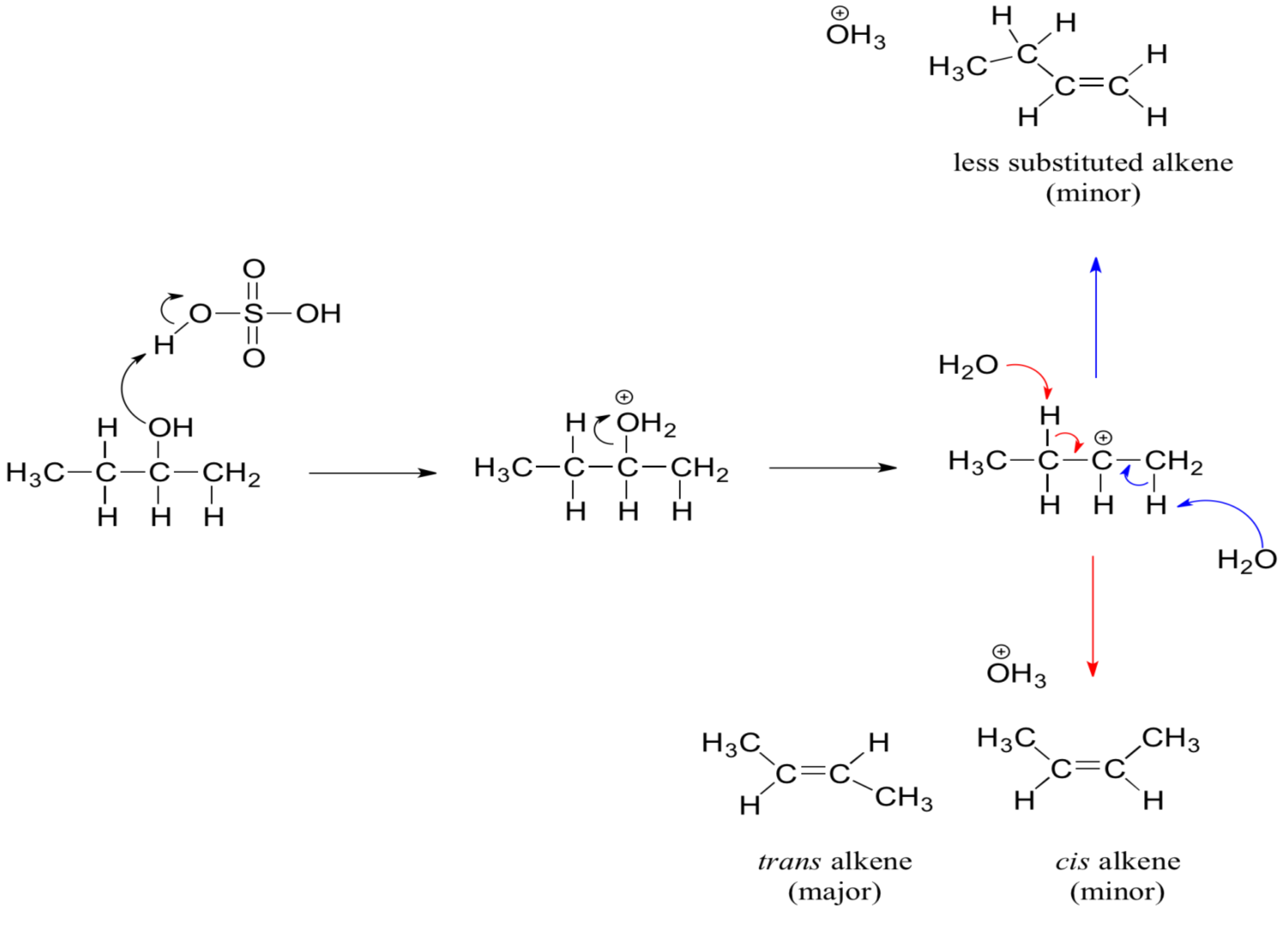
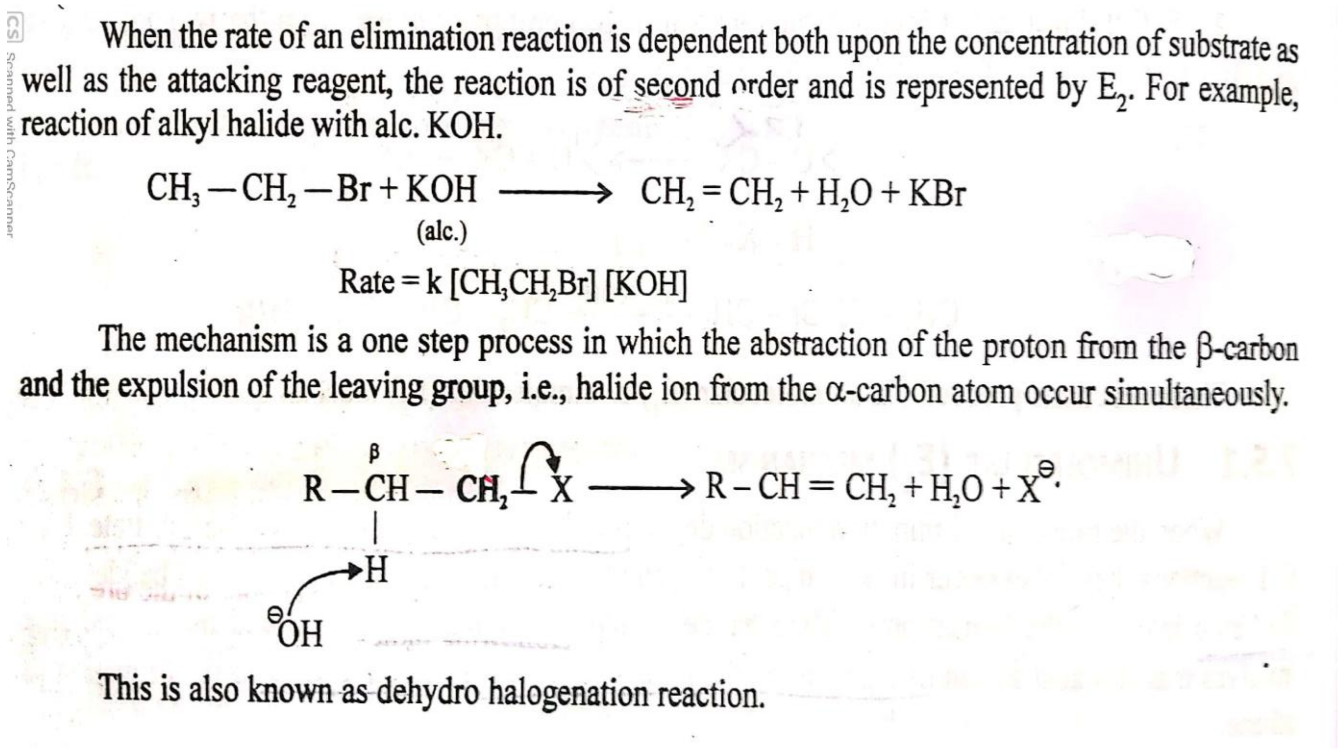


Figure 4. 7.Dehydration of Alcohol (E_1 Mechanism)

E_2 mechanism of dehydration of alcohol



When the rate of an elimination reaction is dependent both upon the concentration of substrate as well as the attacking reagent, the reaction is of second order and is represented by E_2. For example, reaction of alkyl halide with alc. KOH.

$$CH_3-CH_2-Br+\underset{(alc.)}{KOH}\longrightarrow CH_2=CH_2+H_2O+KBr$$

$$\text{Rate}=k\,[CH_3CH_2Br]\,[KOH]$$

The mechanism is a one step process in which the abstraction of the proton from the β-carbon and the expulsion of the leaving group, i.e., halide ion from the α-carbon atom occur simultaneously.

$$R-\overset{\beta}{C}H(H)-CH_2-X+{}^{\ominus}OH\longrightarrow R-CH=CH_2+H_2O+X^{\ominus}$$

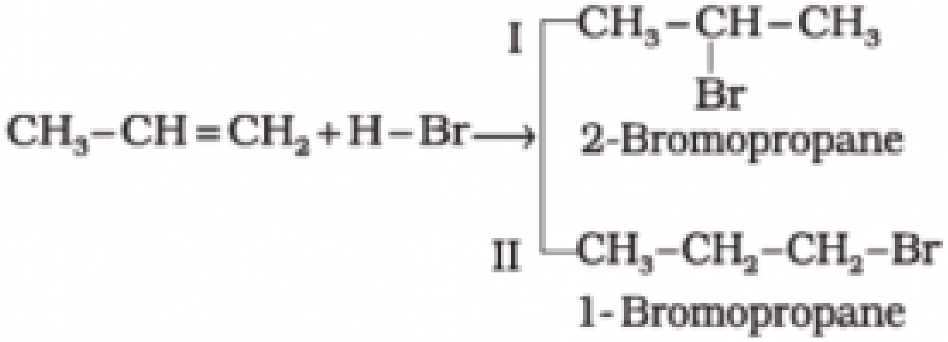
This is also known as dehydro halogenation reaction.

Electrophilic and Free Radical addition in alkenes:

Alkenes belong to the group of unsaturated hydrocarbons that is one molecule of alkene contains at least one double bond. Due to the presence of pi electrons they show addition reactions in which an electrophile attacks the carbon-carbon double bond to form the addition products. These reactions are known as electrophilic addition reactions of alkenes. Sometimes these addition reactions follow free radical mechanism too. Oxidation and ozonolysis reactions are also some of the prominent reactions of alkenes. Some of these reactions are discussed below:

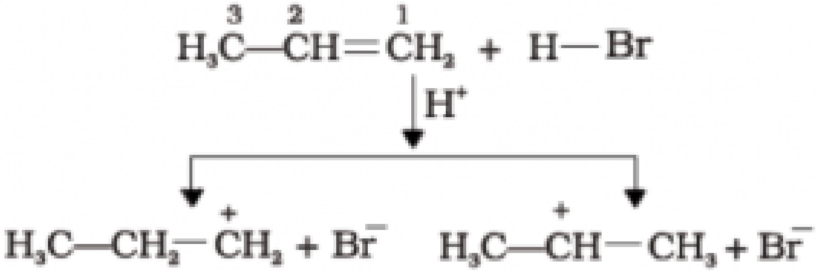
Electrophilic addition reactions of alkenes: Alkenes exhibit wide range of electrophilic addition reactions. Addition of hydrogen halides such as hydrogen bromide and hydrogen chloride is an example of electrophilic addition reactions of alkenes. The general trend of hydrogen halide is given as: HI >HBr> HCl. For symmetrical alkenes such as ethene it is quite easier to predict the end product in comparison to unsymmetrical alkenes such as propene. For example:

$CH_2 = CH_2 + H-Br \rightarrow CH_3-CH_2-Br$



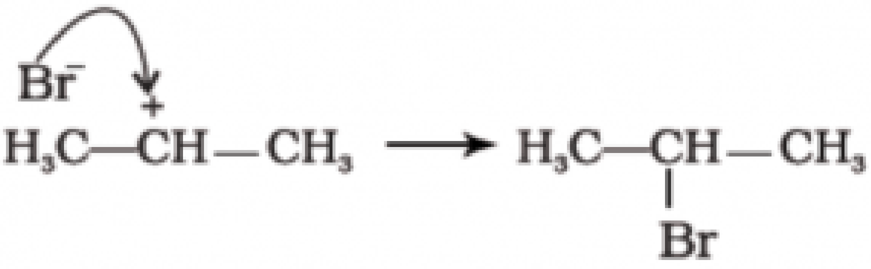
Markovnikov proposed a rule called Markovnikov rule for the prediction of major product in such cases. Markovnikov rule states that negative part of the adding molecule gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus, 2-bromopropane is the expected product by this rule. This can further be explained with the help of mechanism of electrophilic substitution reactions of alkenes. The general mechanism is explained below:

An electrophile, H^+ is generated from hydrogen bromide which attacks on double bond to form carbocation.



Since, the secondary carbocation is more stable than the primary carbocation, the secondary carbocation predominates the formation of ions.

Finally, Br^- attacks the carbocation to form alkyl halides.



Free Radical addition in alkene or Peroxide effect or anti Markovnikov rule

Anti Markovnikov Addition Reaction

Alkenes belong to the group of unsaturated hydrocarbons, that is, one molecule of alkenes contains at least one double bond. Due to the presence of pi electrons, they show addition reactions in which an electrophile attacks the carbon-carbon double bond to form the additional products. When HBr is added to unsymmetrical alkenes in the presence of peroxide, 1-bromopropane is formed contrary to 2-bromopropane (according to Markovnikov's rule). This reaction is better known as anti-Markovnikov addition or Kharasch effect after the name of M. S. Kharasch who first observed it. This reaction is also known as Kharasch effect or peroxide effect.

$$CH_3\text{-}CH{=}CH_2 + HBr \xrightarrow{C_6H_5O_2} CH_3\text{-}CH_2\text{-}CH_2Br$$

Anti Markovnikov addition is also an example of addition reaction of alkenes which is an exception to the Markovnikov's rule. It is one of the few reactions following free radical mechanism in organic chemistry in place of electrophilic addition as suggested by Markovnikov. This reaction is observed only with HBr, not with HCl or HI.

Mechanism of Anti Markovnikov addition

Anti Markovnikov addition reaction is found to follow a free radical mechanism. The peroxide compound involved helps in the generation of free radicals. A general mechanism of anti-Markovnikov addition reaction is discussed below:

Generation of free radical through homolytic cleavage of peroxide compound.

Attack of generated free radical on hydrogen halide to form halide radical through hemolysis

Attack of generated halide radical on alkenes molecule to form alkyl radical through hemolysis.

Attack of a generated alkyl radical on hydrogen halide to form alkyl halide through homolytic cleavagee of hydrogen halide bond.

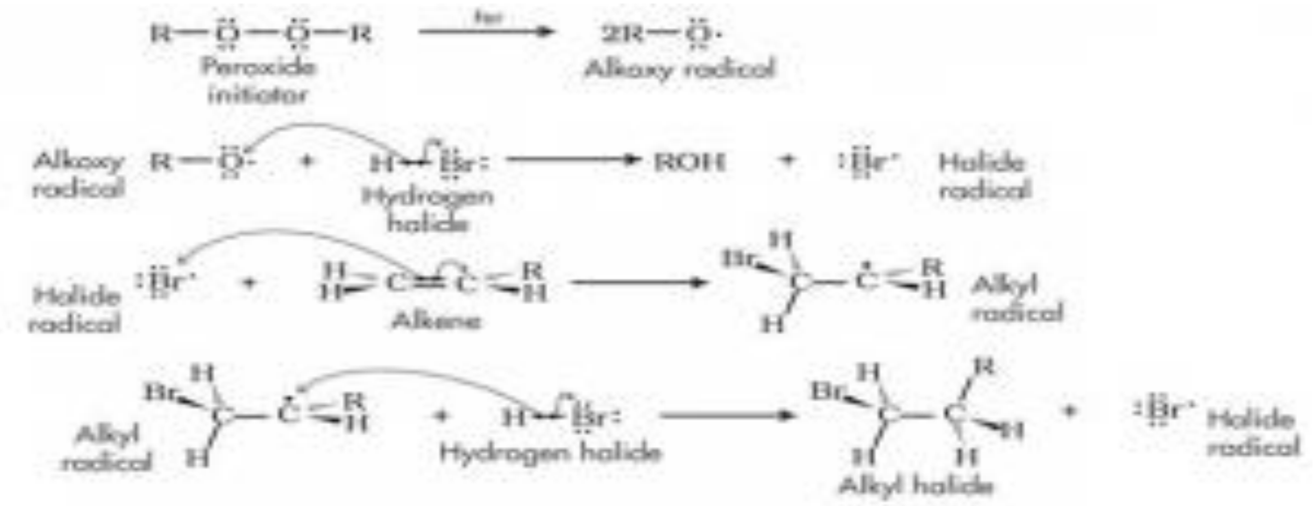
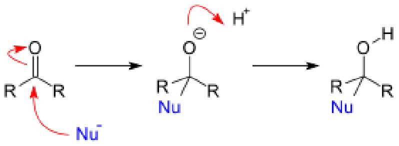


Figure 4.8. Anti Markovnikov addition mechanism

Nucleophilic addition reactions in Aldehyde and ketones:

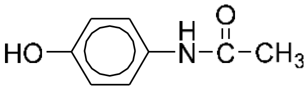
Nucleophilic addition reactions where, nucleophiles with an electrophilic double, triple bond or pie (π bonds) produce a new carbon center with two additional single, or sigma σ, bonds. Addition of a nucleophile to carbon-heteroatom double or triple bonds like -C≡N or>C=O display great variety. These kinds of bonds are polar and have a big difference in their electro negativity among the two atoms; therefore, their carbon atoms transport a slightly positive charge. This creates the molecule of an electrophile and the carbon atom with the electrophilic center; this atom is the prime target for the nucleophile. This kind of reaction is also known as 1,2 nucleophilic addition.



What is paracetamol?

Paracetamol (acetaminophen) is a pain reliever and a fever reducer. The exact mechanism of action of is not known.

Paracetamol is used to treat many conditions such as headache, muscle aches, arthritis, backache, toothaches, colds, and fevers. It relieves pain in mild arthritis but has no effect on the underlying inflammation and swelling of the joint.



Acetaminophin or Paracetamol

Synthetic skills

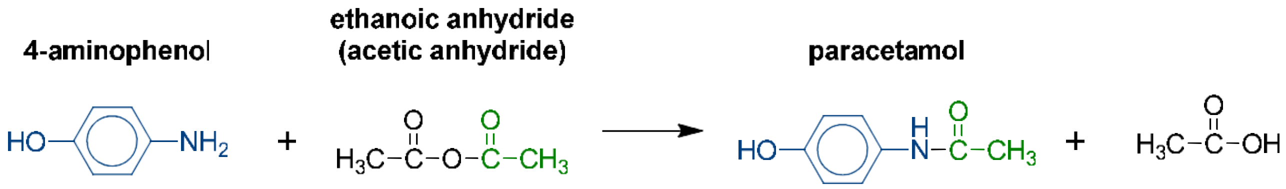
1. weighing and mixing reagents
2. vacuum filtration
3. purification by recrystallisation

Analytic Skills :

1. Thin layer chromatography
2. Melting point determination
3. Infrared (IR) spectroscopy
4. Nuclear Magnetic
5. Resonance (NMR)

Synthesis of Paracetamol (Morning)

Paracetamol is made by reacting 4-aminophenol with ethanoic anhydride (more commonly called acetic anhydride). This reaction forms an amide bond and ethanoic acid as a by- product. When the reaction is complete the paracetamol is then isolated and purified.



The synthesis of paracetamol can be broken down into 3 parts:

Part 1 – mix the reactants together to form paracetamol.

Part 2 – isolate crude paracetamol from the ethanoic acid and unreacted starting materials. Part 3 – purify paracetamol by recrystallisation.

Analysis of Paracetamol (Afternoon)

In the afternoon you will analyze the purity of the paracetamol you have made and interpret the infrared (IR) and nuclear magnetic resonance (NMR) spectra of paracetamol to confirm you have made the correct compound.

The analysis section has 5 parts:

Part 1 – calculating the percentage yield of paracetamol. Part 2 – determine the melting point of your sample.

Part 3 – analyze purity by thin layer chromatography (TLC).

Part 4 – measure and interpret the infrared (IR) spectrum of your compound. Part 5 – interpret the ^1H nuclear magnetic resonance (NMR) spectrum.

Health and Safety

For your health and safety you will need to observe the following protocols:

Laboratory coats and safety spectacles must be worn at all times in the laboratory.

You must carry out your experiments in the fume hoods and not on the benches.

Disposable gloves are available on the shelves next to where you will be working to protect your hands.

No food or drink is allowed.

Chemically contaminated gloves and filter papers go into the yellow bins.

Liquid organic waste is disposed of in special containers located by each large sink in your bay. If the container is full, report it to the demonstrators.

Acetic anhydride, hydrochloric acid and sodium hydroxide are corrosive – wear gloves!

Ethyl acetate and petroleum ether are flammable liquids – no flames or sparks should go near these reagents.

