PERIYAR INSTITUTE OF DISTANCE EDUCATION (PRIDE)

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B.Sc. CHEMISTRY

SECOND YEAR

PAPER – III : GENERAL CHEMISTRY – II

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UNIT –I

1.1 Transition elements and group study

1.1.1 Transition elements:-

The transition elements may be broadly defined as those which as elements or as ions have partly filled d or f subshells. If the d subshell is partly filled, the elements are known as d-block or transition elements.

Position in the periodic Table :-

Electronic configurations :-

The d-block elements consists of three rows called first, second and third transition series.

Elements of first transition series :-

The elements from scandium (Z=21) to Zinc (Z=30) constitute the first transition series. In the first element, Scandium, the 3d subshell starts filling up. It's electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$.

For reasons of space, we shall describe configurations of outer shells only, leaving aside the configuration upto 3p level which the same throughout the period. The outer electronic configuration of scandium may, thus, be written as $3d^1 4s^2$.

The last element, Zinc, has the maximum permissible number of electrons in the d-orbitals. Its outer electronic configuration is $3d^{10} 4S^2$, as shown. But the definition of d-block elements based on the number of electrons in the d-subshell excludes zinc from the first transition series of d-block since neither zinc any of its common ions has a partly filled d subshell.

The atoms of chromium and copper, unlike the others, have a single electron in the 4s orbital. This is due to the additional stativity gained by the atom when the d subshell is exactly half – filled or completely filled. Accordingly, one of the 4s electron moves to the 3d level in the atoms of chromium and copper. The 3d level in the case of chromium gets exactly half filled and that in the case of copper gets completely filled.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d	1	2	3	5	5	6	7	8	10	10
4s	2	2	2	1	2	2	2	2	1	2

Elements of second transition series :-

The ten elements from yttrium to cadmium (Z=39 to 48) constitute the second transition series. In yttrium, 4d subshell begins filling up and its

outer electronic configuration is $4d^1 5s^2$. The filling up of the 4d orbitals continues as we keep moving in this period towards the next nine elements. In cadmium permissible number of 10 electrons, the configuration of the outer shell being $4d^{10} 5s^2$. The electronic configurations of these elements are given below.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
4d	1	2	4	5	5	7	8	10	10	10
5s	2	2	1	1	2	1	1	0	1	2

Elements of third transition series :-

The third transition series starts from hafnium (Z=72) in which the filling of 5d subshell begins. The outer electronic configuration of hafnium is $4f^{14} 5d^2 6s^2$. This process continues thereafter in tantalum to mercury.

	H4	Ta	W	Re	Os	Ir	Pt	Au	Hg
5d	2	3	4	5	6	7	10	10	10
6s	2	2	2	2	2	2	0	1	2

General characteristics of d-block

(1)Metallic character :-

All the transition elements are metals. They are good conductors of heat and electricity. They are also malleable and ductile and form alloys with several other metals. They differ from non-transition metals, however, in being hard and brittle. Mercury is an exception. While the overlapping of unfilled d-orbitals of atoms causes covalent bonding, the valence s-electrons cause metallic bonding. Copper, silver and gold are particularly outstanding in their thermal and electrical conductivities.

2. Molar volumes and densities :-

The molar volumes of transition elements are shown in table 1. These are much lower than those of the S and P block elements of the neighborning groups. The reason is obvious. As a result of decrease in molar volume, there is corresponding increased in density. Accordingly the densities of the transition elements are quite high. Most of these elements have densities greater than 5 or cm^{-3}. Scandium, titanium and yttrium, with density 3.01, 4.51 and 4.47 g cm^{-3}, respectively are the only exceptions.

3. Atomic Radii :-

The atomic radii of the transition elements of a given series are seen to decrease, generally, with increase in the atomic number as expected from the fact that increase in the nuclear charge would tend to attract the electron charge cloud inward. There are, however, a few exceptions.

The radii of the elements, from chromium to copper, however, are very close to one another. As a result of this, the size of the atom does not alter much in moving from chromium to copper.

4. Ionic Radii :-

The ionic radii follow the same trend as the atomic radii. This is evident from the value given in table. It is seen that for ions of the given charge, the radius decreases slowly with increase in atomic number. The radii of the doubly charged ions, although small, are comparable with the radius of Ca^{2+} ion. Their oxides, therefore, are similar to calcium oxide, although somewhat un basic and less soluble in water.

5. Melting points and Boiling points :-

The melting and boiling points of the transition elements are, generally, very high. The melting points of most of the transition elements are above $900^{o}C$. For example, lithium melts at $108.5^{o}C$ and cesium at $28.7^{o}C$.

Zinc, cadmium and mercury which, by definition based on the number of d-electrons, are excluded from the d-block elements, have relatively low melting points, being $419.5^{o}C$, $320.9^{o}C$ and $-38.4^{o}C$, respectively. The covalent bonding. Which is responsible for high melting and boiling points, can occur in the rest of the d – block elements on account of vacant d orbitals.

6. Ionisation energies :-

The atoms are small in size, their ionization energies are fairly high. The indicates that the transition elements are an electropositive than the elements of groups 1 & 2. Although transition elements do from ionic compounds, yet they do not do so as readily as alkaline and alkaline earth metals do. The ionization energy along a given period is generally expected to increase with increase in the atomic number.

The second ionization energies are seen to increase, more or less regularly, with increase in atomic number. The outer electronic configuration of singly charged chromium ion is $3d^5$ and that of singly charged copper ion is $3d^{10}$.

7. Reactivity :-

The atoms of transition elements are rather small and, therefore, ionization energies are fairly high as pointed out above. They require a large amount of energy to change them from solid to vapour state. The metal ions, because of their low positive charge density, do not get hydrated easily. They have rather a tendency to remain unreactive or 'noble'.

8. Oxidation states :-

While discussing the chemistry of transition elements, it is more covenient to use the term oxidation state instead of valency. The oxidation states are given below.

| Elements	Outer electronic Configuration	Oxidation states
Sc	$3d^1 4s^2$	+2,+3
Ti	$3d^2 4s^2$	+2,+3,+4
V	$3d^2 4s^2$	+2,+3,+4,+5
Cr	$3d^5 4s^1$	+1,+2,+3,+4,+5,+6
Mn	$3d^5 4s^2$	+2,+3,+4,+5,+6,+7
Fe	$3d^6 4s^2$	+2,+3,+4,+5,+6
Co	$3d^7 4s^2$	+2,+3,+4
Ni	$3d^{10} 4s^2$	+2,+3,+4
Cu	$3d^{10} 4s^1$	+1,+2,
Zn	$3d^{10} 4s^2$	+2

9. Standard electrode potentials :-

The standard electrode potential of transition element is generally negative compared to the potential of the standard hydrogen electrode. It is expected, therefore, that these metals, excepting copper, would evolve hydrogen gas when reacted with acid solution,

$$M + 2H^+_{(aq)} \longrightarrow M^{2+}_{(aq)} + H_{2(g)}$$
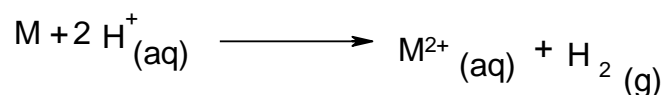
10. Reducing properties :-

They are good reducing agents. The reducing capacity of a metal depends on its tendency to change into aquated ions. But the transition elements do not as good reducing agents as the metals of groups 1,2 and 3.