Synthesis of Paracetamol

CHEMICAL	HAZARD	PRECAUTION	DISPOSAL
Ethyl Acetate	Highly flammable Causes eye irritation	Keep away from heat/open flames/ sparks	Acetone waste container by each sink.
Petroleum ether 40-60 °C  	Highly flammable May cause lung damage if swallowed Vapors may cause drowsiness or dizziness Toxic to aquatic organisms	Keep away from heat/ open flames/sparks Avoid inhalation	Acetone waste container by each sink.
Acetic Acid	Flammable Causes burns	Wear gloves Keep away from heat, open flames and sparks	In a fume hood dilute with water and flush down sink.
4-Aminophenol	Harmful by inhalation and if swallowed Very toxic to aquatic organisms Suspected of causing genetic defects.	Wear gloves Avoid breathing dust. Handle in fume cupboard. Avoid release to the environment	Leave sample tube in your fume cupboard.
Acetic Anhydride	Flammable Harmful by inhalation and if swallowed	Keep away from heat/open flames/ sparks Wear gloves	In a fume hood dilute with water and flush down sink.

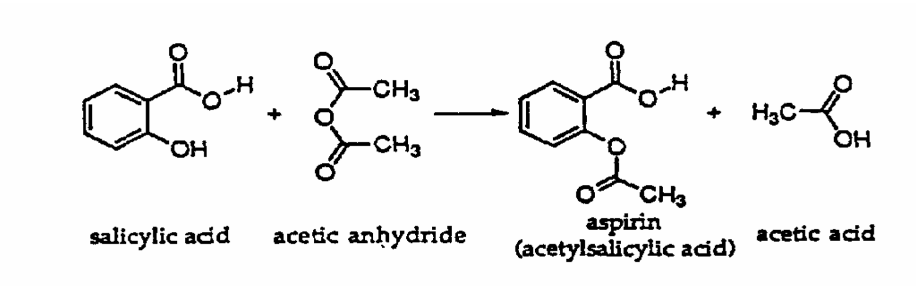
Acetaminophen (paracetamol) ⚠	Harmful Causes skin, eye and respiratory irritation	Wear gloves Avoid breathing dust	Leave sample in your fume hood.

Part 1: Preparation of Aspirin

How it works

The ‘curly’ arrow mechanism below shows the bond forming/breaking process that occurs.

ethanoic anhydride.

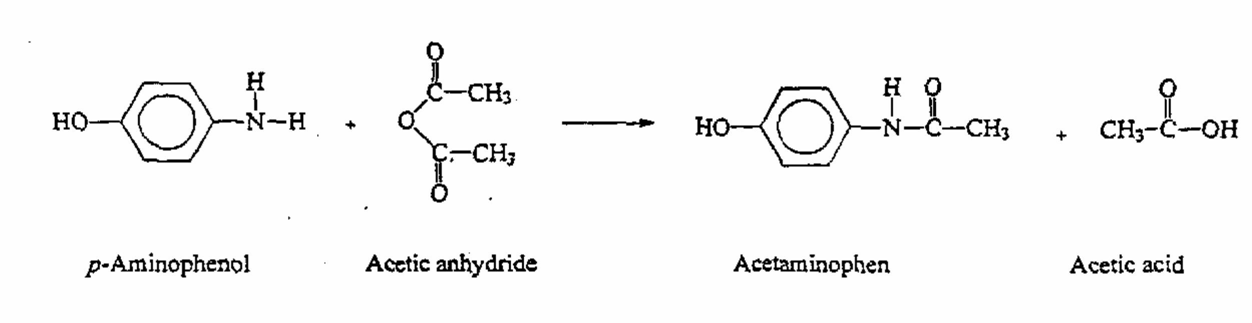


Preparation of Aspirin

Table 4.1. Synthesis of Paracetamol

Safety Precautions

1. Acetic and hydride is corrosive and its vapor irragating respratory system.
2. Sulphuric acid is corrosive. Avoid skin contact.
3. Wear safety glasses in Laboratory.



4-aminophenol

Paracetamol **ethanoic acid**

The lone pair of electrons on the amine of 4-aminophenol attacks the C=O bond of acetic anhydride causing it to break.

Nitrogen has a positive charge but regains electrons by losing a proton. The negative charge on the oxygen comes back in to reform the C=O bond. This causes the other C-O bond to break.

The result is an amide bond formation and a carboxylic acid by-product.

Remember to wear gloves

Preparation of Acetaminophin

Add 2.1 grams of 4-aminophenol (pre-weighed for you in a labeled sample tube) into the round-bottomed flask.

Using your 25 mL measuring cylinder, measure 18 mL of water and add this to the flask. Add a magnetic follower to the round-bottomed flask.

Carefully clamp the flask at the neck and position it in the metal DrySyn block which should be placed on the stirrer hotplate. Stir the reaction mixture using a magnetic follower. Do not apply heat at this stage.

Assemble the apparatus for reflux as shown in the diagram below. Tip: Do not clamp the condenser!

Using a Pasteur pipette, measure 3 mL of ethanoic anhydride (also known as acetic anhydride) into a 10 mL measuring cylinder. Add this to your mixture by lifting the condenser and adding directly to the round-bottomed flask.

Replace the condenser and switch on the heat to your hotplate (set the dial to about 120°C). Tip:

Make sure there is water going through your condenser.

The reaction is heated at reflux for 15 minutes, stirring continuously. The reaction mixture should become colourless.

After refluxing for 15 minutes, switch off the heat and carefully raise the round-bottomed flask away from the DrySyn block using the boss and clamp.

Allow the flask to cool to room temperature.

On cooling, crude paracetamol should form in the round-bottomed flask.

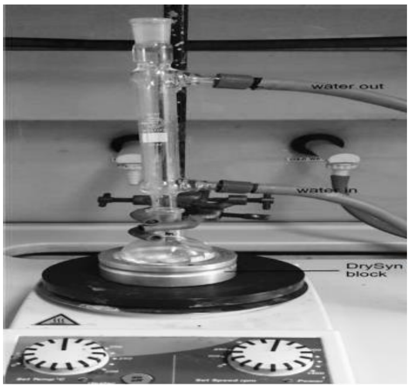


Figure 4. 9 Isolate crude paracetamol from ethanoic acid and unreacted starting materials

How it works

1. The easiest way to collect or remove precipitates is by vacuum filtration. This is a faster method of filtering solids than filtration under gravity as the vacuum pump provides the suction.
2. Set up your vacuum filtration apparatus as shown in the diagram below with the Buchner flask and funnel that you have on the bench.
3. Place your Buchner flask on top of the base of the clamp stand. Clamp the flask around the neck.
4. Place a Buchner (or Hirsch) funnel on top of the flask with a rubber ring or cone in between to create a seal.
5. Place a filter paper inside the funnel. You need to use the appropriate size paper that can lay flat and covers all the holes in the
6. The orange tubing at the back of the fume cupboard is where you will connect your apparatus to the vacuum. Moisten the end of the orange vacuum tubing by dipping it in a beaker of water. This will help you place the tubing onto the side-arm of the Buchner flask.
7. A demonstrator will show you how to switch on the vacuum pump and open the taps required to apply suction to your apparatus.
8. Wet the filter paper with some cold water and gently hold down the funnel. If the water passes through quickly you have a good enough suction. A demonstrator will help you if not.
9. Filter the reaction mixture using water (approximately 5 mL) to rinse out as much of the contents of the reaction flask onto the filter paper.
10. Wash the solid with approximately 2 x 15 mL of ice cold water and leave under suction for a few minutes. This should rinse away any ethanoic acid.
11. Transfer your solid into a clean 100 mL conical flask. Empty the filtrate into the sink at the back of the fume hood and wash out with plenty of water. Clean your funnel with water and remove the used filter paper.

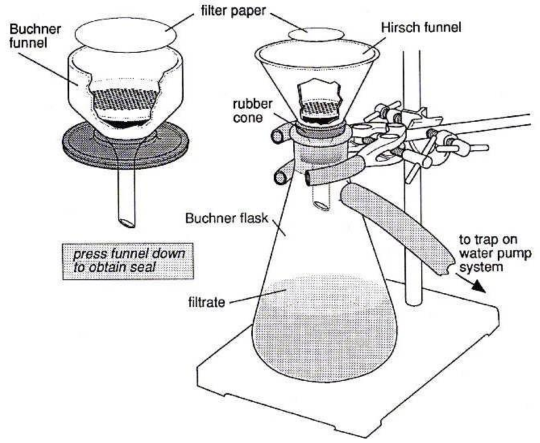


Figure 4. 10. Paracetmole Filtration

Part 3 – Purify paracetamol by recrystallisation

How it works

1. Recrystallisation is a technique that will further purify your product. Paracetamol is not soluble in cold water but it is when the solvent is hot. Any impurities will also dissolve in hot water. When everything has dissolved the solution is cooled. Paracetamol will crystallise but the impurities will remain dissolved.
2. Watch the 'recrystallisation' video on the laptop provided to show how a recrystallisation is set up and performed.
3. With your crude paracetamol in the clean 100 mL conical flask, add 5 mL of water to your solid. Add another 25 mL of water to a 50 mL conical flask.
4. Place both conical flasks onto your hotplate. Switch on the hotplate to heat both flasks gently. Keep gently swirling both flasks until the water is just below its boiling point.
5. Using a Pasteur pipette, add approximately 1 mL (1 pipette full) of hot water from the conical flask to your paracetamol. Tip: do not invert the pipette whilst transferring the water! Swirl your conical flask again to try and get the solids to dissolve. Return the flask to the stirrer hotplate to keep it hot. Continue this until all the solid has dissolved. Careful! If you add a vast excess of water then your paracetamol might not recrystallise on cooling.
6. Once all the solid has dissolved in the minimum volume of hot solvent, allow the flask to cool to room temperature slowly. Why do we want the flask to cool slowly?
7. Set up another vacuum filtration with the filtration apparatus. Pre-weigh an empty watch glass and make a note of the weight g.
8. When no more precipitate appears to have formed, filter your mixture by vacuum filtration. Wash the solid with a small amount (less than 5 mL) of water.
9. Transfer the solid onto the watch glass and leave to dry in a low temperature oven over lunch.
10. After lunch you will calculate the mass of your product and analyze its purity. In the meantime calculate the theoretical yield of paracetamol. You will use this to calculate the yield of your product after lunch.

Analysis of Paracetamol

In this session you will determine yield and purity of the paracetamol you made.

Part 1 – Calculating the percentage yield of paracetamol

Remove your sample from the oven. Record a weight and calculate your yield.

Weight of paracetamol + watch glass

Yield of paracetamol Percentage yield of paracetamol

Part 2 – Melting point of paracetamol

How it works

Comparing the melting point of your synthesized paracetamol to the known melting point is a good way to ascertain its purity. Any impurities present will lower the melting point and increase the range over which the solid melts.

Watch the 'melting point' video on the laptop to help you understand what to do.

When you are ready, press the open end of the capillary tube onto your solid which should transfer some solid into the tube. Invert the tube and tap the sealed end gently onto a hard surface so the solid drops down to the bottom. Repeat this until you have a depth of 2 mm of sample in the sealed end of the tube.

The full operating instructions for the melting point apparatus are provided with the instrument. First you will rapidly heat your sample to a

'plateau temperature' of 160 °C. Above the plateau, the sample will continue to be heated but at a slower rate of 2-3 degrees per minute which will allow you to record an accurate melting range of your compound.

The first temperature is recorded when the first drop of

liquid is apparent. The second temperature is recorded when the entire mass of crystals has been converted into a liquid.

your first temperature here °C Record your second temperature here °C

Give the melting range of your compound here °C

Press stop to finish heating and allow the instrument to cool. Remove your sample tube and dispose in the glass waste bin.

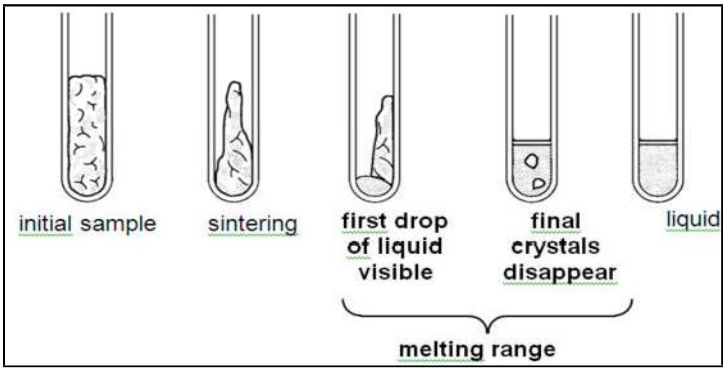


Figure 4.11. Analysis of Paracetamol

Part 3 – analyze the purity of paracetamol by thin layer chromatography (TLC)

How it works

1. Thin layer chromatography (TLC) is a technique that allows you to determine if your sample contains only paracetamol or is contaminated with other compounds (e.g. starting material). A small amount of your sample and some 4-aminophenol is placed on a TLC plate coated in silica gel. A solvent is passed up the plate which causes the compounds present to travel up the plate. 4-Aminophenol and paracetamol travel up the plate at different rates due to their different structures.
2. When the solvent has nearly run to the top of the plate you will visualise the plate under UV light. You should hopefully see just one spot from your sample that corresponds to paracetamol and that it is different to your 4-aminophenol reference. This will confirm that your sample is pure.
3. Watch the 'thin layer chromatography' video on the laptop to help you understand what to do.
4. Pour at least 10 mL of TLC solvent (2:1:0.1 ethyl acetate/40-60 °C petroleum ether/acetic acid) solution into a 100 mL beaker. Line part of the beaker with a piece of filter paper so that it dips into the solvent and also sticks to the walls. Cover the beaker with a watch glass.

Dissolve a few crystals of 4-aminophenol in approximately 2 mL of ethyl acetate in a sample tube. Repeat the same procedure to prepare a TLC sample of paracetamol. Make sure each tube is properly labeled.

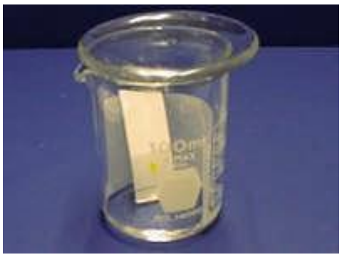


Figure 4. 11. TLC Analysis of Paracetamol

Faintly mark a line above the baseline in pencil. The height of this line 'X' must be higher than the depth of the solvent in the beaker.

TLC plate before elution

Mark 3 points on the baseline so that they are roughly equidistant from each other and the sides of the plate and underneath in pencil label them A, B and C.

Dip a TLC applicator into your 4-aminophenol solution. Capillary action will draw up some of the solution into the applicator. Lightly touch (once or twice) this applicator on
the TLC plates at points A and B (the smaller the applied
X spots the better).

Repeat the same process with your paracetamol solution applied to spot C first then spot B.

Place the TLC plate into the tank with the top of the plate resting against the inside of the beaker (don't forget to replace the watch glass back on top).

You should see solvent travelling up the plate. When the solvent front has reached approximately 1 cm from the top of the plate, remove the plate from the TLC tank. Mark a faint pencil line to indicate how far the solvent has travelled up the plate and allow the solvent to evaporate.

Adverse Effects of Paracetamol:

- **Liver damage**

Acute overdoses of paracetamol can cause potentially fatal liver damage. In 2011, the U.S. Food and Drug Administration (FDA) launched a public-education program to help consumers avoid overdose, warning: "Acetaminophen can cause serious liver damage if more than directed is used.

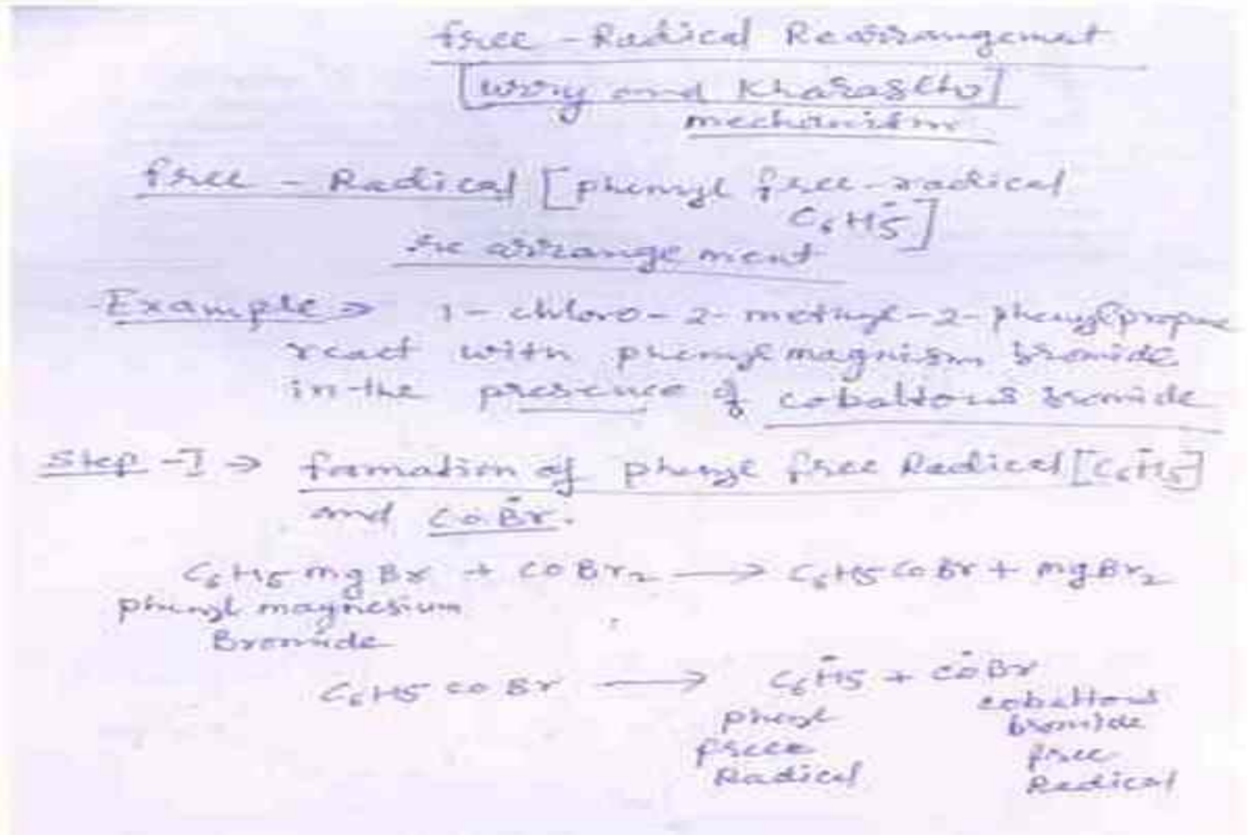
- **Skin reactions**

the U.S. Food and Drug Administration (FDA) issued a warning about paracetamol. It stated that the drug could cause rare and possibly fatal skin reactions such as Stevens–Johnson syndrome (SJS) and toxic epidermal necrolysis

- **Other Factors**

In contrast to aspirin, paracetamol does not prevent blood from clotting (it is not an antiplatelet), thus it may be used in people who have concerns with blood coagulation. Additionally it does not cause gastric irritation.[88] However, paracetamol does not help reduce inflammation, while aspirin does.[89] Compared with ibuprofen—whose side effects may include diarrhea, vomiting and abdominal pain—paracetamol has fewer adverse gastrointestinal effects.[90] Unlike aspirin, paracetamol is generally considered safe for children, as it is not associated with a risk of Reye's syndrome in children with viral illnesses.[91] If taken recreationally with opioids, weak evidence suggests that it may cause hearing loss.[92] Paracetamol use may also inhibit the feeling of empathy for another's pain.[93]

FREE RADICAL REARRANGEMENT



free - Radical Rearrangement
[urry and Kharasch]
mechanism

free - Radical [phenyl free-radical $\dot{C}_6H_5$] rearrangement

Example ⇒ 1-chloro-2-methyl-2-phenylpropane react with phenylmagnesium bromide in the presence of cobaltous bromide

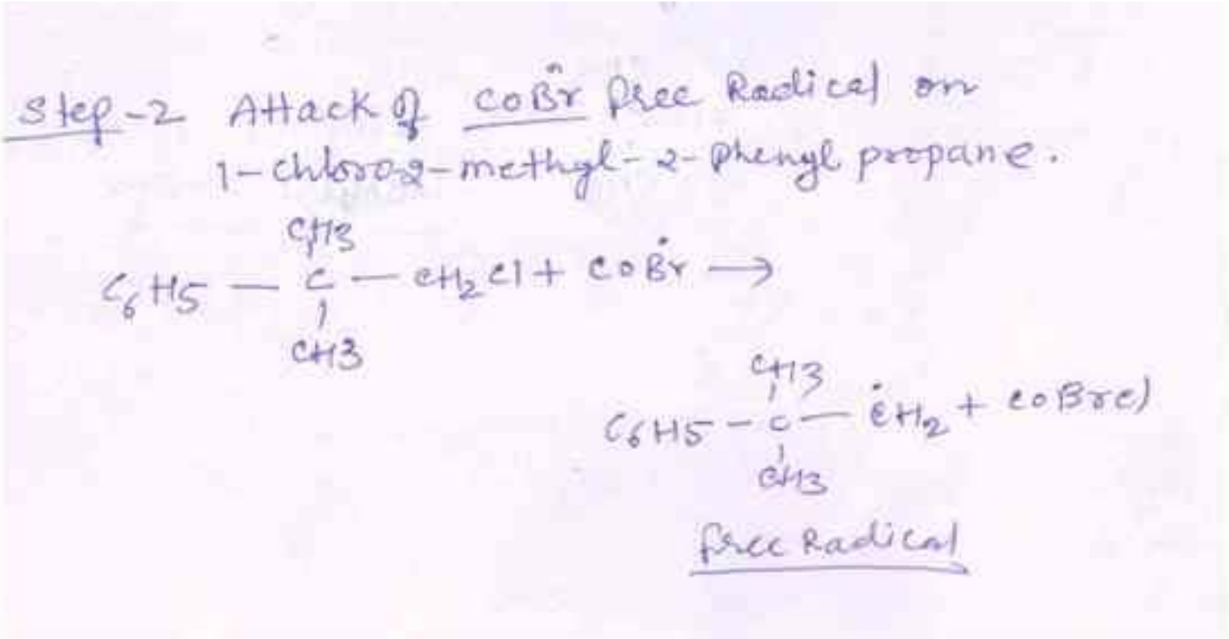
Step-I ⇒ formation of phenyl free Radical [$\dot{C}_6H_5$] and $Co\dot{B}r$.

$$C_6H_5MgBr + CoBr_2 \longrightarrow C_6H_5CoBr + MgBr_2$$

phenyl magnesium Bromide

$$C_6H_5CoBr \longrightarrow \underset{\text{phenyl free Radical}}{\dot{C}_6H_5} + \underset{\text{cobaltous bromide free Radical}}{Co\dot{B}r}$$

PHENYL RADICAL MIGRATION SCHEME BY URRY & KHARASCH IN 1-CHLORO-2 METHYL-2 PHENYLOPROPANE WITH PHENYLMAGNESSIUM BROMIDE IN THE PRESENCE OF CABALTOUS BROMIDE

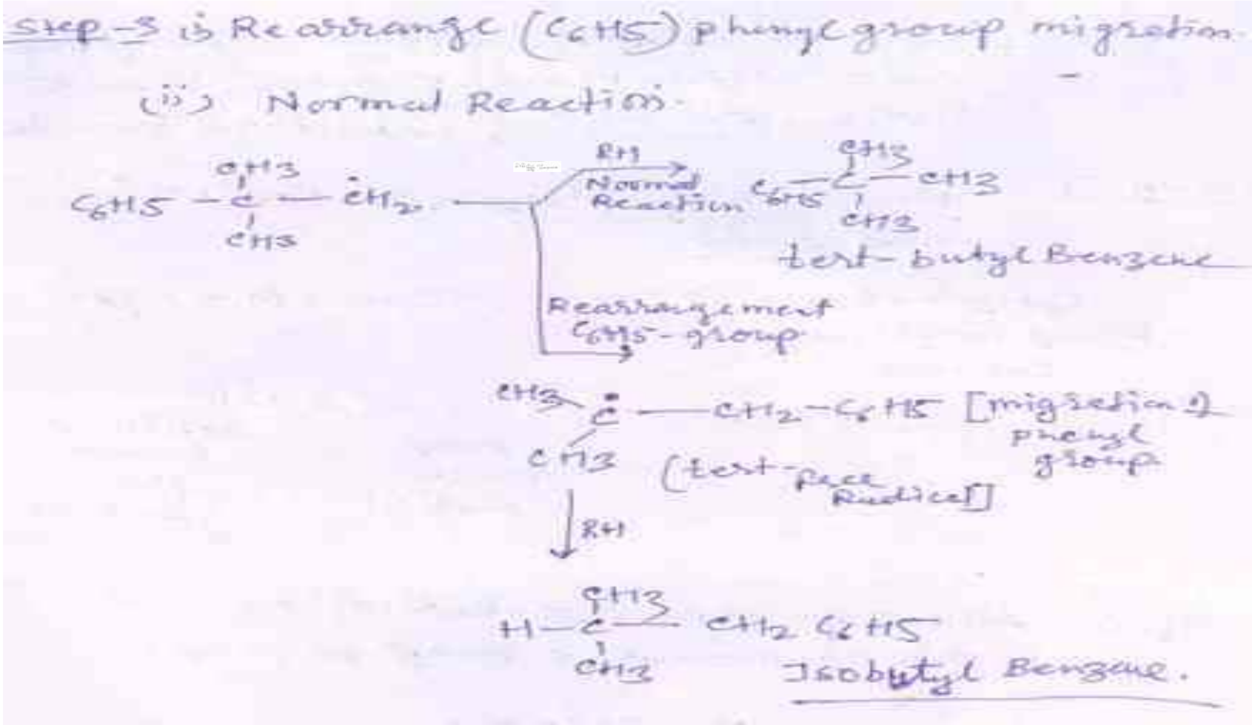


Step-2 Attack of $Co\dot{B}r$ free Radical on 1-chloro-2-methyl-2-phenyl propane.

$$C_6H_5 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2Cl + Co\dot{B}r \longrightarrow$$

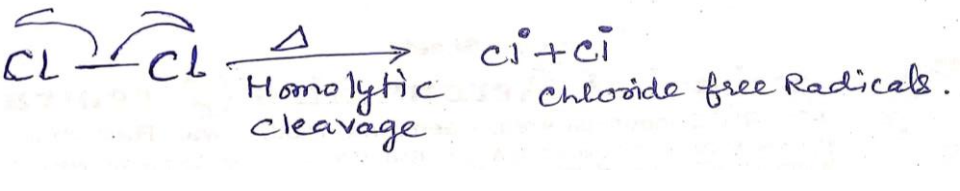
$$C_6H_5 - \underset{CH_3}{\overset{CH_3}{C}} - \dot{C}H_2 + CoBrCl$$

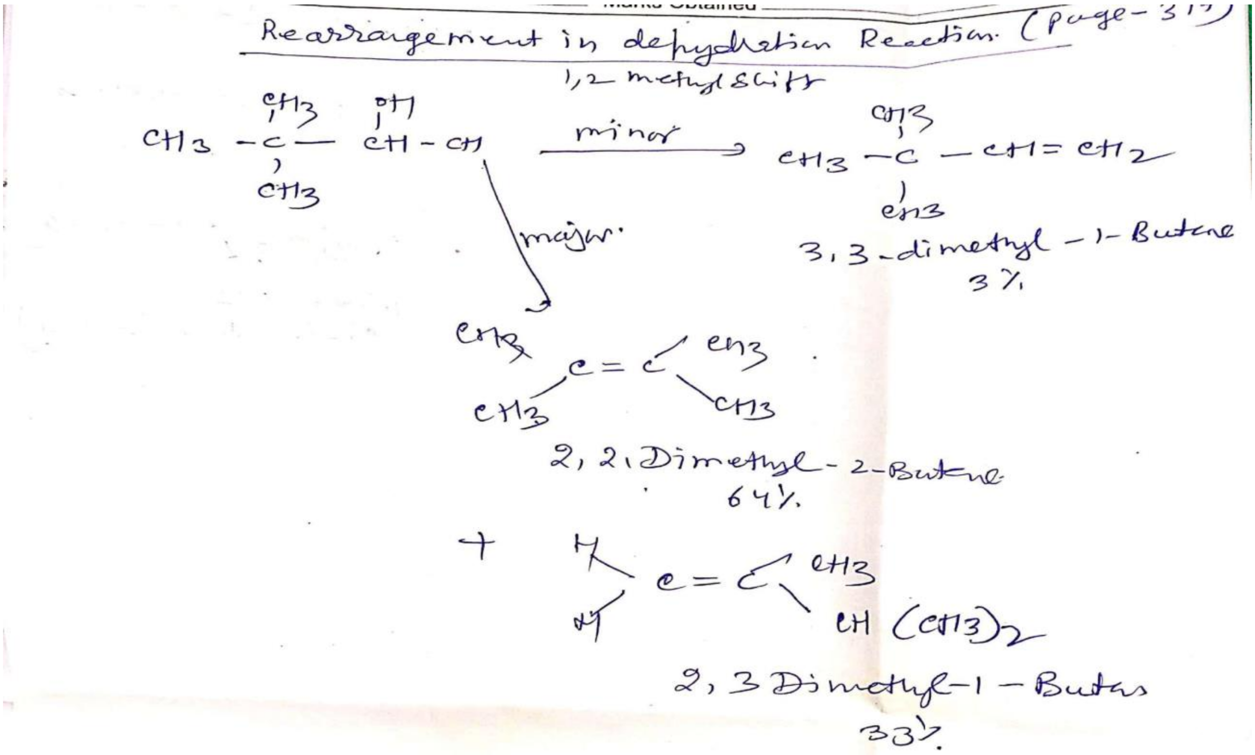
free Radical

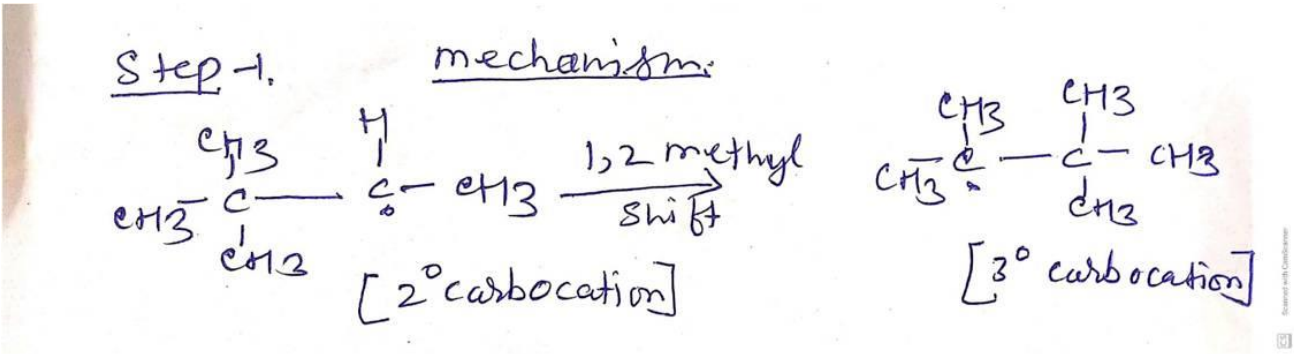


A free radical may be define as an atom or a group of atoms having and odd all unpaid electrons these are generally produce by homolytic cleavage of covalent bond.

REARRANGEMENT IN DEHYDRATION REACTION – 1,2 METHYL SHIFT



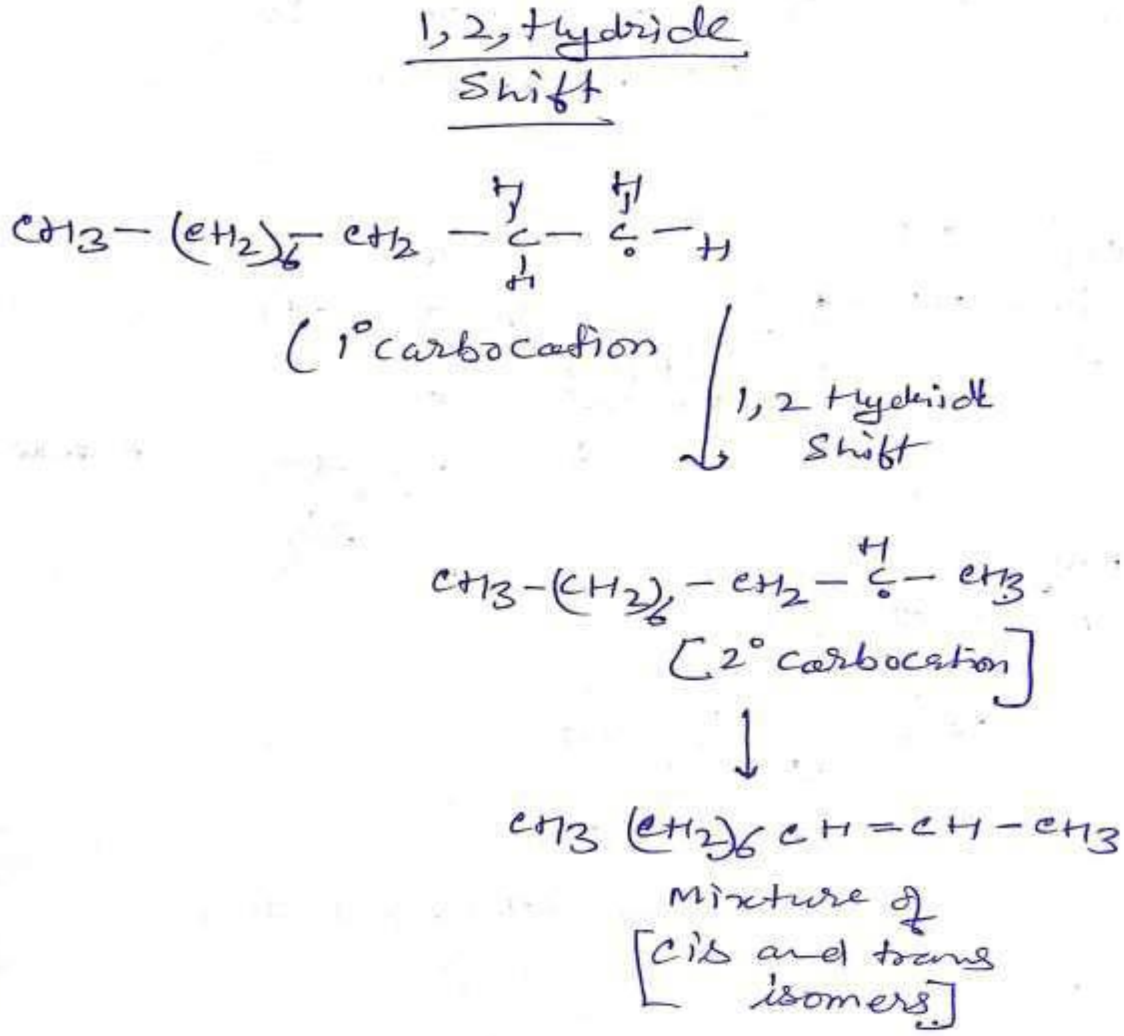




The rearrangement reaction may proceed either through inter molecular or intra molecular mechanism. In intra molecular mechanism, the migrating group does not completely in the process of migration. However, if the rearrangement occurs by inter molecular mechanism, migrating group first completely detaches itself from the molecule and then attaches to the different atom.

In above reaction the radical rearrangement takes place within the molecular from one position to another according to attaining more stability.

1,2 HYDRIDE SHIFT



As it turns out, if a situation exists where an unstable carbocation can be transformed into a more stable carbocation, a rearrangement is possible. One rearrangement pathway where an unstable carbocation can be transformed into a more stable carbocation is called a hydride shift.

Aryl Shift :

A 1,2-aryl shift is a carbocation rearrangement in which an aryl group in a carbocation migrates to the carbon atom bearing the formal charge of +1 (carbon 2) from an adjacent carbon atom (carbon 1).

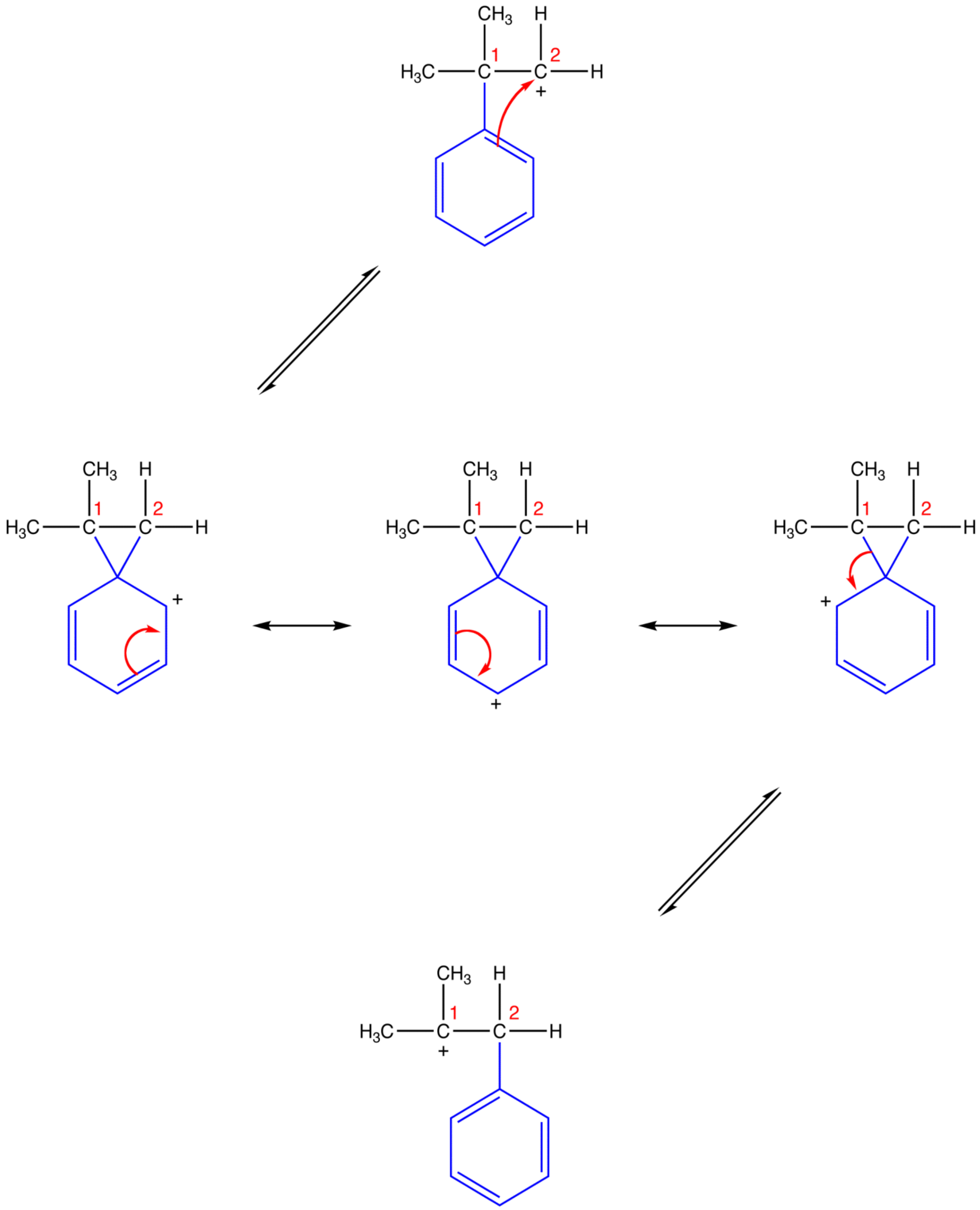
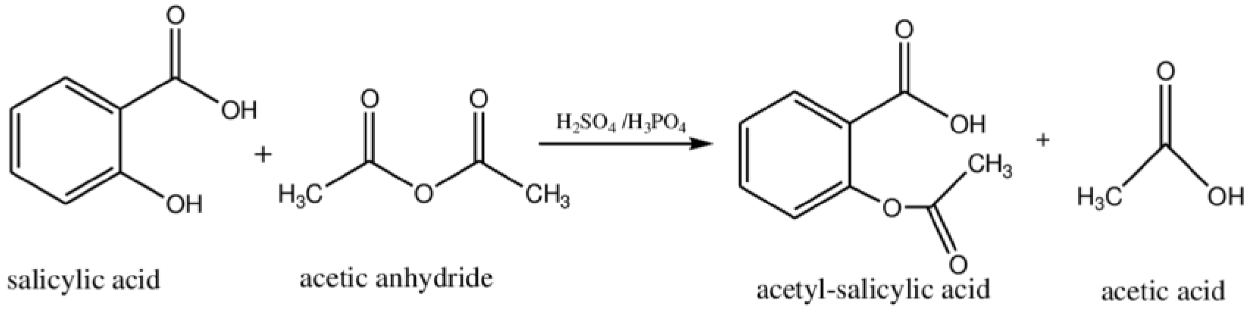