Copper has a positive electrode potential. This means that copper is not able to displace H^+ ions from acid solutions. The reaction.

$$Cu + 2\ H^+_{(aq)} \longrightarrow cu^{2+}_{(aq)} + H_2$$
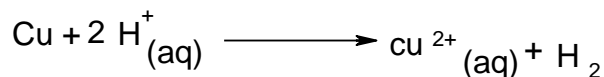
simply does not occur. The tendency of copper to change into cupric ion

is extremely small since E^o for this reaction is negative. Hence, Copper is a particularly poor reductant.

$$Cu \longrightarrow cu^{2+}_{(aq)} + 2\ e^-$$
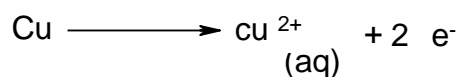
11. Colour :-

Most of the compounds of transition metals are coloured in the solid or in solution states. Colour of substance arises invariably from the property of the substance to absorb light of certain wave lengths in the region of visible light (A = 3800-7600 A^o).

The transition element which have completely empty d orbitals are also colourless. Thus Sc^{3+} and Ti^{4+} ions are colouless.

Colours and outer electronic configurations of important ions are given below.

Ion	Outer electronic configuration	Number of unpaired electrons	Colour of the Ion
Sc^{3+}	$3d^o$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
T_1^{4+}	$3d^o$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light pink
Mn^{3+}	$3d^4$	4	Violet
Fe^{2+}	$3d^6$	4	Green
Fe^{3+}	$3d^5$	5	Yellow
Co^{3+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue

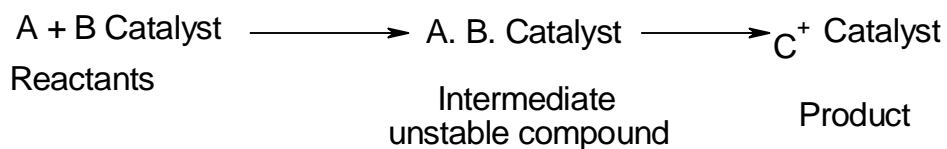|			
Cu^+	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

12. Magnetic properties :-

Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field and diamagnetic substance is one which is repelled by a magnetic field.

Paramagnetism arises from the presence of unpaired electrons in atoms, ions, complex ions or molecules. We may recall from our knowledge of elementary physics that the motion of an electric charge creates a magnetic field.

13. Catalytic properties :-

Most of the transition metals and their compounds have good catalytic properties. Platinum, ion, vanadium pentoride, nickel, etc., are important examples. Vanadium pentonide is also a good catalyst for the same reaction. Nickel is a good catalyst in hydrogenation process.

A + B Catalyst $\longrightarrow$ A. B. Catalyst $\longrightarrow$ C^+ Catalyst

Reactants

Intermediate
unstable compound

Product

The transition elements, on account of their variable valency, are able to form unstable intermediate compounds very readily.

14. Tendency to form complexes :-

The transition metals are almost unique in their tendency to form co-ordination complexes. The tendency of cations of transition elements to form complexes is due to two factors. Firstly, these ions are very small in size and, therefore, have high positive charge density. This facilities acceptance of lone pairs of electrons from other molecules. Second, they have vacant orbitals and these orbitals have the right type of energy to accept lone pair of electrons.

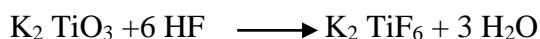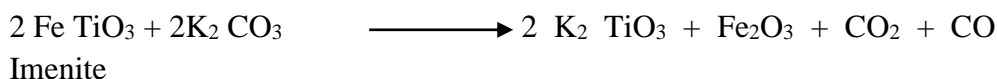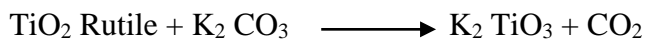**Transition Elements and group study :-**

1. Titanium :

Occurance :

|		
1. Oxide ores	:	a) Rutile - TiO_2
		b) Brookite - TiO_2
		c) Anatase - TiO_2
2. Silicate ores	:	Sphene Ca – Ti-SiO_5
3. Titanate ores	:	Ilmenite $FeTiO_3$

Extraction :

Wholer's Process :-

The finely powdered ore is fused with thrice the weight of K_2CO_3. The fused mass is cooled. The solid obtained is powdered and treated with dilute HF, potassium fluotitanate, K_2TiF_6 is got.

$$TiO_2 \text{ Rutile} + K_2CO_3 \longrightarrow K_2TiO_3 + CO_2$$

$$2 \text{ Fe TiO}_3 + 2K_2CO_3 \longrightarrow 2 \text{ } K_2 \text{ TiO}_3 + Fe_2O_3 + CO_2 + CO$$
Imenite

$$K_2 \text{ TiO}_3 + 6 \text{ HF} \longrightarrow K_2 \text{ TiF}_6 + 3 \text{ H}_2O$$

The potassium fluotitanate is boiled with water and cooled, crystals of $K_2 \text{ TiF}_6$ seperate

The crystals of $K_2 \text{ TiF}_6$ are dissolved in boiling water and treated with NH_4OH, when $Ti(OH)_4$ is precipitated. The precipitate obtained is washed, dried and ignited to get TiO_2. The Oxide cannot be directly used for the extraction of the metal. Therefore it is first converted into $Ticl_4$ by heating a mixture of the TiO_2 and carbon in a current of chlorine.

$$TiO_2 + C + {}_2Cl_2 \longrightarrow TiCl_4 + CO_2$$
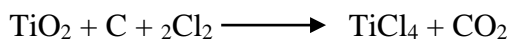
Korll Process :-

In this method $Ticl_4$ is reduced with magnesium in an inert argon atmosphere.

$$Ticl_4 + 2 \text{ Mg} \xrightarrow{1100k} Ti + 2 \text{ Mg Cl}_2.$$
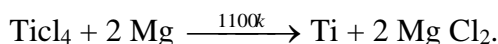
The product is washed in water to remove $Mgcl_2$. A spongy metal is got. It is melted in an electric are under a high vaccum (or) in an atmosphere of inert gas (Helium (or) Argon) to get compact metal.

Refining by van Arkal Process :-

Titanium is heated with iodine when Titanium tetra iodide is obtained. The titanium Tetraiodide is heated on a tungsten filament when it decomposes to give pure metal.

$$Ti + 2I_2 \xrightarrow{350-520k} Ti \text{ I}_4 \xrightarrow[TungstenFilament]{1700k} Ti + 2I_2.$$
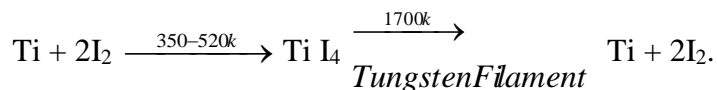
Properties :-

I Physical Properties :-

1. Metallic titanium is a silvery luster and when polished resembles steel appearance
2. Melting Point – 1668°C

3. Boiling point – 3260°C

II Chemical Properties :-

1. Action of air :-

On explosure to air at ordinary temperature, titanium metal reacts with O_2 and N_2 of the air and forms a thin film (or) TiO_2 and TiN on the surface of the metal. This wating prevents the metal from corrosion. This wating remains stable in air up to 400°C.
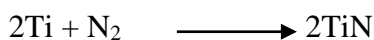
$$Ti + O_2 \longrightarrow TiO_2$$

2. Action of Halogens :-

The metal readily combines with Cl_2 (at 350°C), Br_2 and I_2 to form the tetrahalides, Tix_4.

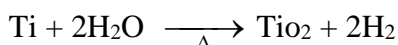$$Ti + {}_2Cl_2 \longrightarrow TiCl_4$$

3. Combination with Non – Metals :-

They combine with B, N_2, H_2, C, to produce TiH_2, TiB, TiC and TiN – These are interstitial compound and hard. These have refractory properties.
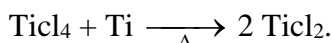
$$2Ti + N_2 \longrightarrow 2TiN$$

4. Action on stem:-

Steam is decomposed by the metal

$$Ti + 2H_2O \xrightarrow{\Delta} TiO_2 + 2H_2$$

5. Cation of $TiCl_4$:-

$TiCl_4$ is reduced to $TiCl_2$ when heated with metal.

$$TiCl_4 + Ti \xrightarrow{\Delta} 2\ TiCl_2.$$

Uses :-

1. Alloys of titanium are useful. Ferrotitanium is used in steel industry. Titanium alloys are used for making filaments for vaccum tubes. This replaces the costly platinum iridium alloy.
2. Used in photo electric cells.
3. Titanium soaps impart special properties to paints and varnishes.
4. Titanium tetrachloride is used for smoke screens.
5. Titanium dioxide is useful in the manufacture of paints and pigments. Titanium compounds are also used for dying.
6. Titanous salts are used in volumetric analysis.
7. TiO_2 is used as a whitener in face powder, ceramics etc.,

2. Zirconium :-

Occurance :-

1. Zircon, Zr SiO_4
2. Baddeleyite, - ZrO_2

Extraction :-

From Baddeleyite, ZrO_2 :-

The ore is powdered and concentrated. The concentrated ore is fused with KHF_2, when fluozirconate is formed.

$$ZrO_2 + 4KHF_2 \longrightarrow K_2Zr\,F_6 + 2KF + 2H_2O.$$

When it is boiled with water, cooled and filtered K_2ZrF_6 crystals are formed. The dried K_2ZrF_6 when mixed with potassium and heated in an iron tube at low temperature gives zirconium metal.

$$K_2\,Zr\,F_6 + 4K \longrightarrow 6KF + Zr.$$

The metal is leached with dil. Hcl then washed with ammonium chloride and finely washed with alcohol when Zr metal is obtained.

Preparation of pure metal (Van Arkal Method):-

Pure Zirconium is obtained by heating impure Zirconium with iodine when Zr I_4 is formed. When this compound is heated on tungsten filament, it decomposes to give pure metal.
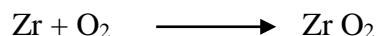
$$Zr + 2I_2 \xrightarrow{\Delta} Zr\,I_4 \xrightarrow[TungstenFilament]{1700k} Zr$$
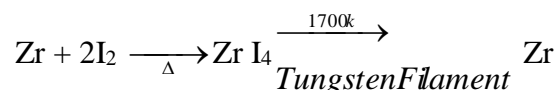
Properties :-

I Physical properties :-

1. It is soft silver white metal m.p. is 1855^oC.
2. It exists in crystalline and amorphous forms.

II Chemical properties :-

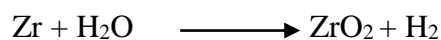**1. With air :-**

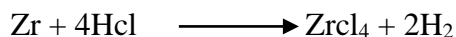When zirconium is heated in air at high temperature to form zirconium dioxide and zirconium nitrate.

$$Zr + O_2 \longrightarrow Zr\,O_2$$

2. With water :-

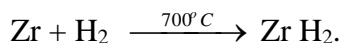It does not react with cold water. But it decomposed steam to give zirconium dioxide and hydrogen.

$$Zr + H_2O \longrightarrow ZrO_2 + H_2$$

3. It reacts with dil. Hcl to form ZrCl₄.

$$Zr + 4Hcl \longrightarrow Zrcl_4 + 2H_2$$

It dissolved in HF and aquaregia

4. It reacts with hydrogen at 700ºC to form Zr H₂.

$$Zr + H_2 \xrightarrow{700^\circ C} Zr H_2.$$

5. With alkalies :-

It react with alkalies only under high temperature to form the alkali Zirconates.

$$Zr + NaoH + [o] \longrightarrow Na_2 ZrO_3 + H_2.$$
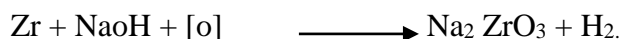
6. Reaction with metals and non – metals :-

It reacts with Cu, Fe and Al to form alloys. At high temperature it reacts with halogens, sulphur, boron, silicon, carbon, phosphorous and nitrogen giving the corresponding compounds.

Uses of Zirconium :-

1. Zirconium steel is a corrosion resistance alloy and it can also withstand wear and tear.
2. Zirconium chloride is used to prepare fire bricks which can withstand very high temperatures.
3. It is also used in nuclear reactors.
4. It is used as a catalyst in the synthesis of ammonia and hydrogenation reactions.
5. It is also used in radio transmitters and flash bulbs.
6. The glasses of Zirconium are not affected

3. Molybdenum:-

Occurance :-

Molybdenum never occurs free in nature. It occurs in the following ores.