Figure 4. 12. Aryl Shift

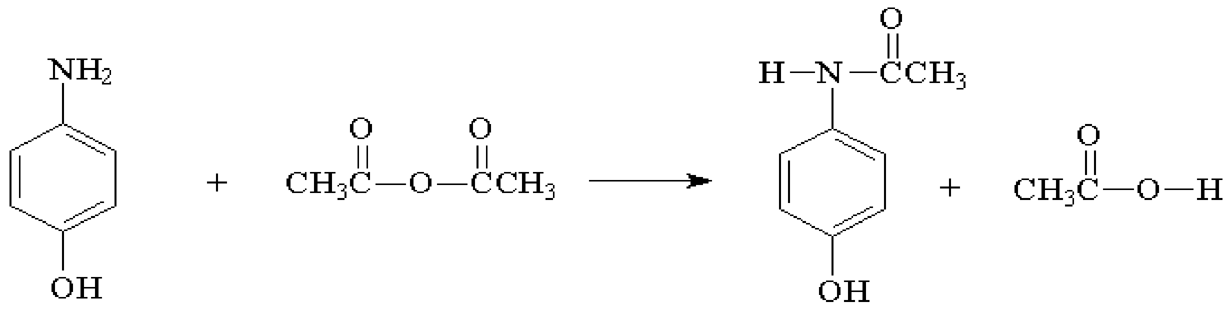
PREPARATION OF ASPIRIN (EMIPIRIN, BUFFERIN)



ASPIRIN

2 ACETOXY BENZOIC ACID

PARACETOMOL (METACIN,TYLENOL, TAPAR, CALPOL)

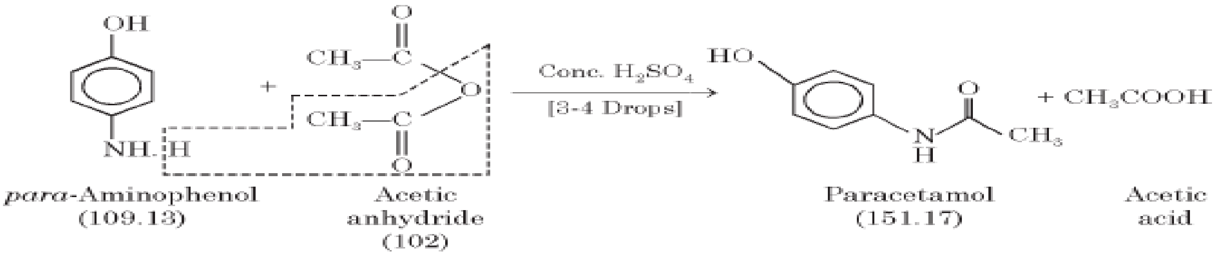


4-AMINO PHENOL

ACETIC ANHYDRIDE

4 ACETAMIDO PHENOL

ACETIC ACID



QUESTIONS FOR REVISION

PART- A

1. What is organic chemical reaction
2. Where the substitution reaction takes place?
3. What are the different types of substitution reaction?
4. What is electrophile? Give electrophile examples?
5. Why electrophile approach benzene ring
6. Give an example of reaction which goes through free radical substitution
7. What do you mean by free radical
8. Why free radical is reactive
9. What do you mean by elimination reactions in organic compound
10. What is alpha and beta elimination?
11. Give reaction between propene and HBr
12. Explain the structure and stability of carbokataine
13. Give examples of neutrophile
14. Give reaction of formation of aspirin and Paracetmole

PART-B

1. What is 1,2 hydride shift in isopropine and carbokataine
2. Write reaction of formation of $C_6H^{\circ}_5$, $CoBr^{\circ}$.
3. Give example of neutrophile addition to aelilhide and ketones
4. What is statement of Markonikoff rule of addition in propene
5. Give reaction mechanism of E_1 and E_2 elimination

PART- C

1. Give reaction mechanism of SN_1 and SN_2 substitution reaction
2. Give energy profile for SN_1 and SN_2 reaction
3. Give reaction mechanism of aspirin and Paracetmole
4. Give chemical tests to ascertain purity of aspirin and Paracetmole

EXTRA NOTES ON REACTIVE INTERMEDIATES:

1. Carbocation
2. Carbanion
3. Free Radical
4. Carbene

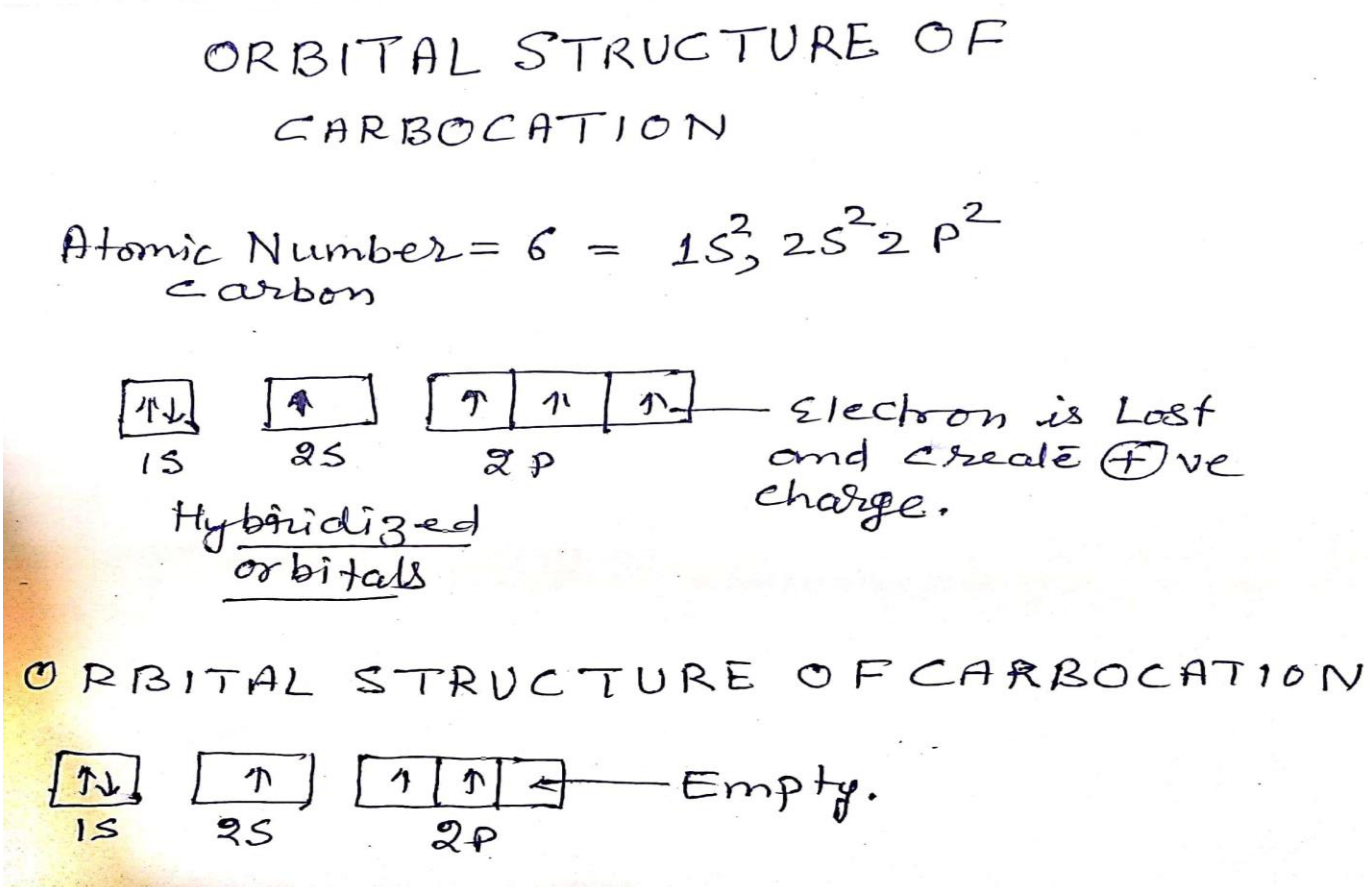
The reactive species are short lived highly reactive chemical species through which the majority of organic reactions occurs

These reactive species are carbocation,carbanion, free radical , carbene and Nitrenes

- **Carbocation:**

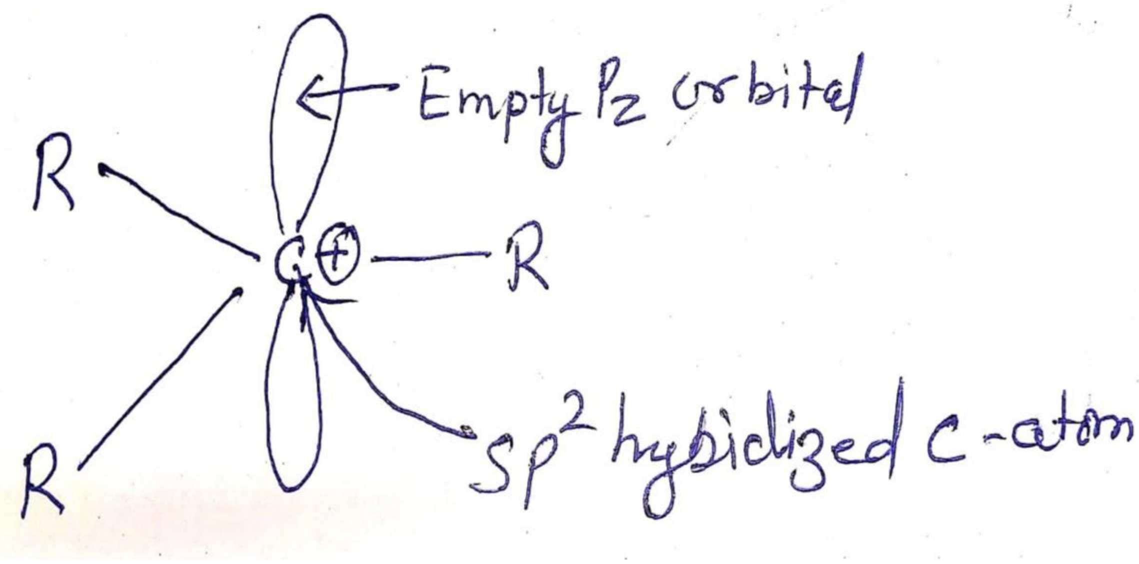
Chemical species baring in positive charge of carbon and carrying six electrons in its valency shell are called carbocation.

These are the formed by heterolytic cleavage of covalent bonds in which the leaving group takes away with it shared pair of electron of covalent bond.



The carbocation planer chemical species. The carbon atom carrying the positive charge is sp^2 hybridized. The three sp^2 hybridized orbitals at this carbon atom form three **σ bonds** with monovalent atoms or groups, which lie in a plane and are inclined at an angle of 120˚.

The unhybridized $2Pz$ orbital which is perpendicular to the plane of three **σ bonds** is however empty.



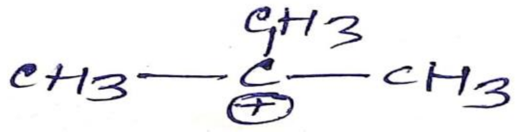
Orbital Structure of Carbocation

Classification :

Carbocation are classified as primary (1˚), secondary (2˚) and tertiary (3˚) according as the positive charge is present on a primary , secondary and tertiary carbon atom respectively

$CH_3-\overset{\oplus}{C}H_2 \rightarrow$ [Ethyl carbocation]
1°

$CH_3-\overset{\oplus}{C}H-CH_3$ [2°]
Iso-propyl carbocation.



$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3$$

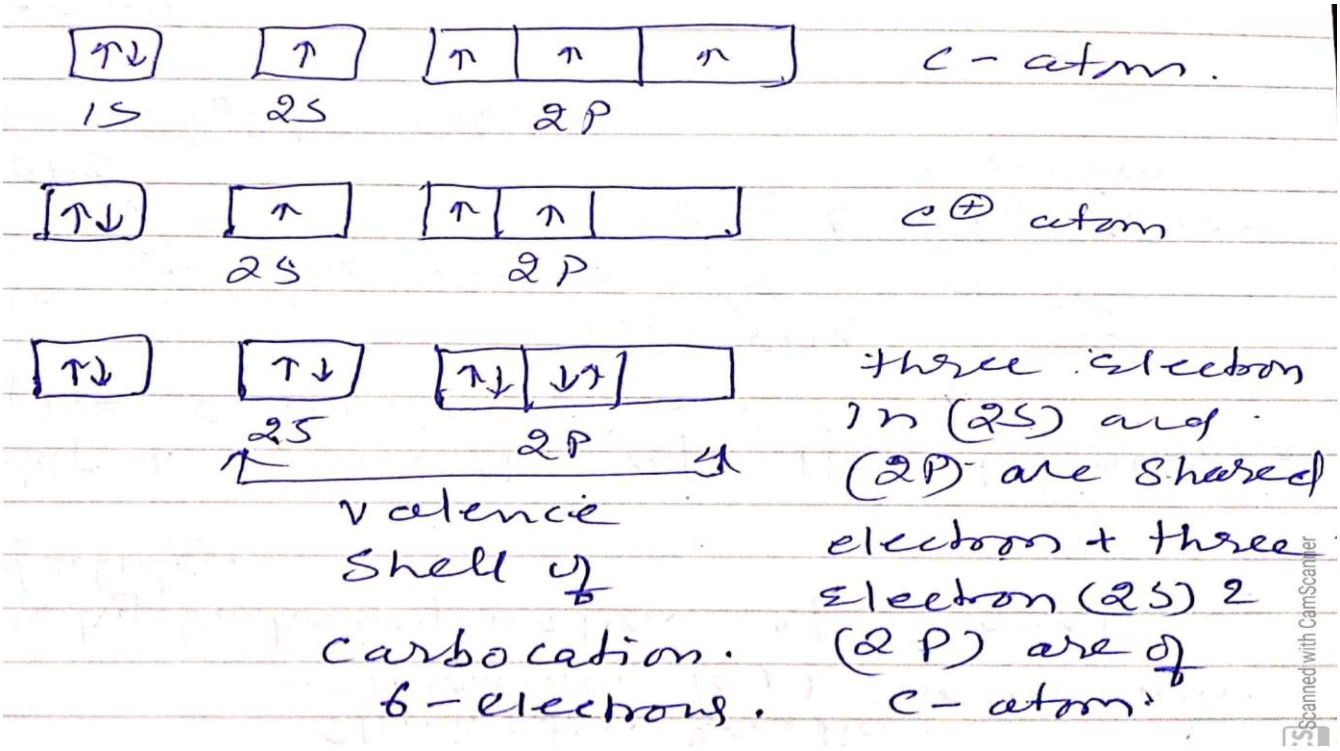
tert- Butyl carbocation.

Stability of carbocation:

The order of the stability of carbocation follows the sequence → 3˚> 2˚> 1˚

This order of the stability of carbocation can be easily explain on the basis of dispersal of positive charge by +I effect (electron releasing inductive effect) of alkyl groups.

Greater the number of alkyl groups on carbon atom carrying positive charge, greater would be dispersal of charge of more stable would be carbocation. Carbocation are highly reactive chemical species since carrying positive charge as only six electrons in its valency shell and have strong tendency to complete one octane.

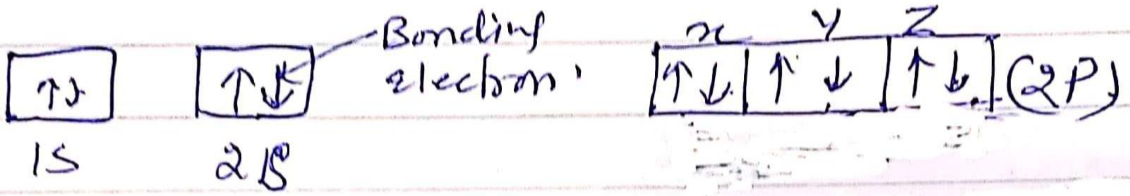


valence Shell of carbocation. 6-electrons.

three electron in (2S) and (2P) are shared electron + three electron (2S) 2 (2P) are of C- atom.

Carbanion:-

Carbanion → Chemical species bearing a negative charge on carbon and possessing ~~etc~~ eight electron in its valence shell are called Carbanion



$2S \rightarrow$ 2-electron } Take part in Bonding
$2P_x \rightarrow$ 2 electron
$2P_y \rightarrow$ 2 electron
$2P_z$ — 2 electron remain as lone pair.

② carbanion are produced by heterolytic cleavage of covalent bonds in which the shaped pair of electrons remain with the carbon-atom

$$HO^- + H-CH_2-CHO \rightarrow$$

$$H_2O + \overset{\ominus}{:}CH_2-CHO$$

acetaldehyde carbanion.

$H_2N^- + H-C\equiv C-H \longrightarrow$

Amide ion

Acetylene

$^-:C\equiv C-H + NH_3$.

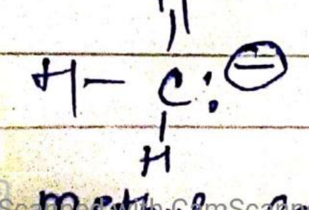
① Classification:- like carbocation, carbanion are also classified as primary (1°), secondary (2°) and tertiary (3°), according as the negative charge is present on a primary, secondary and a tertiary carbon atom respectively

② $R-CH_2^-$
primary
caranion (1°)

R_2CH^-
secondary
carbanion (2°)

Stability:- The order of carbanions is just opposite to that of carbocations and free radicals

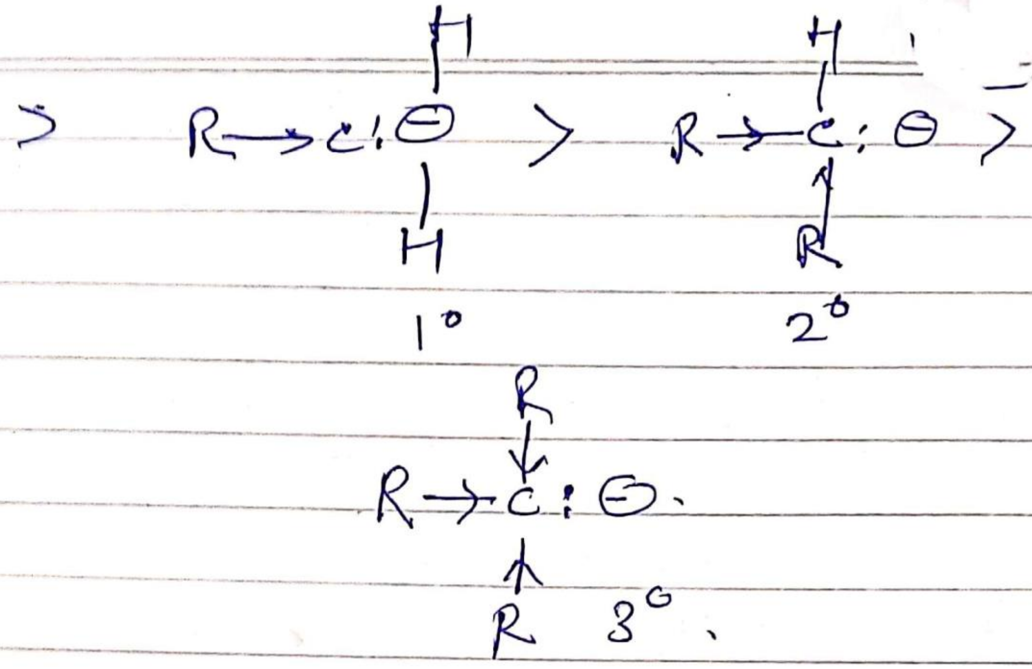
$1° > 2° > 3°$



$$H-\overset{H}{\underset{H}{C}}:^{\ominus}$$

methyl carbanion

PTO



$$> R \rightarrow \overset{H}{\underset{H}{C}}:\ominus > R \rightarrow \overset{H}{\underset{R}{C}}:\ominus > R \rightarrow \overset{R}{\underset{R}{C}}:\ominus$$

③ The order of stability can be easily explained in terms of +I effect of the alkyl groups.