1. Molybdenite   - MoS_2
2. Wulfinite   - $Pb\ MoO_4$
3. Molybdite   - $FeO_3.\ MoO_3.\ H_2O$
4. Hermaite   - $MoO_2\ 4\ MoO_2$

Extraction :-

Molybdenum is commonly extracted from molybdenite.

1. Concentration of the ore:-

The ore molybdenite is crushed into fine powder. The crushed ore is concentrated by froth floatation process.
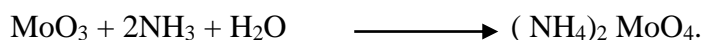
2. Roasting :-

The crushed and concentrated ore of molybdenite is heated strongly in a current of air. Molybdenum trioxide MoO_3 is formed.
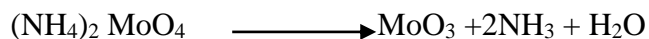
$$2MoS_2 + 7O_2 \longrightarrow 2MoO_3 + 4SO_2$$

3. Purification of MoO3:-

Impure molybdenum trioxide is dissolved is ammonia to get ammonium molybdate.

$$MoO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2 MoO_4.$$

Ammonium molybdate is purified by recrystallisation crystals of ammonium molybdate are heated to decompose it to form molybdenum trioxide.

$$(NH_4)_2 MoO_4 \longrightarrow MoO_3 + 2NH_3 + H_2O$$

4. Metallurgy :-

Metallic molybdenum can be obtained in several ways form MoO_3. It may be reduced with hydrogen (or) carbon.

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

$$MoO_3 + 3C \longrightarrow Mo + 3Co$$

Aluminothermic reduction of MoO_3 gives almost 99% pure metal.

$$MoO_3 + 2Al \longrightarrow Mo\ Al_2O_3.$$

99% pure metal can be prepared by the reduction of the oxide with calcium shaving (or) Zinc dust.

$$MoO_3 + 3Ca \longrightarrow Mo + 3CaO.$$

In all these methods Mo is obtained in the form of powder. The metal is obtained in compact form by pressing it at about 2600^oC (near its melting point). This heating is done in an atomosphere of hydrogen.

Preparation of pure molybdenum metal :-

Thermal decomposition of molydenum pentachloride on an electrically heated molybdenum filament gives pure metal.

$$2MoCl_5 \xrightarrow[\Delta]{Filament} 2Mo + 5Cl_2$$
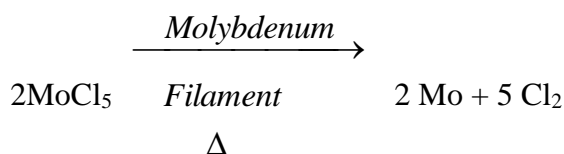
Properties:-

I. Physical Properties :-

It is a silvery white metal, fairly hard and melts at 2610°C.

Chemical Properties :-

1. It is not attacked by air at ordinary temperatures but when heated strongly (500-600°C) it gets slowly oxidised to the trioxide MoO_3.

    $2Mo + 3O_2 \longrightarrow 2\ MoO_3$.
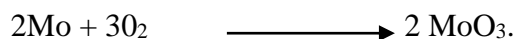
2. It is also attacked by the halogens giving the corresponding halides.

    $Mo + 3F_2 \longrightarrow MoF_6$.

    $2Mo + 5Cl_2 \longrightarrow Mo_2Cl_{10}$.

    $2Mo + 5Br_2 \longrightarrow Mo_2Br_3$.

3. It does not reacts with sulphur and phosphorous.

4. It is only gradually attacked by acids. Hot and concentrated nitric acid, oxidises the metal to the trioxide, MoO_3. However, it soon becomes passive.

5. It is not attacked by alkalies but dissolves in fusion mixture of KNO_3 and $NaoH$.

Uses:-

1. It is used as an anticathods in x-ray tubes.

2. Molybdenum and tungsten form thermocouple for high temperature measurements.

3. Used in the manufacture of standard weights.

4. Used as a promotor in the Haber's process for the manufacture of ammonia.

5. Molybdenum steels are used for making high speed lathe tools and rifle barrel.

6. It is used as a substitute for platinum for electric resistance in resistance furnaces.

7. Sodium molybdate is used in ceramics for colouring pottery and porcelain, in the textile industry for dyeing silk and wool.

8. It is used as a mordant.

4. Tungsten:-

Occurance :-

Tungsten is also known as wolfram. It is not found in nature. In the combined state it occurs in the following ores.

1. Wolframite   - $FeWO_4$ and $MnWO_4$
2. Tungsite   - WO_3
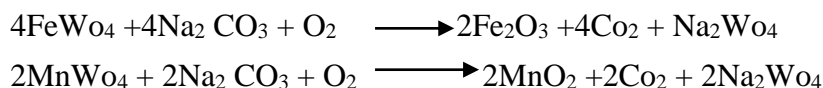3. Scheelite   - $CaWO_4$
4. Hubnrite   - $MnWO_4$

Extraction :-

1. Concentration :-

  The wolframite ore is crushed to a fine powder. It is concentrated by electtromagnetic seperation since the ore contains magnetic impurities.

2. Roasting :-

  The crushed ore is roasted with sodium carbonate. Soluble sodium tungstate is formed. Iron and manganese get oxidised to their respective oxides.

$$4FeWO_4 + 4Na_2CO_3 + O_2 \longrightarrow 2Fe_2O_3 + 4CO_2 + Na_2WO_4$$

$$2MnWO_4 + 2Na_2CO_3 + O_2 \longrightarrow 2MnO_2 + 2CO_2 + 2Na_2WO_4$$

3. Conversion to WO_3:-

  The roasted mass is then extracted with hot water. Sodium tungstate is soluble in water and hence it dissolves. Oxides of iron and manganese are removed by filtration. The filtrate containing sodium tungstate is treated with acid. tungsten trioxide, WO_3 is precipitated. WO_3 is washed with water and then dried.

4. Reduction :-

  Tungsten may be obtained in metallic state by several methods.

  WO_3 can be reduced with hydrogen, carbon, zinc, aluminium, magnesium and silicon.

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

$$WO_3 \; 2Al \longrightarrow W + Al_2O_3.$$
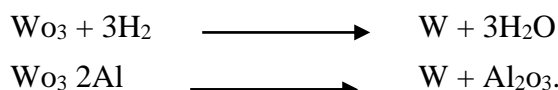
  A pure variety of tungsten in powder form is obtained by heating tungsten oxide in quartz tubes in a carefully controlled furnace in a current of hydrogen.

Preparation of pure tungsten:-

  Pure tungsten metal can be obtained

  i) by heating the tungstic acid, H_2WO_4 is a current of H_2

   $$H_2WO_4 + 3H_2 \longrightarrow W(Pure) + 4H_2O.$$

  ii) By thermal decomposition of WCl_6 Vapour on a tungsten electric air.

$WCl_6 \longrightarrow W \text{ (Pure)} + 3Cl_2$

Properties :-

I Physical Properties:-

1. Pure tungsten resembles platinum possessing steel lustre.
2. The powder form is hard and brittle, but the crystalline form is malleable and ductile.
3. It can withstand high pressure and stress and strain.

Chemical properties :-

1. Reaction with air :-

At high temperature it reacts with air forming its trioxides.

$2W + 3O_2 \longrightarrow 2WO_3$
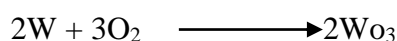
2. Reaction with water :-

Red hot tungsten decomposes steam into hydrogen

$W + 2H_2O \longrightarrow WO_2 + 2H_2$

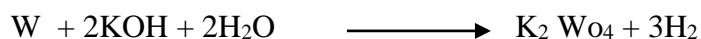**3. Reaction with acids:-**

It does not easily react with even hot concentrated acids. It dissolves in aquaregia.

4. Reaction with alkalis:-

It react with alkalis forming its compounds.

$W + 2KOH + 2H_2O \longrightarrow K_2WO_4 + 3H_2$

5. Reaction with halogens:-

Tungsten reacts with halognens at red hot conditions forming the halides.

$W + 3F_2 \longrightarrow WF_6$

$W + 3Cl_2 \longrightarrow WCl_6$

$2W + 5Br_2 \longrightarrow 2WBr_5$

$W + I_2 \longrightarrow WI_2$
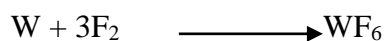
6. Reaction with non – metals:-

It does not reacts with nitrogen. It reacts with sulphur and phosphorous in their vapour state.

$W + 2S \longrightarrow WS_2$

Uses:-

1. It is mainly used for preparing special steels and filaments for electric lamps, pen and strings of musical instruments.
2. It is used as an anticathode in X-ray tubes.

3. It is used in making surgical instruments, gramophone needles, voltage regulators, contract points etc.,

4. Sodium tungstate is used as a mordant in dyeing.

5. Wo_3 is used as a yellow pigment while lead tungstate is used as a substitue for white lead.

6. Tungsten – Molybdenum thermo –couples are used for high temperature work.

7. Lead – tungsten alloys finds use in making bullets and shots.

8. Oxides of tungsten are used in ceramics to impart different shapes in glass and porcelain.

9. Tungsten has been tried as a catalyst for many reactions.

5. Platinum :-

Occurance :-

Platinum occurs native in nature in the form of alloys.

Important ores:-

1. Sperrylite   - $Pt\ AS_2$

2. Cooperite   - $Pt\ (AsS)_2$

3. Braggite   - $(Pt, Pd, Ni)S,$

Extraction :-

The heavier metallic particles are first seperated from alluvial sand and gravel by washing. Gold if present, is removed by the amalgamation process. The rest of the ore is digested with aguaregia which dissolves all the platinum metals forming chlorides, except osmium which is seperated by the solution containing, chlorides of the metals of the platinum family (Pt, Pd and Rh) is evaporated to dryness and the residue heated to $175^{o}C$. Palladium and Rhodium tetrachlorides are thus converted into the lower chlorides, $pdcl_2$ and $RhCl_2$, which are insoluble while platinumtetrachloride and iridiumtetrachloride remains as such. On adding water, platinumtetrachloride together with iridium tetrachloride (Which is present in small quantity only) passes into solution while the lower chlorides of palladium and rhodium remains as the residue.

The solution acidified and ammonium chloride is added when the sparingly soluble salt, $(NH_4)_2\ pt\ cl_6$, gets precipitated.

$$Ptcl_4 + 2NH_4\ cl \longrightarrow (NH_4)_2\ Pt\ cl_6$$
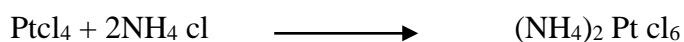
The precipitate of ammonium chloro platinate is ignited when it decomposes to give spongy platinum.

$$(NH_4)_2 \, Ptcl_6 \longrightarrow 2NH_4cl + 2cl_2 + Pt$$
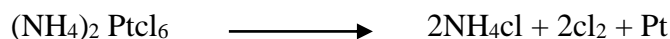
It is heated to redness and hammered to get the metal in the form of coherent sheets.

Properties :-

I. Physical Properties:-

Platinum is a lustrous bluish white metal. When pure it is extremely ductile. It is highly malleable. Platinum wires and foils can be sealed into glass without cracking.

II. Chemical Properties:-

1. With Oxygen:-

At ordinary temperature platinum is resistant to oxidation. It combines with oxygen at high temperature and pressure to give the oxide PtO.

2. With acids:-

Pure platinum is not attacked even by not concentrated hydrochloric acid, nitric acid and sulphuric acid. If the metal is impure, it slightly reacts with sulphuric acid. It is dissolved by aque regia forming chloroplatinic acid, $H_2 [ptcl_6]$

$$Pt + 2 \, Hcl + 4 \, cl \longrightarrow H_2 [Ptcl_6]$$

3. With alkalis:-

Platinam is commonly considered as an inert element. But it is attacked by fused alkalis.

4. With halogens:-

It combines with fluorine and chlorine at red heat. With fluorine it gives platinum tetrafluoride Pt F_4 and with chlorine it gives platinum dichloride, $Ptcl_2$.

Uses:-

1. Since platinum is almost inert, it is used in jewellery.
2. Sine it is inert to chemicals, it is used for making crucibles, dishes etc.,
3. It is used as electrodes in various electrolytic processes.
4. It is used as an important catalyst in the form of platinised asbestos.
5. Platinum is used for plating fancy and other presentation articles.
6. It is used to make dental plates and pins.

1.1.3. Chemistry of Titanium dioxide:-

It is obtained by heating TiO_2 with Ti. It is a non-stoichiometric compound with composition TiO 0.75. It changes readily to TiO_2. Due to this reaction, it acts as a strong reducing agent, for instance, it readily reduces water to hydrogen.

$$TiO + H_2O \longrightarrow TiO_2 + H_2$$

It is basic and ionic in character.