④ Greater the number of alkyl groups on the carbon atom carrying the negative charge, greater would be the intensity of the negative charge on carbon and hence Less stable would be the carbanion.

⑤ Like carbocations, free radicals carbanion are also short-lived highly reactive chemical

PTO

species.

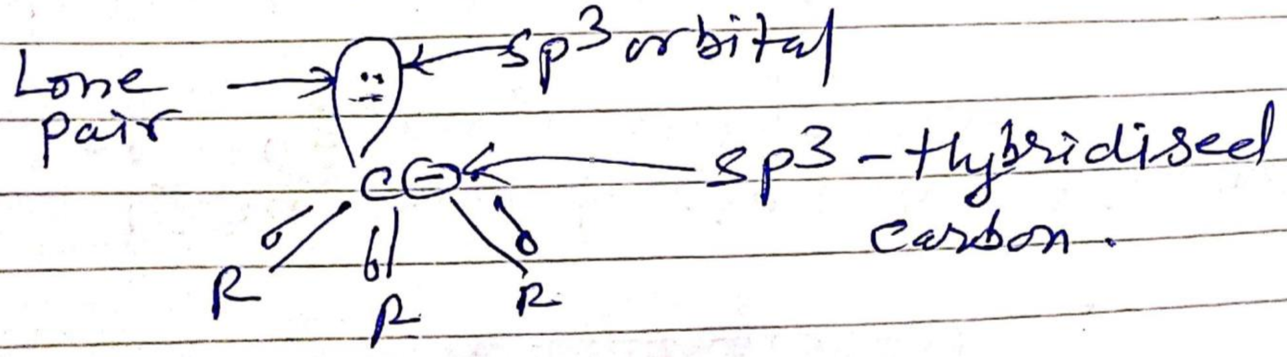
Instability of carbanions is believed to be due to the presence of a formal charge on them.

Orbital Structure

① The structure of simple carbanions is usually pyramidal just like those of ammonia, amine

② The carbon atom carrying the negative charge is sp^3 hybridised.

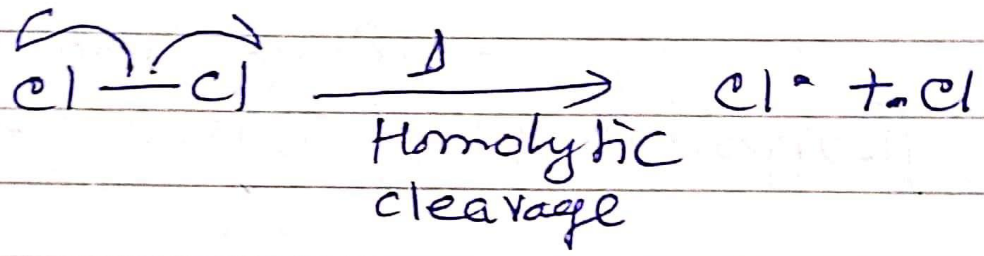
3) Three of the four sp^3-hybridised orbitals form three σ bonds with monovalent atoms or groups while the fourth sp^3 orbital contains the lone-pair of electrons.



Free - Radical

A free radical may be defined as an atom or a group of atoms having an odd or ~~uppo~~ unpaired electron.

These are generally produced by homolytic cleavage of a covalent bond. for Example

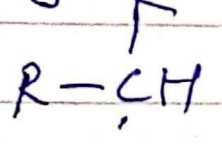


$$Cl-Cl \xrightarrow[\text{Homolytic cleavage}]{\Delta} Cl^{\bullet} + {}^{\bullet}Cl$$

Classification:- ① Like carbocations and carbanion, free radicals are also classified as primary (1°), secondary (2°) and tertiary (3°), according the unpaired electron is primary, secondary and tertiary respectively.

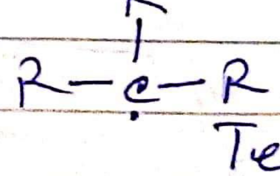
$R-\dot{C}H_2$

primary (1°)



$$R-\underset{\bullet}{\overset{R}{\overset{|}{C}}}H$$

secondary



$$R-\underset{\bullet}{\overset{R}{\overset{|}{C}}}-R$$

Tertiary (3°).

① Stability → The order of stability of free radicals is the same as that of carbocations i.e, 3° > 2° > 1°

② The order of stability cande easily explained on the basis of hyperconjugation.

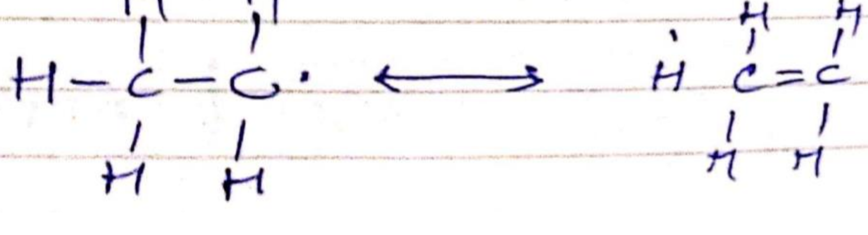
The greater the number of hyperconjugation structures, more will be the resonance energy and greater will be stability of free radical,

③ Primary free radical has three hyperconjugation structures secondary has six and tertiary has nine.

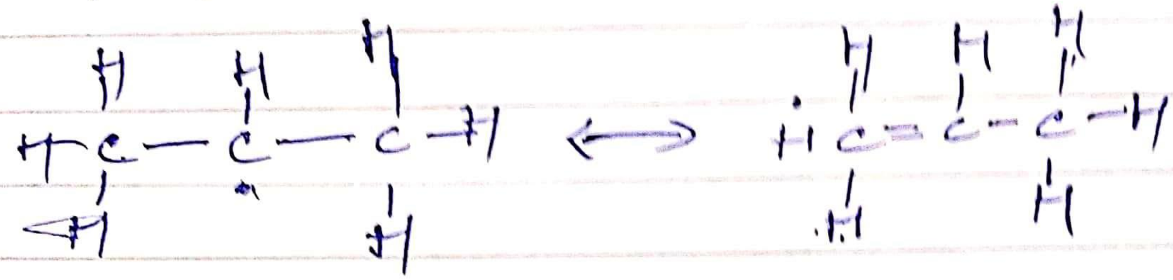
Hence tertiary free radical is most stable

Example →

Ethyl free Radical

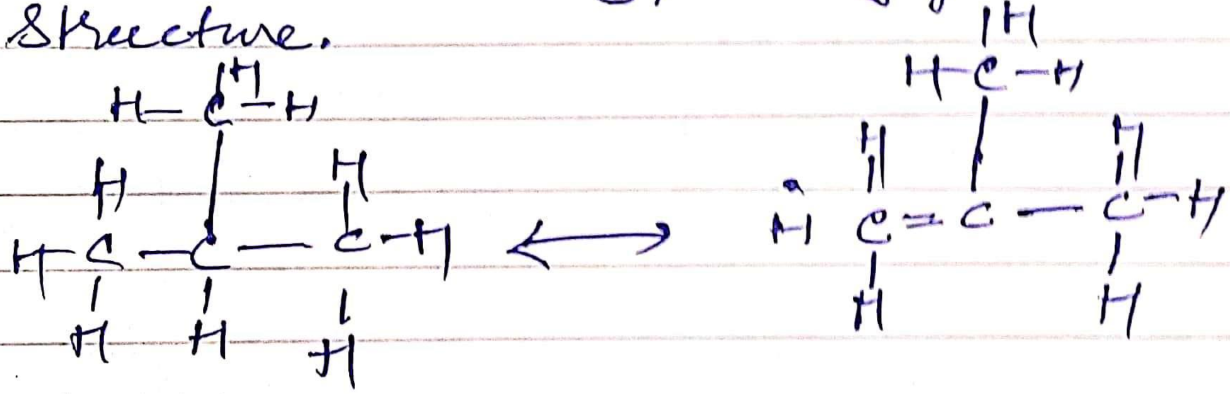


Isopropyl free Radical



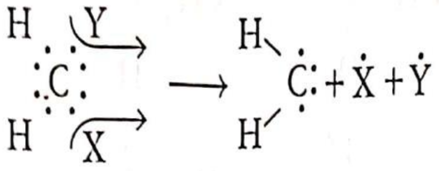
Isopropyl free radical may have six hyperconjugation structure

Tertiary butyl free radical :- May have nine hyperconjugation structure.

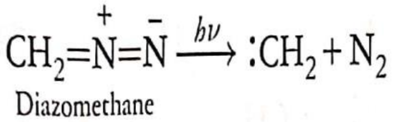


Carbene

These are highly reactive species containing divalent carbon having no charge and surrounded by a sextet of electrons. For example, $:CH_2$ is called methylene carbene and $:CCl_2$ is known as dichlorocarbene. There are two non-bonded electrons on the carbon in carbenes. These non-bonding electrons are derived by the homolytic fission of bonds.



They are generated by photolytic cleavage, for example, methylene carbene is generated by photolysis of diazomethane.



$$CH_2{=}\overset{+}{N}{=}\overset{-}{N} \xrightarrow{h\nu} :CH_2 + N_2$$

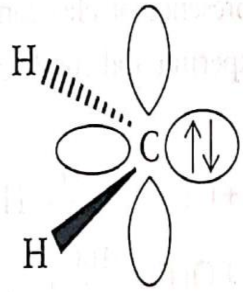
Diazomethane

Since the C atom in carbenes has six electrons, it is an electron deficient species.

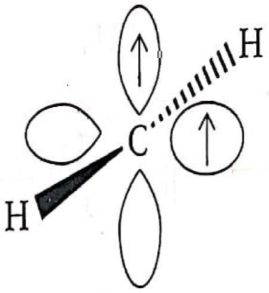
Structure

Carbenes exist in two forms: singlet or triplet.

1. **Singlet:** If both non-bonding electrons are in one orbital (antiparallel spin) then the carbene is said to be in a singlet state. This is a diamagnetic state. It has a trigonal geometry with carbon undergoing sp^2 hybridization.



2. **Triplet:** If both non-bonding electrons go into different orbitals (unpaired spins) then the carbene is said to be in triplet state. This is a paramagnetic state. The triplet carbene can be linear (*sp* hybridized) or bent (sp^2 hybridized).



UNIT -3

MODULE- 5

ORGANIC FUEL

TOPICS:-

- Solid fuels: Coal, Classification of Coal, Proximate and Ultimate analyses of coal and its significance, Gross and Net Calorific value, Determination of Calorific value of coal by Bomb Calorimeter. Metallurgical coke, Carbonization processes; Otto-Hoffmann by- product oven method.
- Liquid fuels : Advantages of liquid fuels, Mining, Refining and Composition of petroleum, Cracking, Synthetic petrol, Reforming, Knocking, Octane number, Anti-knocking agents, Cetane number
- Gaseous fuels; Advantages, manufacturing, composition and Calorific value of coal gas and oil gas, Determination of calorific value of gaseous fuels by Junker's calorimeter
- Numerical problems based on determination of calorific value (bomb calorimeter/Junkers Calorimeter/Dulongs formula, proximate analysis & ultimate and combustion of fuel.

UNIT –III

MODULE -5

ORGANIC FUELS

INTRODUCTION:

Fuels are the main energy sources for industry and domestic purposes.

"A fuel is a substance containing carbon as the major substituent which provides energy on combustion for industry and domestic purposes".

The combustion is the process of oxidation that provides heat energy. Every combustion is an oxidation but every oxidation is not combustion.

Example: - Combustion of wood, Petrol and kerosene gives heat energy.

Classification of Fuels:-

Classification of fuels is based on two factors.

- Occurrence (and preparation)
- The state of aggregation

1. **Occurrence (and preparation)**

On the basis of occurrence, the fuels are further divided into two types.

- Natural or primary fuels: -These are found in nature such as Wood, peat, coal, petroleum, natural gas etc.
- Artificial or secondary fuels: - These are prepared artificially from the primary fuels.

Example: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc.

Characteristics of a good fuel:-

- The fuel should be easily available.
- It should be dry and should have less moisture content. Dry fuel increases its calorific value.
- It should be cheap, easily transportable and has high calorific value.
- It must have moderate ignition temperature and should leave less ash after combustion.
- The combustion speed of a good fuel should be moderate.
- It should not burn spontaneously to avoid fire hazards.
- Its handling should be easy and should not give poisonous gases after combustion.
- The combustion of a good fuel should not be explosive.
- Combustion should be easily controable.
- A good fuel should burn efficiently without smoke.

2. The state of aggregation

The second classification is based upon their state of aggregation like:

1. Solid fuels
2. Liquid fuels and
3. Gaseous fuels.

Type of fuel	Natural or primary fuel	Artificial or secondary fuel
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.

Table 5.1. Types of Fuels

Characteristic properties of solid, liquid and gaseous fuels:

S.NO	Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
1	example	Coal	Crude oil	Coal gas
2	Cost	Cheap	Costlier than solid fuels	Costly
3	Storage	Easy to store	Closed containers should be used for storing	Storage space required is huge and should be leak proof.
4	Risk towards fire hazards	Less	More	Very high, since these fuels are highly inflammable
5	Combustion rate	It is a slow process	Fast process	Very rapid and efficient

S.NO	Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
6	Combustion control	Cannot be controlled	Cannot be controlled or stopped when necessary	Controlled by Regulating the supply of air
7	Handling cost	High since labour is required in their storage & transport.	Low, since the fuel can be transported through pipes	Low, similar to liquid fuels, these can be transported through pipes
8	Ash	Ash is produced and its disposal also possess problems	No problem of ash	No problem of ash
9	Smoke	Produce smoke invariably	Clean, but liquids associated with high carbon and aromatic fuels produce smoke	Smoke is not produced
10	Calorific value	Least	High	Highest
11	Heat efficiency	Least	High	Highest efficiency
12	Application	It cannot be used in internal combustion engine	It can be used in internal combustion engine	It can be used in internal combustion engine

Table 5.2. Characteristic properties of Fuels

Solid Fuels:-

The main solid fuels are wood, peat, lignite, coal and charcoal.

Coal: - Coal is a fossil fuel which occurs in layers in the earths crust. It is formed by the partial decay of plant materials accumulated millions of years of ago and further altered by action of heat and pressure. The process of conversion of wood into coal can be represented as Wood, Peat, Lignite, Bituminous Coal, and Anthracite

Peat:- Peat is brown-fibrous jelly like mass.

Lignite:- these are soft, brown coloured, lowest rank coals.

Bituminous coals:- These are pitch black to dark grey coal.

Anthracite:- It is a class of highest rank coal.

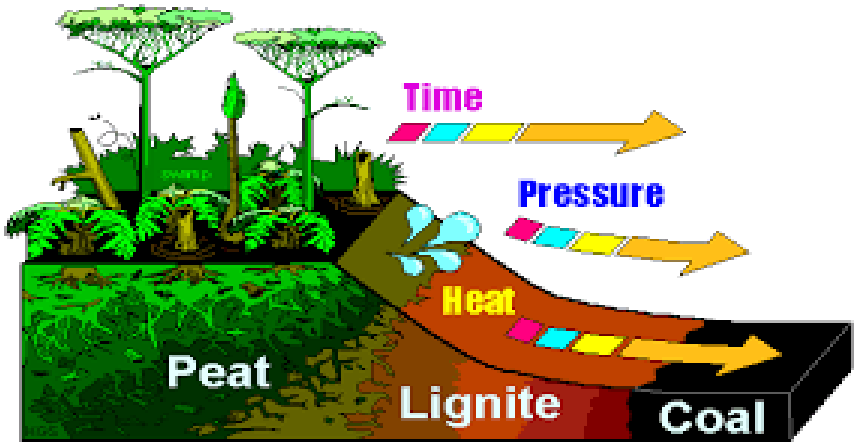


Figure 5. 1. Formation of Coal

Fuel	**Percentage of carbon**	**Calorific value (k.cal/kg)**	**Applications**
Wood	50	4000-4500	Domestic fuel
Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	In households and for steam raising

Table 5.3. Percentage of Carbon in types of Coal

Analysis of Coal:-

The analysis of coal is helpful in its ranking.

The assessment of the quality of coal is carried out by these two types of analyses.

1. Proximate analysis
2. Ultimate analysis

a. Proximate analysis: In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

- Moisture content
- Volatile matter
- Ash
- Fixed carbon

Moisture Content: About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110 ^{0}C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.

$$Percentage\ of\ \text{Moisture} = \frac{Loss\ in\ Weight}{Weight\ of\ coal\ taken} \times 100$$

Volatile Matter: The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 + 20C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of Volatile Matter} = \frac{Loss\ in\ Weight}{Weight\ of\ coal\ taken} \times 100$$

Ash: The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 + 50 C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis. Thus,

$$\text{Percentage of Ash} = \frac{Weight\ of\ ash\ left}{Weight\ of\ coal\ taken} \times 100$$

Fixed carbon:

Percentage of fixed carbon = 100 - % of (Moisture + Volatile matter + ash)

Significance of proximate analysis

Proximate analysis provides following valuable information's in assessing the quality of coal.

Moisture: Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover over, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".

Volatile matter: a high volatile matter content means that a high proportion of fuel will distil over as gas or vapors, a large proportion of which escapes un-burnt, So, higher volatile content in coal s undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinkers, which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

Fixed carbon: Higher the percentage of fixed carbon, greater is it's calorific and betters the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

b. Ultimate analysis:

This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

Carbon and Hydrogen: About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$C + O_2 \rightarrow CO_2$

$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$ $H_2 + ½ O_2 \rightarrow H_2O$

$CaCl_2 + 7 H_2O \rightarrow CaCl_2.7H_2O$

$$\text{Percentage of Carbon} = \frac{Increase\ in\ weight\ of\ KOH\ \times 12}{Weight\ of\ coal\ taken\ \times 44} \times 100$$

Nitrogen: About 1 gram of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\text{Percentage of Nitrogen } = \frac{Volume\ of\ acid\ consumed\ by\ \mathrm{NH_3} \times Normalityof\ Acid\ \times 14nx}{Weight\ of\ Caol\ taken} \times 100$$

Sulphur: Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted in to Sulphate. The washings are treated with Barium chloride solution, when Barium- sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of Sulpher } = \frac{Weight\ of\ BaSO_4 \times 32}{Weight\ of\ Caol\ taken\ \times 233} \times 100$$

Ash: The residual coal taken in the crucible and then heated without lid in a muffle furnace at $700 + 50^0$c for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis. Thus,

$$\text{Percentage of Ash } = \frac{Weight\ of\ Ash\ left}{Weight\ of\ Coal\ taken} \times 100$$

Oxygen: It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

Percentage of Oxygen = 100 – percentage of (C + H + S + N + Ash)

Significance of ultimate analysis:

Carbon and Hydrogen:

Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile mater and hence, it affects the use to which the coal is put.

Nitrogen: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little Nitrogen content.

Sulphur: Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2, SO_3, which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion.

Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

Oxygen: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Liquid Fuels: Liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum:-

Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust. Crude oil is a source of many liquid fuels that are in current use. The composition of crude petroleum approximately is C = 80-85%, H= 10-14% , S= 0.1-3.5% and N=0.1-0.5%.

Bomb calorimeter:

A calorimeter is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. Differential scanning calorimeters, isothermal micro calorimeters, titration calorimeters and accelerated rate calorimeters.

Construction of Bomb Calorimeter:

Our calorimeters require approximately 0.5g of sample matter (i.e. food) weighed in a crucible. We need to have the weight entered with four decimal places (i.e. 0.4972g) . Place crucible inside the stainless steel container ("the bomb vessel") and fill bomb vessel with 30 bar (435psi or 30 atm) of pure oxygen.