Chemistry of Titanium Tetrachloride:

It can be prepared in the laboratory by passing chlorine over a not mixture of titanium dioxide and carbon.

$$TiO_2 + C + Cl_2 \longrightarrow TiCl_4 + CO_2$$

1. It is colourless, fuming liquid at ordinary temperatures and boils at 137^oC.

2. It gets readily hydrolysed by water yielding titanium dioxide.

$$TiCl_4 + 2 H_2O \longrightarrow TiO_2 + 4 HCl$$
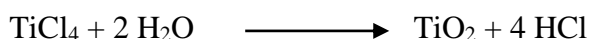
If water is not present in excess, hydrolysis takes place only to a limited extent yielding titanium oxochloride, $TiOCl_2$

3. It is reduced to metallic titanium on treatment with Mg or Na.

4. It dissolved in con. HCl yielding chloro complexes having formulae $[TiCL_5 (H_2O)]^-$ and $[TiCL6]^{2-}$

5. Titanium chloride is a strong lewis acid and accepts electrons from strong oxygen – does not like ethers, alcohols, and esters yielding addition compounds of the type $(R_2O) TiCl_4 (R_2O_2)_2$ $TiCl_4$.

Uses:-

$TiCl_4$ is used for producing dense white smoke screens and for making writings in the sky in army operations. This is because the spraying of liquid $TiCl_4$ into moist air results in its hydrolysis forming dense white smoke of TiO_2.

It is also used as a catalyst in the manufacture of polyethylene.

Chemistry of Vanadium Pentoxide:

This is perhaps the most compound of vanadium (V). This is obtained as a red or orange solid on thermal decomposition of ammonium metavanadate, NH_4VO_3.

$$2NH_4VO_3 \longrightarrow V_2O_5 + 2NH_3 + H_2O$$

Vanadium pentoxide is also formed as a brick red precipitate when ammonium vanadate solutions are treated with dil. H_2SO_4.

It is also prepared by using the metal in oxygen.

It melts at about 650° C and is insoluble in water.

Vanadium (V) oxide has all its outer electrons fully paired in covalent bonds. There is no incomplete electron shell. The compound therefore should be colourless. But actually it is orange – red in colour. The reason of this anomoly lies in defects in the solid state due to which charge transfer transition in the visible region are possible.

Chemistry of Zirconium dioxide:

It is obtained as a gelatinous precipitate on adding an alkali to Zirconium (IV) solution. On strong heating, the hydrous oxide gives ZrO_2. The hydrous oxide is also obtained by vapour of $Zrcl_4$. This is done by passing the vapour of $Zrcl_4$ mixed with air through a special flame produced by burning a hydrocarbon in excess of oxygen.

It is a hard and white pigment like TiO_2 and is used as such. It is insoluble in water. It has an extremely high melting point, viz., 2700° C. It resists attack by both acids and alkalies. It has good mechanical properties and is used in making crucibles and furnaces. ZrO_2 is more basic in TiO_2.

Chemistry of Zirconium halides:

$ZrCl_4$ is made in the same way as $TiCl_4$ i.e., by passing chlorine over the dioxide heated with carbon.

It gets easily hydrolysed yielding oxochloride.

$$ZrCl_4 + H_2O \xrightarrow{\hspace{3cm}} H_2o\ ZrOcl_2 + 2HCl$$

The oxochloride crystallises from the solution as the octahydrate, $ZrOcl_2$. $8H_2o$. $Zrcl_4$ resembles $Ticl_4$ in most of its properties.

$ZrBr_4$ and ZrI_4 are also known. These are made by direct combination of the elements and are similar in properties to $Zrcl_4$. $ZrBr_4$ is yellow while ZrI_4 is red – brown in colour. ZrF_4 is also known as a white crystalline solid.

The trihalides ZrX_3 are known but these are not stable.

These are oxidised by water to +4 state.

Chemistry of Tungsten trioxide:

This is the most important oxide of tungsten. It is obtained from Wolframite. It is a yellow powder, insoluble in water and has amorphous nature. It dissolves in alkalies forming tungstates. When heated mildly in a current of hydrogen, it changes into tungsten dioxide, WO_2 which is a brown

powder. It is soluble in water. It has a complicated structure containing W – W bonds.

The oxide WO_3, when fused with alkali or alkaline earth oxides, gives mixed oxides whose structures and properties are very similar to those of the corresponding mixed oxides of Mo.

Chemistry of Tungsten Bronzes:

By reducing alkali metal tungstates (e.g. Na_2WO_4 or K_2WO_4) with tungsten deeply coloured substances are obtained. These substances called tungsten bronzes, are unreactive towards common acids and alkalies, but are good conductors of electricity. They have metallic lusture and have the general formula M_xWO_3 (where M = Li, Na and K). The value of X<1. These are evidentally, non – stoichiometric substances in which M+ ion is always present in intersitial sites created by three – dimensional network formed due to corner sharing of WO_6 octahedra.

Tungsten bronzes can also be prepared by (i) heating the metal tungstates in a current of hydrogen (ii) reducing the tungstates electrolytically (iii) reducing WO_3 with alkali metals in the vapour phase.

The colours of the tungsten bronzes depend upon the amount of alkali or alkaline earth metal ions. These ions depending upon their amount, produce varying extents of lattice defects and hence impart different colours to the tungsten bronzes. Thus the colour of $NaxWO_3$ varies from golden yellow (x=0.9) to blue violet (x=0.3). The electrons produced due to ionisation of alkali metal M to M+ ions in these tungsten bronzes are completely delocalised over the whole of the lattice and are therefore, free to move throughout the lattice. As a result, the tungsten bronzes become conducting. The tungsten bronzes with x<0.3 are metals. The conductance of tungsten bronzes deceases with increase in temperature. The tungsten bronzes are largely used as metallic paints.

Chemistry of Chloroplatinic acid:

It is the best known complex of platinum (IV). It is prepared by the action of aqua regia on platinum.

$$2NHO_3 + 8HCl + Pt \longrightarrow H_2[PtCl_6] + 4H_2o + 2NOCl$$
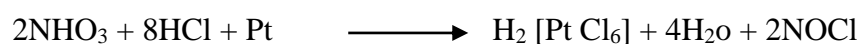
The solution is evaporated to drive off nitric acid before crystallising chloroplatinic acid.

It is reddish brown crystalline substance associated with 6 molecules of water of crystallisation, $H_2[PtCl_6].6H_2o$.

On heating in chlorine at 360 – 370 C, it decomposes into platinum (iv) chloride.

$$H_2 [Pt Cl_6] \longrightarrow Pt Cl_4 + 2HCl$$
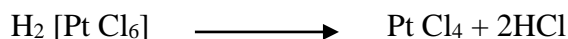
It is a strong dibasic acid, ionising as

$$H_2 [Pt Cl_6] \longrightarrow 2H + [Pt Cl_6]^{2-}$$

It forms stable salts. The lithium and sodium salts ($Li_2PtCl_6.6H_2o$, $Na_2PtCl_6.6H_2o$) are soluble while potassium and ammonium salts (K_2PtCl_6 $(NH_4)_2 PtCl_6$) are yellow precipitates.These salts decompose on heating and leaving a residue of platinum.

$$K_2 Pt Cl_6 \longrightarrow Pt + 2KCl + 2Cl_2$$

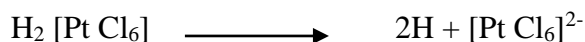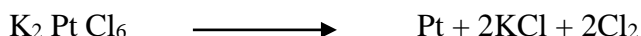Some other well known complexes of Pt(iv) are [Pt $(NH_3)_6$] , [Pt $(NH_3)_5$ Cl], etc.

Chemistry of Barium Platinocyanide:

It is a very important compound of bivalent platinum and is prepared by treating chloroplatinic acid with barium hydroxide solution and hydrocyanic acid and passing in sulphur dioxoide till the solution becomes colourless.

$$H_2 [Pt Cl_6] + 5Ba(OH)_2 + 4HCN + SO_2 \longrightarrow$$

$Ba[Pt (CN)_4] + BaSo_4 + 3BaCl_2 + 8H_2o. + 3BaCl_2 + 8H_2O$
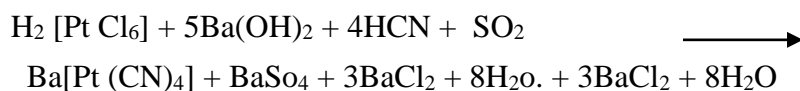
The complex anion [Pt $(CN)_4$] is diamagnetic and like [Pt Cl_4] , it has a square planar geometry.

Chemistry of Molybdenum blue :

It can be made by reducing molybdic acid with zinc or sulphur dioxide. It is also formed when powdered molybdenum is allowed to remain in constact with a suspension of the trioxide in water at ordinary temperature.

Its constitution is not certain, probably it contains molybdenum is both the +5 and +6 states.

It is a dark blue substance and forms a blue colloidal solution.

It is used as a pigment for rubber etc.

Chemistry of Ammonium Molybdate :

Ammonium molybdate is obtained from molybdenite mineral. The mineral is first oxidised to trioxide, the trioxide is boiled with ammonium hydroxide solution to give ammonium molybdate $(NH_4)_2 MoO_4$.

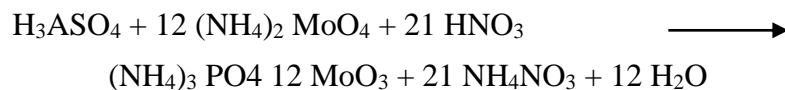This solution on evaporation gives crystals of para molybdate ($NH_4)_6 Mo_7 O_{24}. 4H_2O$ are formed.

It is yellow crystalline substance. It is soluble in water.

It forms a yellow precipitate with phosphorous and arsenate.

$H_3PO_4 + 12 \ (NH_4)_2 \ MoO_4 + 21 \ HNO_3 \longrightarrow$

$\qquad (NH_4)_3 \ PO_4 \ 12 \ MoO_3 + 21 \ NH_4NO_3 + 12 \ H_2O$

Ammonium phospho molybdate

$H_3ASO_4 + 12 \ (NH_4)_2 \ MoO_4 + 21 \ HNO_3 \longrightarrow$

$\qquad (NH_4)_3 \ PO4 \ 12 \ MoO_3 + 21 \ NH_4NO_3 + 12 \ H_2O$
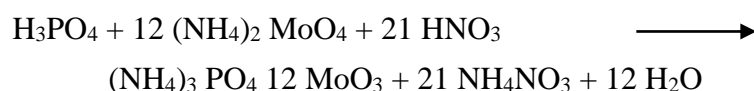
Ammonium phospho molybdate

Uses :

It is used in the laboratory for the identification and determination of phosphate and arsenate.

1.1.4. Group study of Ti, V And Cr Groups

1. Group study of Titanium group

A Comparative study of the Element :

The titanium group (IVB) of the transition elements comprises of three elements namely, Titanium, Zirconium and Hafnium. They have similar electronic configurations, namely $(N-1)d^2 \ ns^2$.

Element			Outer electronic Configuration
Titanium	:	Ti	$3d^2 4S^2$
Zirconium	:	Zr	$4d^2 5S^2$
Hafnium	:	Hf	$5d^2 6S^2$

Position in the periodic table :

They are transition elements in the sense that their last electron enters the d-orbital. They are placed between group   III B and V – B in the preiodic table as shown below.

Group III B	Group IV B	Group V B
SC	Ti	V
Y	Zr	Nb
La	Hf	Ta

The inclusion of these elements in the same sub group in the preiodic table and the position of these elements are justified by the similarities and regular gradation in their properties discussed below.

1. Abundance :

Titanium and zirconium are relatively abundant elements. Titanium is the ninth most abundant element. Hafnium occurs much less abundantly.

2. Oxidation state :

They exhibit +2, +3 and +4 oxidation states the +2 oxidation state is exhibited when they use only two S-electrons. +3 and +4 oxidation states are exhibited. When one or both the d-electrons are used along with the two S-eletrons. The +4 oxidation state is the most stable state for each element. The +2 and +3 states are not so common in the chemistry of hafnium.

3. Physical Properties :-

The anhydrous compounds of these elements in the +4 state are covalent. This is because the ionisation energy is very large. It is not certain whether M^{4+} ions exist even in solution. There elements are metallic in nature, have high melting point and boiling point. Their electronegativity decreases from Ti to Hf. Ionic radii, atomic radii and covalent radii increases from Ti to Hf. Their densities, melting point and boiling point increase from Ti to Hf.

4. Chemical Properties :

The lower oxidation state undergo disproportionation. For example.

$$2Ti^{3+} \xrightarrow{\quad Heat \quad} Ti^{2+} + Ti^{4+}$$

$$2Ti^{2+} \xrightarrow{\quad H_2O \quad} Ti^{2+} + Ti^{4+}$$
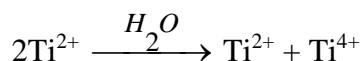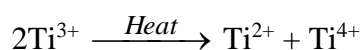
They are highly reactive towards most of the oxidising agents. There metals donot react with dilute acids or alkalis. This is probably due to the formation of a protective oxide film. Titanium dissolves slowly in hot and concentrated acids. It exploes with fuming nitric acid. Zirconium dissolves in aquaregia and to a smaller extent in hot concentrated sulphuric acid. Titanium dissolves freely in HF. This is because of the tendency of Ti to form hexafluoride complexes.

The atomic radii of group IV B elements are peculier the data are as follows.

Ti 132 PPm

Zr 145 PPm

Hf 144 PPm

As we move down a periodic table the atomic radii should increases. But the case of VI period elements which follow lanthanam behave in a peculier fashion due to lanthanide contraction. So the size of hafninum atom and ion is the same that of zirconiumion and so the seperation of hafnium and zirconium is difficult.