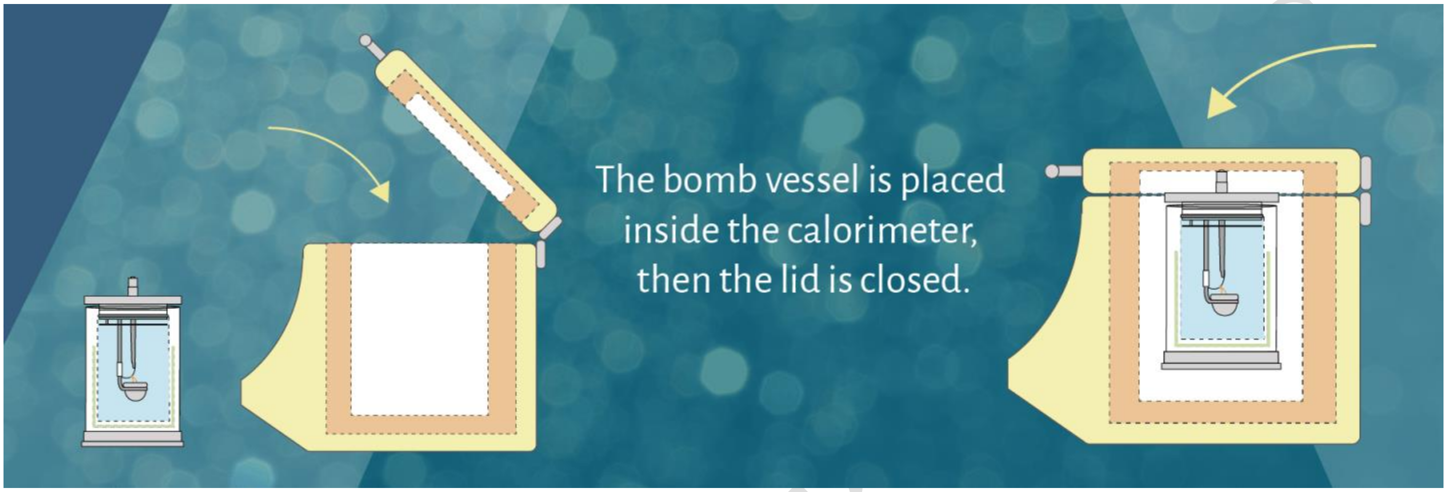


Figure 5.2 (a). View of Bomb Calorimeter

Place the filled bomb vessel inside the calorimeter and close the lid. The bomb vessel is now sealed and isolated from outside temperature influences. Once the bomb vessel temperature has stabilized in the bomb well, the sample is then ignited.

An electrical ignition charge instantly heats the ignition wire, which in turn burns the attached firing cotton. The burning cotton thread falls into the fuel sample below causing the sample to ignite.

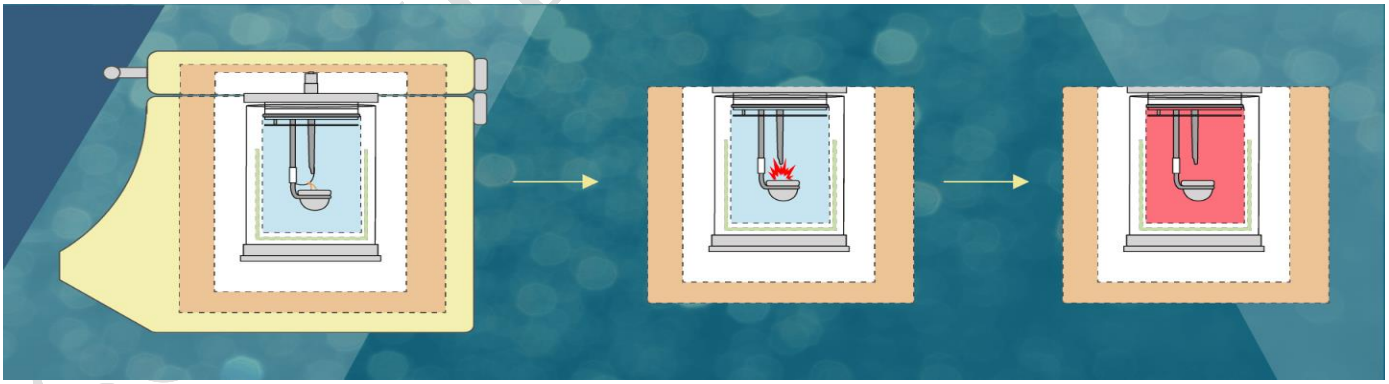


Figure 5.2(b). View of Bomb Calorimeter

During the burning of the fuel sample, the crucible can momentarily rise to above 1000 Deg C with the pressure spiking to 3 x the initial pressure. Within seconds, the heat of the reaction starts to dissipate into the bomb vessel and the pressure starts to subside.

To accurately measure the temperature of the vessel, sensitive high resolution temperature sensors are used, measuring every 6 seconds for the duration of the determination.

Once the determination is complete, typically within 4 minutes (depending on which model you have), the calorimeter calculates the Calorific Value (CV) of the fuel sample. At this point in time, the bomb vessel is removed from the bomb well to be cooled. Typically the bomb vessel is now between 8 to 14 Deg C higher in temperature.

Once the bomb vessel is sufficiently cooled in a cooler, it can be reused again.

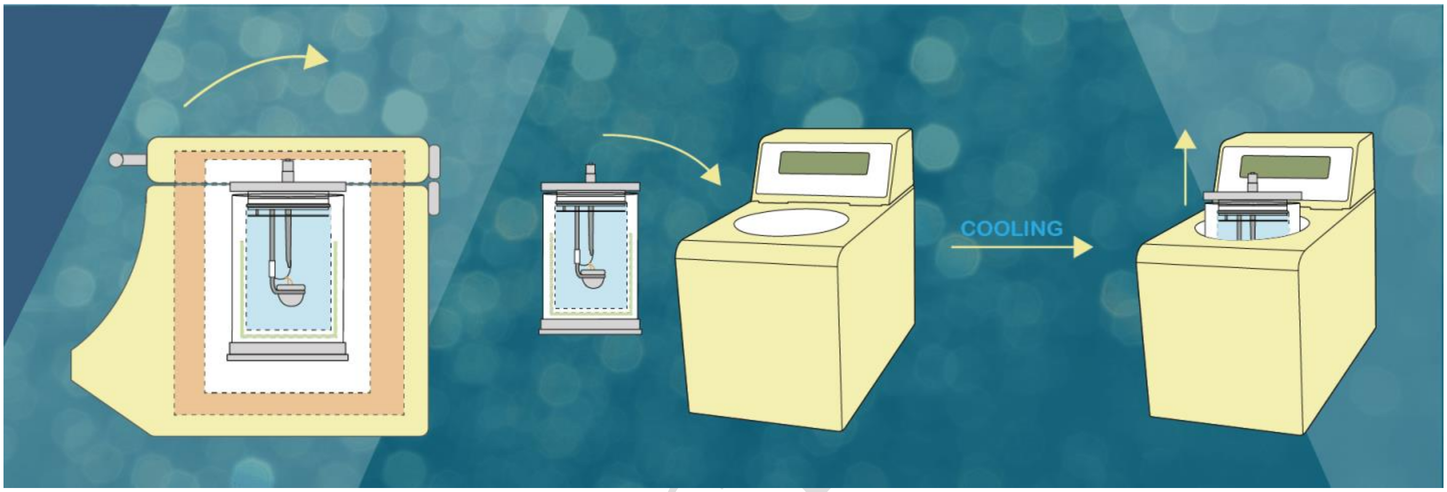


Figure 5.2(c).View of Bomb Calorimeter

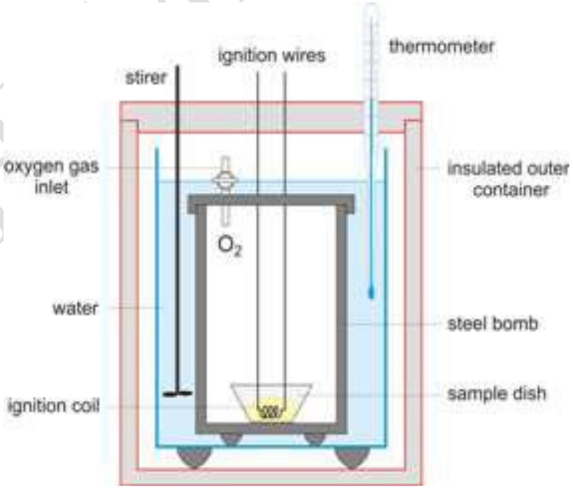


Figure 5.3 Bomb Calorimeter Internal view

Calculation of Bomb Calorimeter:

Weight of fuel (benzoic acid) taken in the crucible in x gm

Weight of water taken in calorimeter = W gm

Water equivalent of calorimeter, Stirrer, thermometer, bomb etc.,= w gm (water equivalent of apparatus = weight of apparatus X specific heat of material from which bomb Is made.

Initial temperature of water in calorimeter = t_1° C

Final temperature of water in calorimeter = t_2° C

Let higher calorific value of fuel = L cal/gm

Calculation:

Heat liberated by burning of fuel = xL calorie

Heat absorb by water and apparatus = [(W+w) × (t_2-t_1)

Heat liberated by furl = heat absorbed by water and apparatus

xL= [(W+w) × (t_2-t_1)

$$\mathrm{L} = \frac{(W+w)\times(\mathbf{t}_2-\mathbf{t}_1)}{\mathrm{x}}\,\mathrm{cal}/\boldsymbol{gm}$$

If H = percentage of hydrogen in fuel

$$(\mathrm{HCV})\mathrm{L} = \frac{9H}{100} = \text{mass of water from 1 gm of fuel} = 0.09\mathrm{H}$$

LCV= (HCV-0.09H × 587) cal/gm

Correction:

$$\mathrm{HCV} = \frac{[(W+w)\times(\mathrm{t}^2-\mathrm{t}^1) + \text{ cooling correction}] - [\text{Acid} + \text{Fusewire correction}]}{mass\ of\ fuel\ (x)}$$

Theoretical calculation of calorific value of fuel by Dulong Formula

Dulong's formula for calorific value from the chemical composition of fuel is

HCV = 1/100 [8,080 C + 34,500 (H – O/8)+ 2,240 S] kcal/kg

Where C, H, O, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water,

Carbonization of Coal:

Coke is the solid carbonaceous residue that remains after certain types of coal are heated to a high temperature out of contact with air. The process of heating coal in this manner is referred to as carbonization or coke making. High-temperature carbonization, with which this section is concerned, is practiced to produce a coke having the requisite properties for metallurgical use, as in blast furnaces or foundry cupolas. Low-temperature carbonization was once practiced widely to produce a coke suitable for residential heating, but residential furnaces are now fired almost exclusively by oil and natural gas.

High-temperature carbonization reactions

In high-temperature carbonization, coal is heated to temperatures of 900–1,200 °C (1,600–2,200 °F). At these temperatures, practically all the volatile matter is driven off as gases or liquids, leaving behind a residue that consists principally of carbon with minor amounts of hydrogen, nitrogen, sulfur, and oxygen (which together constitute the fixed-carbon content of the coal). Carbonization reactions can be illustrated in the following simplified manner:

The exact extent and nature of the products depend on the temperature and heating rate of the coal particles during the carbonization process.

Carbonization processes

For a high-temperature carbonizing process to be commercially satisfactory, it is necessary to (1) pass large quantities of heat into a mass of coal at temperatures up to 900 °C or more, (2) extract readily the completed coke from the vessel in which it is carbonized, (3) avoid atmospheric pollution and arduous working conditions for the operators, and (4) carry out the whole operation on a large scale and at a low cost.

Coke ovens:

Modern coke ovens can be as large as 6.5 metres (21 feet) high, 15.5 metres (50 feet) long, and 0.46 metre (1.5 feet) wide, each oven holding up to about 36 tons of coal. The coking time (i.e., between charging and discharging) is about 15 hours. Such ovens are arranged in batteries, containing up to 100 ovens each. A coking plant may consist of several such batteries. Large coking plants in the United States carbonize approximately 5,500,000 to 11,200,000 tons of coal annually, but older coking plants are still operating throughout the world with quite small ovens and annual throughputs of only 112,000 to 336,000 tons. Modern coke ovens are highly mechanized, thus minimizing atmospheric pollution and lessening the labour needed. Massive machines load coal into each oven, push coke sideways away from the oven, and transfer red-hot coke to a quenching station, where it is cooled with water. In some plants the red-hot coke is cooled in circulating inert gases, the heat abstracted being used to generate steam. This is called dry quenching.

Recovery of by product:

- **Recovery of Tar:**

Coal, oven gas its pass to a tower in which liquid ammonia and sprayed tar and dust are removed.

- **Recovery of ammonia:**

The gases are passed to another tower in which is sprayed, NH_3 gas goes into solution.

- **Recovery of naphthalene**

Napthane are removed to avoid blockage of pipe.

- **Recovery of benzene:**

The remaining gases are sprayed with petroleum and benzene and homologues can be covered.

- **Recovery of H_2S :**

The resultant gases are passed over moist Fe_2O_3 to retain H_2S

Significance of Recovery of by product:

The coke oven gas are mainly removed from cola gas because of their utility value and also improve the quality of gas

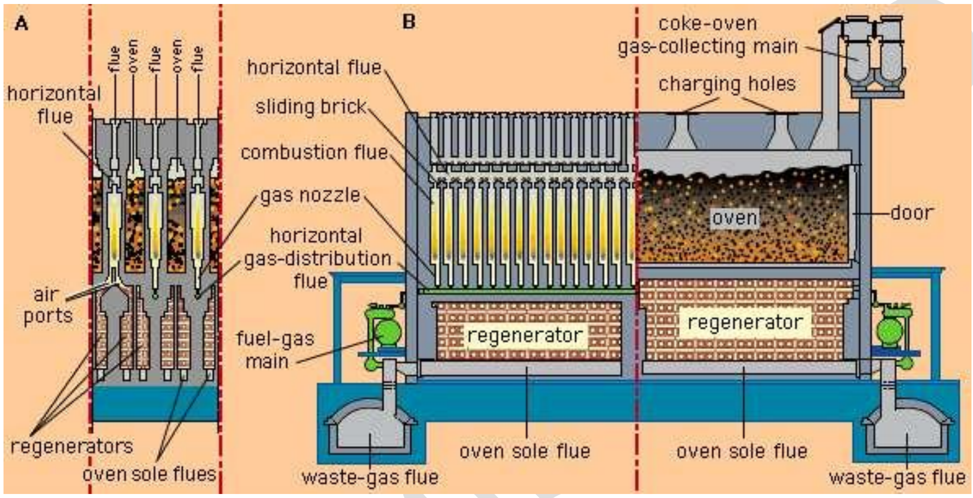


Figure 5.4. coke oven

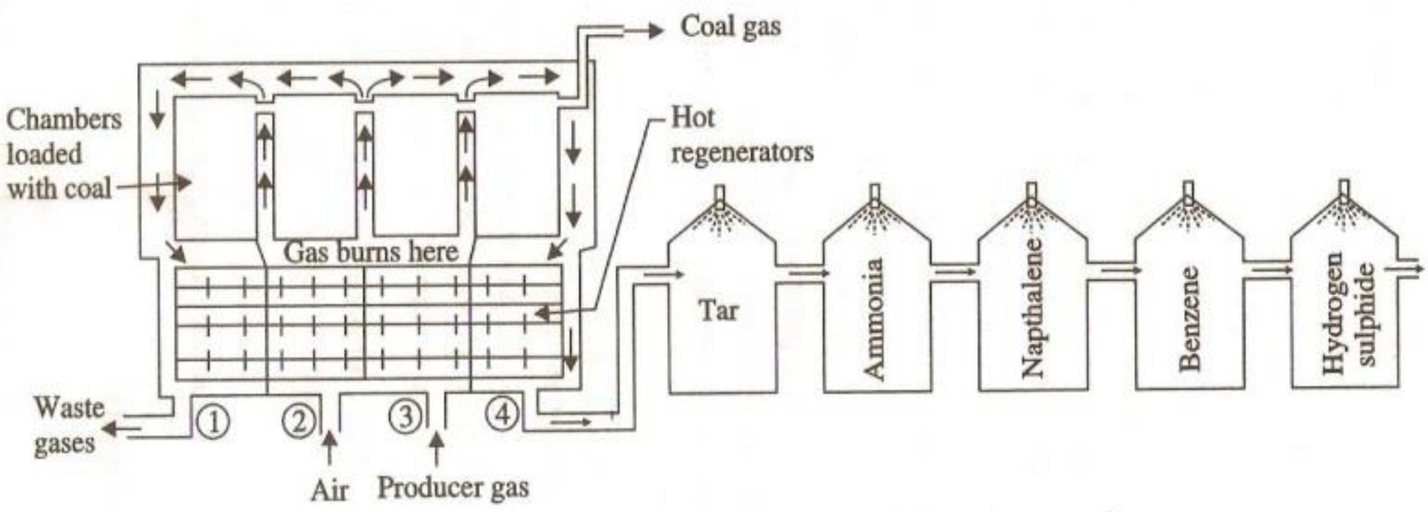


Figure 5. 5. Otto-Hoffman by product

Coking coals

Although chemical composition alone cannot be used to predict whether a coal is suitable for coking, prime coking coals generally have volatile matter contents of 20 to 32 percent—i.e., the low- and medium-volatile bituminous ranks. When heated in the absence of air, these coals first become plastic, then undergo decomposition, and finally form coke when the decomposed material resolidifies into a hard and porous solid. In addition to the coal rank, various maceral groups exhibit strong effects on coking behaviour and the resultant coke properties. In general, the vitrinite and liptinite maceral groups are considered reactive and inertinite macerals unreactive.

The preparation of the coal charge for coke ovens becomes increasingly important as prime coals become less available. Formerly, single coals were used on their own to yield good strong coke, but today there is rarely enough of such coal to supply large plants. Consequently, less good coking coals have to be used. However, by judicious selection and crushing followed by intimate blending, equally good cokes can be made from a variety of coals. Broadly speaking, suitable blends can be obtained by mixing high-volatile with low-volatile coals, and often small additions of ground, small coke and anthracite are helpful. Drying the coal and even preheating it to 200 °C (390 °F) may also be helpful and economic. Thus, in modern plants the facilities for preparing the blend may be quite elaborate.

Types and sizes of coke

During the last hours in the ovens, the coke shrinks and fissures. When it is discharged, it is partly in discrete pieces up to 200 millimeters (8 inches) long or more. After the coke leaves the quencher, it is screened into various sizes and the larger pieces may have to be cut. The bulk of oven coke (sized about 40 to 100 millimeters) is used throughout the world in blast furnaces to make iron. Exceptionally large strong coke, known as foundry coke, is used in foundry cupolas to melt iron. Coke in 10- to 25-millimetre sizes is much used in the manufacture of phosphorus and calcium carbide; from the latter, acetylene, mainly for chemical purposes, is made. Large quantities of the smallest sizes (less than 12 millimeters), known as coke breeze, are suited for sintering small iron ore prior to use in blast furnaces. Any surplus breeze serves as an industrial boiler fuel.

By-products

Another important and expensive part of the coking plant is the by-product plant. Hot tarry gases leaving the ovens are collected, drawn away, and cooled. Crude tar separates and is removed for refining. The crude coke oven gas is scrubbed free of ammonia, and then usually crude benzol is removed from it. Some of the remaining gas (mainly methane, hydrogen, and carbon monoxide) is used to heat the coke ovens, while the rest is available for use in blast furnaces and in soaking pits for heating steel ingots.

Refining of Petroleum:-

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

FRACTIONAL DISTILLATION

Fractional distillation is the process of taking a chemical mixture and using heat to separate out the various components in that mixture. When you think of this process, the first word that should come to mind is separation. In other words, as a chemist in the laboratory, you would use this process when you are interested in isolating one or more compounds present in a mixed sample containing as few as two and up to an endless amount of compounds.

Because heat is used in this separation technique, boiling points play a very important role in fractional distillation. Essentially, you are able to determine what given component is separated out from the mixture by its boiling point. Remember that boiling point is a physical property. Specifically, it is the temperature where a phase change occurs from liquid to vapor.

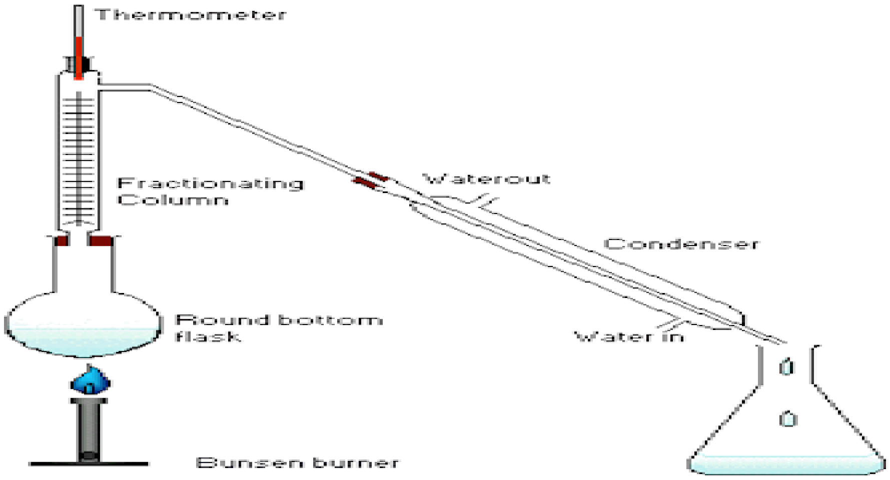


Figure 5.6. Fractional Distillation

Naphtha: It is derived as a refine petroleum distillate containing main saturated ring structure.

Gasoline: Gasoline is straight run petrol from refinery which needs further reforming and cracking.

Straight run naphtha: – A major source of petroleum refinery. The over head liquid distillate refinery is called benzene or straight run naphtha.

Refining of petroleum is done in different stages:

Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and $MgCl_2$ it present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.

Fractional distillation: Heating of crude oil around 400^0C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

Advantages of Fractional Distillation:

1. It's easy to implement.
2. It's highly effective and efficient.
3. It helps produce much-needed fuel.

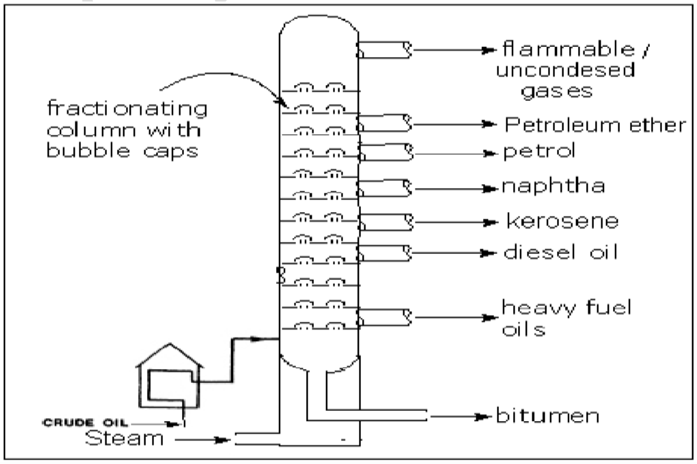


Figure 5.7. Refining of Petroleum by fractional distillation

REFORMING PROCESS

Thermal reforming

In a thermal reforming process, the feedstock, such as 205°C (400°F) end-point naphtha or a straight-run gasoline, is heated to 510-595°C (950-1100°F) in a furnace, much the same as a cracking furnace, with pressures from 400 to 1000 psi (2758 to 6895 kPa). As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha and then enters a fractional distillation tower where the heavy products are separated. The remainder of the reformed material leaves the top of the tower and is separated into gases and reformate. The reformate has a high octane number due to cracking of the longer-chain paraffins into higher-octane olefins.

The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (about 1%). The amount and quality of gasoline, known as reformate, is very dependent on the temperature. As a rule, the higher the reforming temperature, the higher the octane number, but the lower the yield of reformate.

Catalytic reforming

Catalytic reforming is a process whereby light petroleum distillates (naphthas) are contacted with a platinum-containing catalyst at elevated temperatures and hydrogen pressures ranging from 345 to 3,450 kPa (50–500 psig) for the purpose of raising the octane number of the hydrocarbon feed stream. The low octane, paraffin-rich naphtha feed is converted to a high-octane liquid product that is rich in aromatic compounds. Hydrogen and other light hydrocarbons are also produced as reaction by-products. In addition to the use of reformate as a blending component of motor fuels, it is also a primary source of aromatics used in the petrochemical industry.

The need to upgrade naphthas was recognized early in the 20th century. Thermal processes were used first but catalytic processes introduced in the 1940s offered better yields and higher octanes. The first catalysts were based on supported molybdenum oxide, but were soon replaced by platinum catalysts. The first platinum-based reforming process, UOP's Plat forming^{-} process, came on-stream in 1949. Since the first Plat forming unitwas commercialized, innovations and advances have been made continuously, including parameter optimization, catalyst formulation, equipment design, and maximization of reformate and hydrogen yields. The need to increase yields and octane led to lower pressure, higher severity operations. This also resulted in increased catalyst coking and faster deactivation rates.

The first catalytic reforming units were designed as semi regenerative (SR), or fixed bed units, using Pt/alumina catalysts. Semi regenerative reforming units are periodically shut down for catalyst regeneration. This involves burning off coke and reconditioning the catalyst's active metals. To minimize catalyst deactivation, these units were operated at high pressures in the range of 2,760 to 3,450 kPa (400–500 psig). High hydrogen pressure decreases coking and deactivation rates.

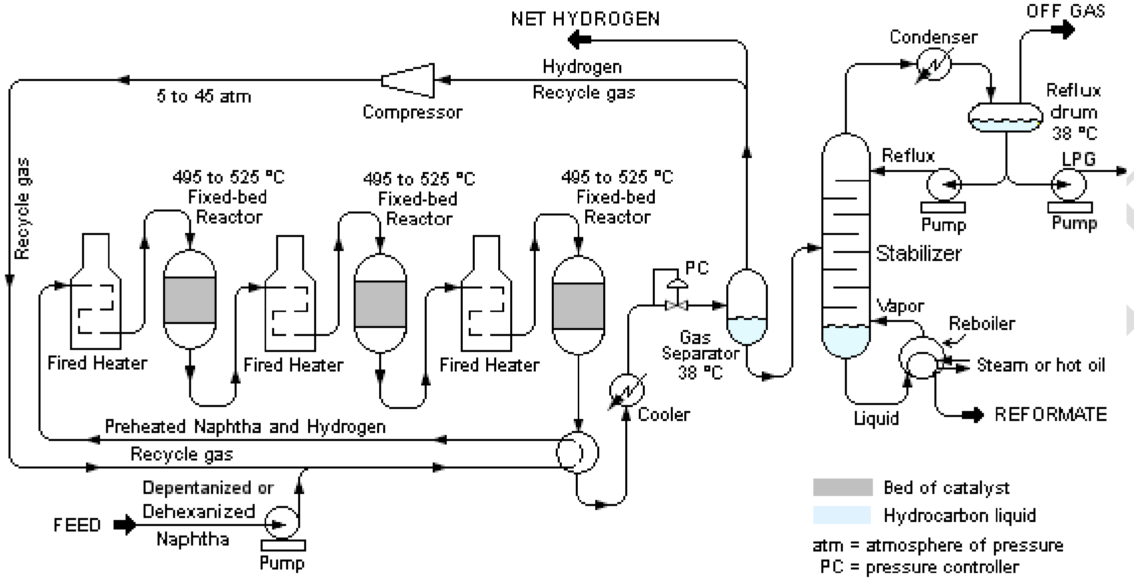


Figure 5.8.Fixed Bed Catalytic reforming Process

Cracking:

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking. Cracking

Example. $C_{10}H_{12} \rightarrow C_5H_{12} + C_5H_{10}$

(Decane) (Pentane) (Pentene) Cracking is mainly two types:

1. Thermal Cracking
2. Catalytic Cracking

Thermal cracking: If the cracking takes place at high temperature then it is thermal cracking.

It may take place by two ways. They are

i) Liquid-phase Thermal cracking

ii) Vapor-phase Thermal cracking

The liquid phase cracking takes place at 475^0C to 530^0C at a pressure 100kg/cm^2. While the vapor phase cracking occurs at 600 to 650^0C at a low pressure of 10 to 20 kg/cm^2

Catalytic cracking: If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. Catalytic cracking may be fixed bed type or moving bed type.

i) Fixed bed catalytic cracking: The oil vapors are heated in a pre-heater to cracking temperatures (420 – 450 ^{0}C) and then forced through a catalytic chamber maintained at 425 – 450 ^{0}C and 1.5 kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed. The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a 'stabilizer', where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

The advantages of catalytic cracking over thermal cracking are as follows

- Catalytic cracking takes place at lower temperature and pressure (3000C -400^{0}C and 1-5kg/cm^2) as compared to that of thermal cracking (500^{0}C-600^{0}C and kg/cm^2)
- Catalytic cracking yields a higher quantity of branched-chain, unsaturated, aromatic hydrocarbons as compared to thermal cracking.
- Catalytic cracking is a better-controlled process than thermal cracking.
- Petrol obtained by catalytic cracking has lesser sulfur content.

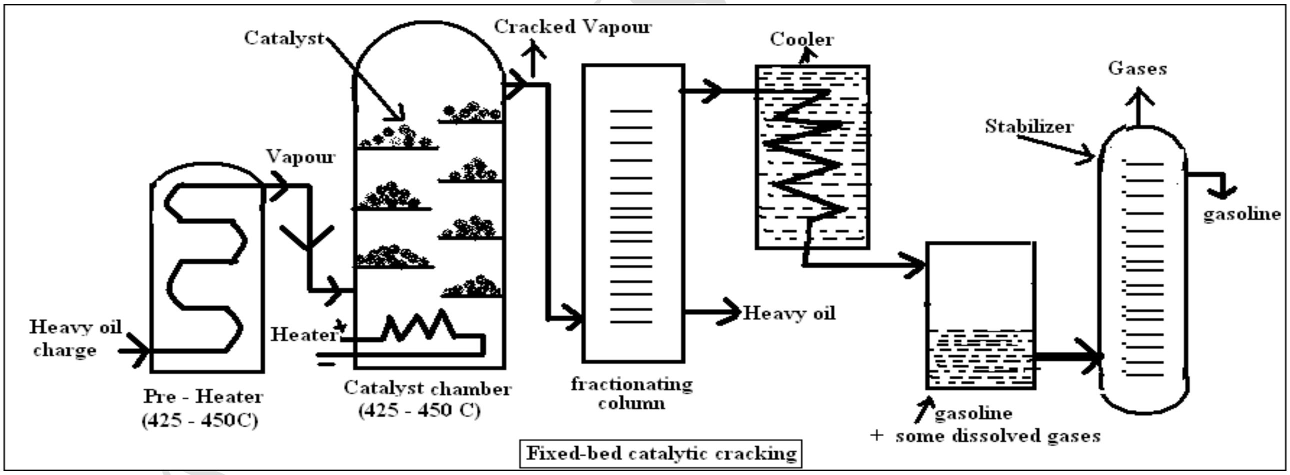


Figure 5.9.Fixed bed catalytic cracking

ii). Moving bed catalytic cracking:

Heated oil vapors go up in the reactor and catalyst comes down through the hopper which is the significance in the moving bed catalytic cracking process. After the cracking of vapors the spent catalyst is removed from the bottom. It is regenerated and sent again to the catalyst hopper through the elevators. The cracked vapors after the separation of dust separated go to the fractionators where gas oil is separated from vapors of gas and gasoline. Gas oil is withdrawn from the bottom. The gas and the gasoline vapors are condensed in the condenser and are separated.

Other methods of synthesis of gasoline are by polymerization, alkylation, Fischer-Tropsch method and liquefaction of coal or hydrogenation of coal.

Normally the gases obtained from the cracking of petroleum are ethylene, propene, butene and saturated hydrocarbons like methane, ethane, propane and butane. Polymerization also classified by catalysis to obtain motor fuel.

Advantage of moving bed catalytic cracking:

1. Better contact with the feed and catalyst, enabling uniform temperature and efficient transfer
2. Catalyst can be regenerated and used again for cracking

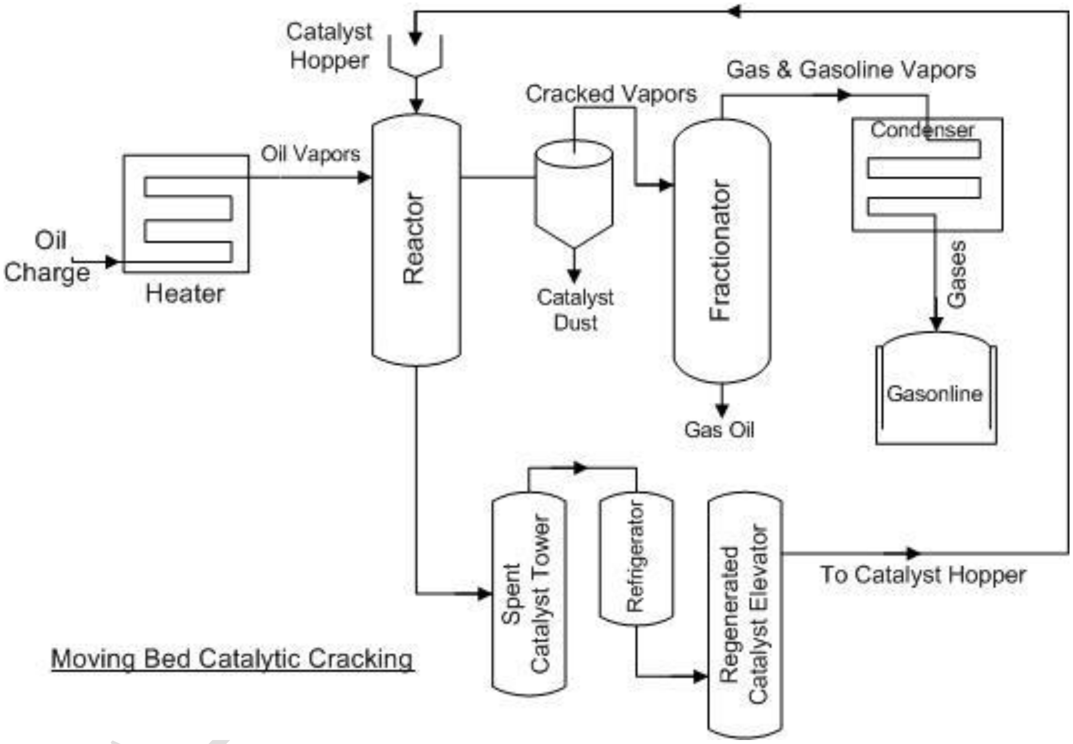


Figure 5.5 Moving Bed catalytic Cracking

Knocking

Premature and instantaneous ignition of petrol – air (fuel-air) mixture in a petrol engine, leading to production of an explosive violence is known as knocking.

In an internal combustion engine, a mixture of gasoline vapor and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio. The efficiency of an internal combustion engine increases with the compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.

Some of the effects of knocking or detonation are:

- Carbon deposits on liners and combustion chamber
- Mechanical damage
- Increase in heat transfer
- Noise and roughness
- Decrease in power output and efficiency

Preignition

The knocking can be controlled or even stopped by the following methods:

- Increasing engine r.p.m
- Reducing pressure in the inlet manifold by throttling
- Retarding spark
- Making the ratio too lean or rich, preferably latter.
- Water injection increases the delay period as well as reduces the flame temperature.

Use of high octane fuel can eliminates detonation. High octane fuels are obtained by adding additives known as dopes like tetraethyl lead, benzol, xylene to petrol.

Chemical structure and knocking:

The tendency of fuel constituents to knock in the following order.

Straight-chain paraffins > Branched-chain paraffins (i.e., iso paraffins) > Olefins > Cyclo paraffins (i.e., naphthalenes) > aromatics.

Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffin and so on.

Octane number:

The knocking characteristic of a fuel can be easily expressed by octane number. The anti- knocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereas the anti-knock value of Iso-octane is approximately taken as 100 because Iso-octane knocks very little. Actually the octane number is the percentage of Iso-octane in a mixture of n-heptane in order to matches the knocking characteristics of the fuel. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20

mixture in Iso-octane and n-heptanes. Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead (C2H4)4Pb and diethyl-telluride (C2H4)2Te

A sample of petrol gives as much knocking as a mixture of 80% Iso octane and 20 % n-Heptane, its octane number is 80.

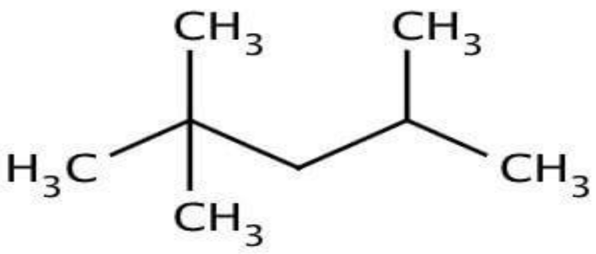


Figure 5. 6(a). 2, 2, 4- Trimethyl pentane (Iso-octane)

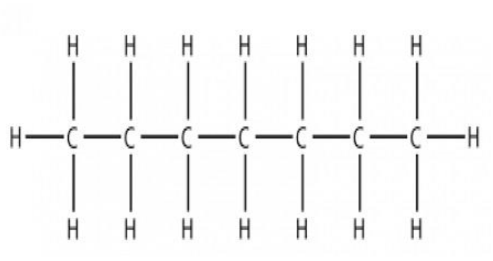


Figure 5.11(b). n-heptane

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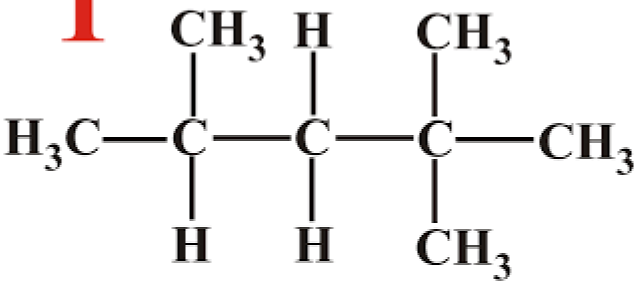


Figure 5.7. Isooctane (2,2,4 Trimethyl pentane

Octane rating: It has been found that n-heptane, Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – Trimethyl pentane). It gives very little knocking, so its anti-knock value has been given as '100'. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test.

In knocking characteristics. In this way, an "80-octane" fuel is one which has the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

Advantages:

Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way.

When tetra ethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

The mechanism of action is as follows:

First TEL will be transformed into finely divided particles of PbO which looks like a cloud. This takes place in the cylinder. Then the PbO particles react with hydrocarbon peroxide molecules formed, thus slowing down the oxidation process and prevent early detonation. Thus either knocking may be stopped or greatly reduced.

Disadvantages: Deposits of PbO are harmful to engine. So PbO must be eliminated from the engine. For this purpose, little amount of ethylene dibromide is added to petrol. It converts the harmful PbO to volatile $PbBr_2$ and eliminated through exhaust. Presence of any sulphur compounds reduces the efficiency of TEL.

Cetane Number:-

Cetane number is defined as the percentage of hexadecane (n-Cetane) present in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristic of diesel fuel in test. Generally diesel fuels with Cetane numbers of 70-80 are used.

The knocking tendency of diesel fuel is expressed in terms of Cetane number. Diesel engines works on the principle of compression ignition. Cetane (n-Cetane) or hexadecane [$CH3 – (CH_2)_{14}-CH_3$] is a saturated hydrocarbon, its Cetane number is arbitrarily fixed as 100. A methyl naphthalene is an aromatic hydrocarbon, its Cetane number is arbitrarily fixed as zero.

Synthetic Petrol

Synthetic fuel or synfuel is a liquid fuel, or sometimes gaseous fuel, obtained from syngas, a mixture of carbon monoxide and hydrogen, in which the syngas was derived from gasification of solid feedstocks such as coal or biomass or by reforming of natural gas.

Common ways for refining synthetic fuels include the Fischer–Tropsch conversion,[1] methanol to gasoline conversion, or direct coal liquefaction.

(a)Bergius process (indirect method):

The Bergius process is a method of production of liquid hydrocarbons for use as synthetic fuel by hydrogenation of high-volatile bituminous coal at high temperature and pressure. It was first developed by Friedrich Bergius in 1913. In 1931 Bergius was awarded the Nobel Prize in Chemistry for his development of high pressure chemistry.

1. Finely powdered coal + heavy oil+ catalyst powder (tin or nickel) is made into a paste.
2. The paste is pumped along with hydrogen gas into the converter, where the paste is heated to 400-450ċ under a pressure of 200-250atm.
3. During this process hydrogen combine with coal to form saturated higher hydrocarbons, which undergo further decomposition at higher temperature to yield mixture of lower hydrocarbons.
4. The mixture is led to a condenser, where the crude oil is obtained.

The crude oil is then fractionated to yield.

Gasoline (ii) Middle oil (iii) heavy oil

- **Middle oil:** The middle oil is further hydrogenated in vapors phase to yield more gasoline.
- **Heavy oil:** The heavy oil is recycled for making paste with fresh coal dust. It is dank and viscous due to high ratio of aromatics and nephatha to linear alkane and high amount of nitrogen, sulphur, oxygen.
- **Gasoline:** The yield of gasoline is about 60% of the coal.

About 60% of coal is converted into crude oil which is refine fractional distillation.

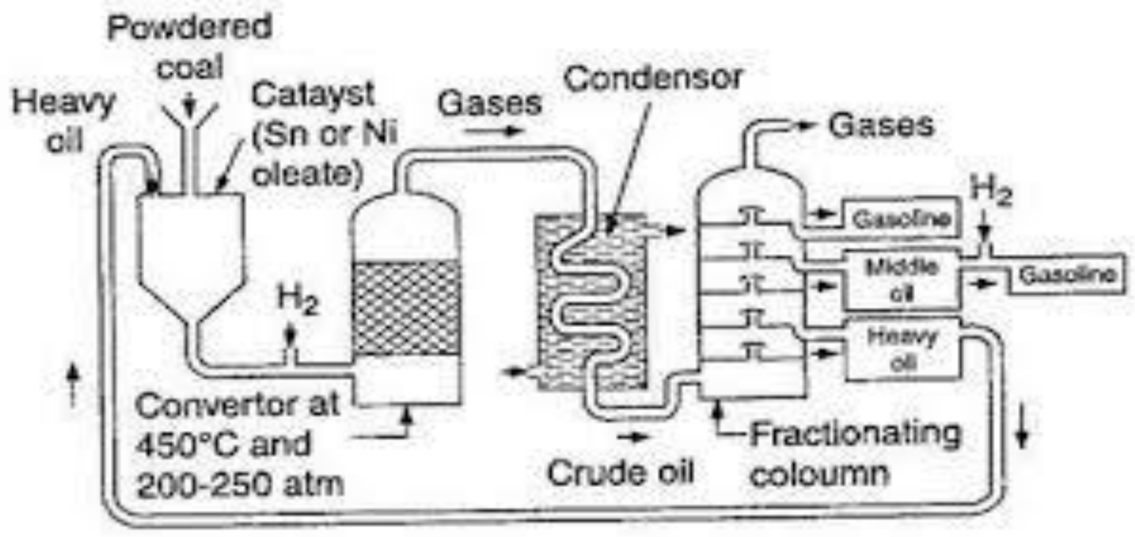


Figure 5.8. Bergius process of hydrogenation of coal to gasoline

b. Fischer- Tropsch process (indirect method):

In this process coal is first converted into coke. Then water gas is produced by passing steam over red hot coke

$$C + H_2O \xrightarrow{1200\dot{c}} \underset{\text{(Water gas)}}{CO + H_2}$$

1. The water gas is mixed with hydrogen and the mixture is purified by passing through $Fe_2O_3 + Na_2CO_3$ (to remove sulphur compounds).
2. The purified gas is compressed to 5 to 25 atm and then led through a converter, which is maintained at a temperature of 200-300°C.
3. The converter is provided with a catalyst bed consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts kieselgurh earth.
4. A mixture of saturated and unsaturated hydrocarbon is produced as a result polymerization.

$$n\,CO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$
$$n\,CO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

5. The out coming gaseous mixture is led to condenser, where the liquid crude oil is obtained.

The crude oil is fractionated to yield (i) Gasoline and (ii) Heavy oil.

The heavy oil is used for cracking to get more gasoline.

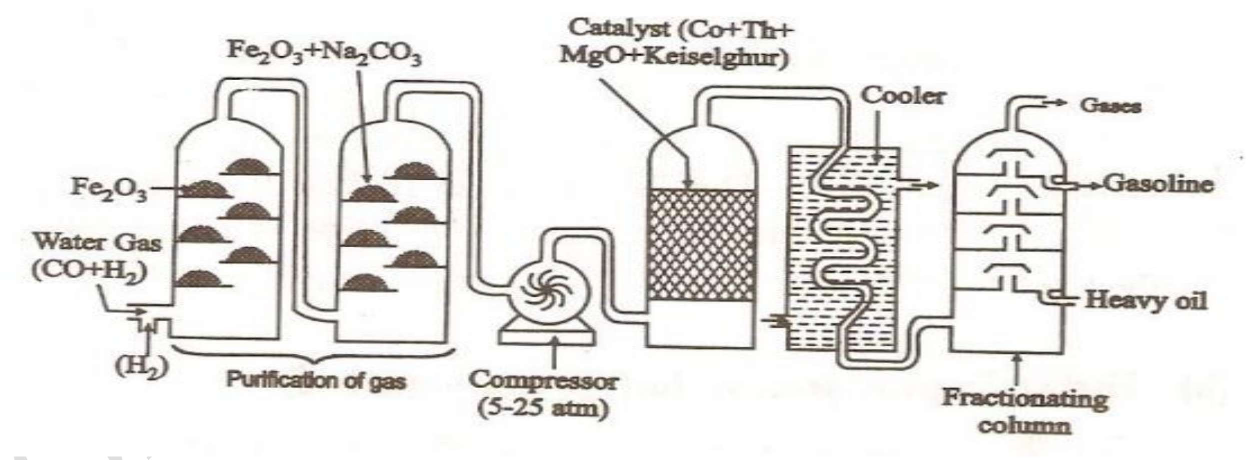


Figure 5.13.. Fischer-Tropsch process

The whole process is exothermic therefore the hot products lead to cooler and liquid resembling to gasoline to obtain, which is further purify to get gasoline and heavy oil. Heavy oil can be reused for cracking to get more gasoline.

Gaseous Fuels:-

The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. These are classified into two types.

1. Primary fuels Ex:- Natural gas
2. Secondary fuels ex: - Coal gas, producer gas, water gas.

Natural Gas:-

The natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons.

If the lower hydrocarbons are present, the gas is called dry gas or lean gas but if the hydrocarbons having the higher molecules are present, the gas is known as rich or wet gas.

The average composition of natural gas is as follows. Methane – 88.5%, Ethane – 5.5%, Propane – 3.7%

Butane – 1.8%,

Pentane, hydrogen and higher hydrocarbons – 0.5%

The calorific value of natural gas varies from 8000-14000 K.cal/m^3.

Applications:-

- It is an excellent domestic fuel and industrial fuel.
- It is also used as raw material for the manufacture of carbon-black, methanol, formaldehyde etc.
- Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.

LPG (Liquefied Petroleum Gas)

The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products. Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG are n-butane, Iso butane, butylenes and propane (traces of propene and ethane). The hydrocarbons are in gaseous state at room temperature and 1 atmospheric pressure but can be liquefied under higher pressure.

LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides which are added specially for safety measure.

Characteristics of LPG:-

- It has high calorific value (27,800 kcal/m^3)
- It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
- It gives moderate heat which is very good for cooking
- Its storage is simple. It is colourless

- It has tendency to mix with air easily
- Its burning gives no toxic gases though it is highly toxic
- It neither gives smoke nor ash content
- It is cheaper than gasoline and used as fuel in auto vehicles also
- It is dangerous when leakage is there

Applications:

- **In Food industry:** LPG is widely used in the food industry like hotels, restaurants, bakeries, Canteens etc. Low sulphur content and controllable temperature makes LPG the most Preferred fuel in the food industry.
- **In Glass & Ceramic**: The use of a clean fuel like LPG enhances the product quality thereby reducing technical problems related to the manufacturing activity of glass and ceramic products.
- **In Building Industry:** LPG being a premium gaseous fuel makes it ideal for usage in the Cement manufacturing process.
- **In Automotive Industry:** The main advantage of using automotive LPG is, it is free of lead, Very low in sulphur, other metals, aromatics and other contaminants.
- **In Farming industry:** LPG in the farming industry can be used for the following:

a. Drying of crops
b. Cereal drying
c. Curing of tobacco and rubber
d. Soil conditioning
e. Horticulture etc

LPG is used in metal industry, aerosol industry, textile industry and it can also be used in Steam rising.

CNG (Compressed Natural Gas)

Natural gas contains mainly CH_4. When natural gas is compressed at high pressure (1000atm) or cooled to -160^oC, it is converted to CNG. It is stored in cylinder made of steel. It is now replacing gasoline as it releases less pollutant during its combustion. In some of the metro cities, CNG vehicles are used to reduce pollution.

Characteristics of CNG:-

- Natural Gas being lead/sulphur free, its use substantially reduces harmful engine emissions.
- Natural gas being lighter than air, will rise above ground level and disperse in the atmosphere, in the case of a leakage.
- Natural Gas in the gaseous state, and is colourless.
- Predominantly Methane is available in the lean gas, hence CNG contains mostly methane.

Applications:-

- It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and Air conditioners.
- Natural gas is also consumed in homes for space heating and for water heating
- It is used in stoves, ovens, clothes dryers and other appliances.
- In some of the metro cities, CNG vehicles are used to reduce pollution.

Combustion

Combustion may be defined as the exothermic chemical reaction, which is accompanied by heat and light. It is the union of an element or a compound with oxygen.

Example: $C(s) + O_2 (g)\ CO_2 (g) + 97$ kcal

In common fuels it involves the burning of carbon and hydrogen in air and also to a much smaller extent of sulphur.

The presence of moisture in coal is undesirable, because it causes waste of heat; moisture may be present in coal naturally or by adding i.e. moistening the coal before use. The presence3 of some sort of moisture in coal helps to keep the temperature of the fire bars low and prevents the formation of clinkers. The excess presence of moisture leads to heavy smoking and leads to slow starting of combustion process. Optimum free moisture content is 7 to 9% when coal has minimum density. The presence of moisture in combustion makes the combustion process successful.

Calorific value:

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of w fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”. **Or**

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and in usually expressed as cal gm^{-1} or kcal gm^{-1} or B.Th.U. **Or**

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

a. Calorie 3. British thermal unit (B.Th.U) and b. Kilocalorie4. Centigrade heat unit (C.H.U)

Calorie: It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

1 k.cal = 1000 cal

Kilocalorie: This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

1 k.cal = 3.968 B.Th.U

British thermal unit (B.Th.U): This is the unit of heat in English system, it is defined as "the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.

1 B.Th.U = 252 cal = 0.252 k.cal.

Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

1 k.cal = 3.968 B.Th.U = 2.2 C.H.U

Inter conversion of various units of heat:

On the basis that 1 kg = 2.2 lb and 1 ^{0}C = 1.8 ^{0}F we have

1 k.cal = 1000 cals = 3.968 B.Th.U = 2.2 C.H.U

1 B.Th.U = 252 cals Units of calorific value:

For solid or liquid fuels: cal/g or k.cal/kg, B.Th.U/lb For gaseous fuels: k.cal/cubic meter or k.cal/m^3 B.Th.U/ft^3 or B.Th.U/cubic feet

Relation between various units:

1 k.cal/kg = 1.8 B.Th.U/lb = 1 cal/g

1 k.cal/m^3 = 0.1077 B.Th.U/ft^3

1 B.Th.U/ft^3 = 9.3 k.cal/m^3

Gross calorific value:-

Gross calorific value is the heat liberated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature. This heat includes the latest heat of condensation of water. Because when a fuel containing hydrogen is burnt, the hydrogen present is converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam, so liberated, is included in the gross calorific value.

Higher calorific value (HCV) or gross calorific value is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to 60 ^{0}F or 15 ^{0}C.

Net calorific value or lower calorific value (LCV): lower calorific value is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape.

Net calorific value is the gross calorific value excluding the latent heat of condensation of water (the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

LCV or NCV = HCV – Latent heat of water vapors formed

Net calorific value = Gross calorific value – (Mass of hydrogen per weight of fuel burnt x 9 x latent heat of vaporization of water).

Net calorific value = Gross calorific value – 52.83 x %H Where % H = percentage of hydrogen.

The gross and net calorific values of coal can be calculated by bomb calorimeter.

Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

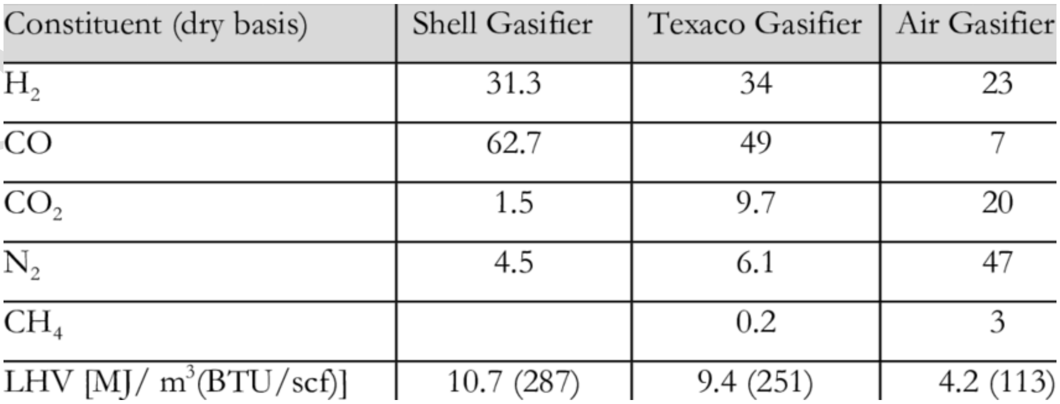
Manufacture of Coal Gas:

Coal gas is a flammable gaseous fuel made from coal and supplied to the user via a piped distribution system. It is produced when coal is heated strongly in the absence of air. Town gas is a more general term referring to manufactured gaseous fuels produced for sale to consumers and municipalities.

Coal gas contains a variety of calorific gases including hydrogen, carbon monoxide, methane, ethylene and volatile hydrocarbons together with small quantities of non-calorific gases such as carbon dioxide and nitrogen.

Composition

The composition of coal gas varied according to the type of coal and the temperature of carbonization. Typical figures were:



Constituent (dry basis)	Shell Gasifier	Texaco Gasifier	Air Gasifier
H_2	31.3	34	23
CO	62.7	49	7
CO_2	1.5	9.7	20
N_2	4.5	6.1	47
CH_4		0.2	3
LHV [MJ/ m^3(BTU/scf)]	10.7 (287)	9.4 (251)	4.2 (113)

Table 5.3. Average Composition of coal gas

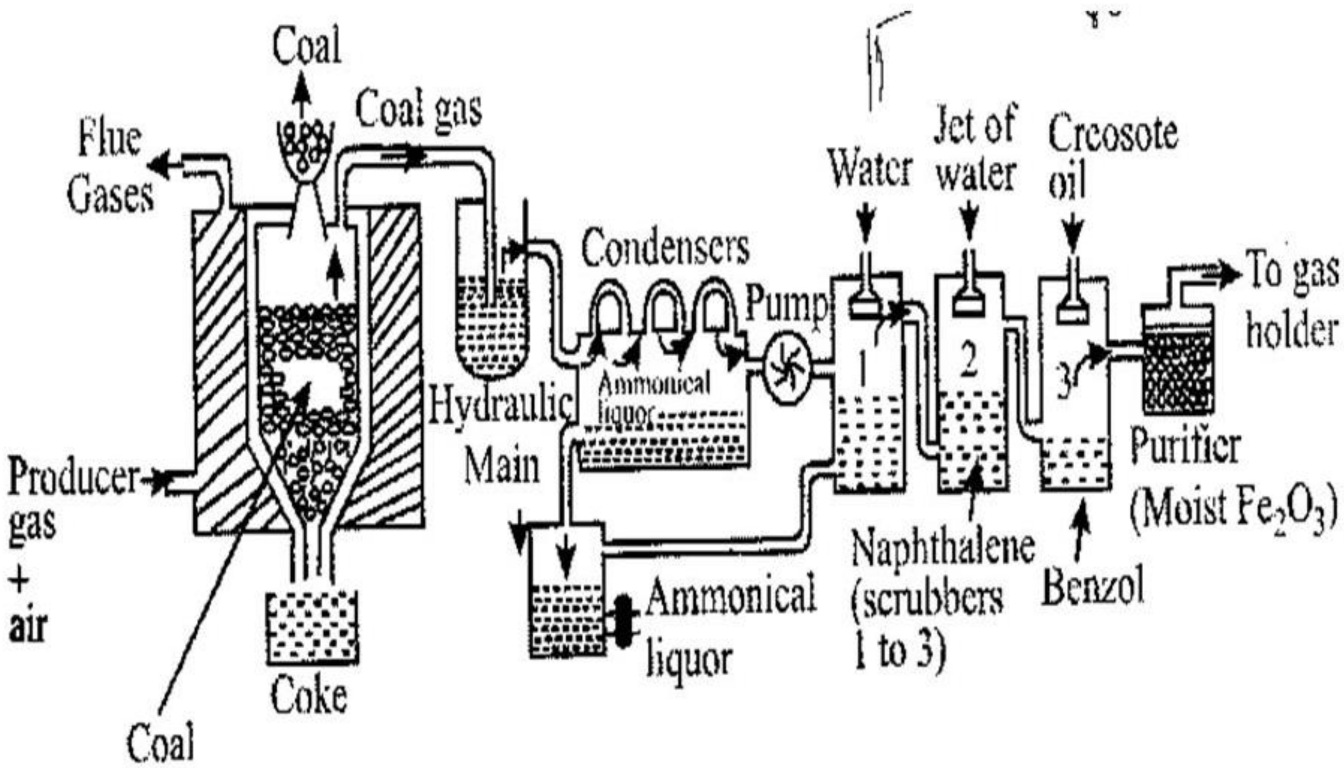


Figure 5.14. Manufacture of coal gas

Process:

Coal is obtained of carbonization of coal in 1300 ˚C in coke oven. The coal Is enter into the top of large vertical silica retort heated externally to 1300 ˚C by producer gas burner. The coal gas is the first sent to hydraulic main which remove tar by cooling the gas in big water cooling heat exchanger called condenser.

Ammonia any other tar is present in the coal gas are removed by scrubbing with water in a scrubber number 1 Benzol, naphthalene etc., are removed by scrubbing with creosote oil scrubber number 3. Sulphur compounds like hydrogen sulphide is removed by passing gas over moist ferric oxide.

Application of coal gas:

1. As a fuel.
2. Domestic commercial Illumination.
3. In metallurgical operation.

The coal gas can be converted into gasoline and diesel to additional treatment via Fisher Tropsch process.

Oil gas :

Manufacturing of oil gas:

The oil gas is prepared by cracking or thermal decomposition of mineral oil like kerosene oil.

$$C_{12}H_{26} \xrightarrow{\text{Cracking}} CH_4 + C_2H_6 + C_2H_4 + C_3H_8 + C(\text{Tar})$$

QUESTIONS FOR REVISION

PART -A

1. Distinguish between Gross and Net Calorific Value of Fuel?
2. What are the different varieties of coal found inside the earth?
3. What is ignition temperature ?
4. What is Cetane value of diesel oil?
5. Discuss relative merits and demerits of solid, liquid, and gaseous fuel?
6. Explain recovery of by products from coke oven gas?

PART-B

1. Name highest ranking coal gives its approximate calorific value
2. What is Knocking and anti Knocking agent
3. What is the process of cracking and its objectives?
4. What is octane number? What are the addictives that may be used as octane number as enhancer?
5. What is synthetic petrol? Name two methods of its preparation?

PART -C

1. Define Fishers Tropsch with neat labeled diagram
2. Describe the manufacturing of metallurgical coke by Otto Hoffman method
3. What is reforming? Explain various reforming process of gasoline
4. How is calorific value of a fuel determine by bomb calorimeter with neat diagram
5. What is meant by proximate analysis of coal? What are the quantities estimated in this analysis and their significance
6. How is coal gas produced? State its composition and application?

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