2. Group study of Vanadium Group

A Comparative study of the elements:-

The vanadium group (VB) of the transition elements comprises of three elements namely, Vanadium, Niobium and Tantalum. They have similar electronic configurations namely (n-1) $d^2 ns^2$ (exception : Niobium)

Element			Outer electronic Configuration
Vanadium	:	V	$3d^2 4S^2$
Niobium	:	Zb	$4d^2 5S^1$
Tantalum	:	Ta	$5d^3 6S^2$

1. Abundance :

They do not occur abundantly as these of the titanium group. They have odd atomic numbers are relatively rare elements.

2. Oxidation states :

The chemistry of these elements is further complicated because of the formation of an additional oxidation state of +5. The +5 oxidation state becomes more stable on moving down the group. i.e. from V → Nb → Ta. It is for this reason vanaduim (V) compounds are good oxidising agents while, the Nb and Ta compounds are not good oxidising agents, because they are stable. Lower oxidation state becomes more stable in the order Ta < Nb < V.

3. Physical Properties :-

These elements are metallic in nature. They have high melting and boiling point. Their extraction is difficult because of their high melting point and reactivity at high temperatures. Their electronegativities are almost the same. Ionic radii, density, melting points increase in the order V → Nb → Ta. However their boilding point are in the order V < Nb < Ta. The atomic radii are in the order V<Nb <Ta. This is because titanium follows after lanthanides. Therefore due to lanthanide contraction the atomic radii of Nb and Ta are the same. So it is difficult to seperate them.

4. Chemical Properties:

All the three elements are unreactive at ordinary temperatures. However, on heating, they become quite reactive. Thus, on heating with halogens, Vanadium yeilds VF_5, VCl_4, VBr_3. Nb and Ta react under similar conditions giving Nb X_5 and Ta X_5 (Where X = halogen).

The metals, when heated also react with oxygen to give the pentoxides $M_2 O_5$. In these pentoxide, the oxidation state of the metal is +2. Vanadium gives VO_2 also in which the oxidation state of vanaduim is +5.

The metals on heating with nitrogen and carbon to give interstitial nitrides and carbides.

3. Group Study of Chromium Group

A Comparative study of the elements:

The chromium group (VI –B) of the transition elements comprises of three elements namely, chromium, Molybdenum and tungsten. They have similar electronic configurations, namely $(n-1)d^3 ns^1$ (exception tungsten)

Element			Outer electronic Configuration
Chromium	:	Cr	$3d^5 4S^1$
Molybdenum	:	Mo	$4d^5 5S^1$
Tungsten	:	W	$5d^4 6S^2$

1. Physical Properties:

All the three elements of this group are metals they have small atomic volume, extreme hardness and very high melting point. They are highly resistant to corrosion these metals have very low volatility. Tungsten has the highest melting point next only to carbon. All the metals are silver white. Melting point, boiling point and density increases regularly from Cr to W. The atomic radii are in the order Cr < Mo =W. This is because tungsten follows after lanthanides. Therefore, due to lanthanide contraction the atomic radii of Mo and W are same.

Hence, there is very close resembles between there two elements. They have similar properties. So it is difficult to seperate them.

2. Reactivity :

The elements of this group like elements of vanadium group have low reactivity at ordinary temperatures. Chromium dissolves in dil. HCl and H_2SO_4 giving Cr^{2+} ion. Molybdenum and tungsten do not dissolve in these acids. Chromium dissolves in alkalis giving chromites. All the three metals react readily when heated with oxygen, nitrogen and halogen giving compounds of the type M_2O_3. Chromium absorbs hydrogen while morybdenum and Tungsten do not. Chromium is a strong reducing agent Mo and tungsten do not have strong reducing character.

3. Oxidation State :

From the electronic configuration, it appears that Cr and Mo should have oxidation states 1 to 6 while tungsten should have oxidation states 2 to 6. But actually all the elements show the same oxidation states varying form

O to 6. The most oxidation state of chromium is +3 while for the other two is 6. This is show that increase in atomic number, the higher oxidation.

State becomes more stable while the lower oxidation state becomes less stable.

Zero Oxidation State :

Metal carbonyl such as $Cr(Co)_6$, $Mo(Co)_6$ are examples in which these elements exhibit the oxidation state zero. The electrons for binding are denoted by the carbonyls group. The carbonyls are soluble, in organic solvents.

+1 Oxidation State :

Chromium and Mo have d^5s^1 configuration. So +1 Oxidation state is expected from them. Even tungsten may be expected to exhibit this state by losing one of the two outer selectrons. But this oxidation state of +1 is not very common in these metals.

Examples:

$[Cr(dipyridyl)_3]Clo_4$ and $K_3[Cr(CN)_3NO]$. Mo^+ and W^+ are also known as ions such as $(C_6H_6)_2Mo+$ and $(C_6H_6)W^+$

+2 Oxidation State :

$[Cr(H_2O)_6]^{2+}$, $[Cr(CN)_5]^{4-}$, $[Cr(NH_3)_6]^{2+}$

+3 Oxidation State :

Compounds of chromium in +3 oxidation state are commonly known as chromic compounds. These are ionic in character. They have Cr^{3+} ion they are considered to the most stable compounds of chromium. There are several complexes of Cr^{3+} ion some examples are give below.

$[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[CrCL_6]^{3-}$, $[Cr(CN)_6]^{3-}$
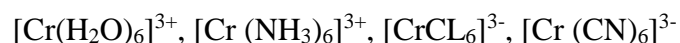
+4 Oxidation State:

Molybdenum and tungsten form dioxides. MoO_2, WO_2. In these compounds these metals exhibit +4 oxidation state. These oxides are inert. They are refractory in character. Chromium in +4 state is found in chromium tetra fluoride $Cr F_4$, which is a brown volatile solids.

+5 Oxidation State:

The +5 oxidation state is more common in Mo than in W. It is rare in Cr.

+6 Oxidation State:

The compounds of chromium in +6 oxidation state, like Cr_3O7^{2-} are strong oxidising agent. But Mo and W in +6 oxidation state do not behave as oxidising agents, because +6 state in the most stable oxides MoO_3 and WO_3

and stable halides MoF_6 and Wx_6. In these compounds Mo and W are in +6 state.

1.2. Natural Radioactivity

Discovery of Radioactivity

Some time after the discovery of X- rays in 1895, Becquerel started studying phosphorescent substances. He left, accidentally, a pile of a mineral containing the heavy metal uranium, on a photographic plate covered with black paper and placed in a dark room. When the photographic plate was developed he found a dark spot in it exactly in the place over which the pile of mineral was placed.

On further examination, it was found that the uranium mineral was sending out mysterious radiations which were more penetrating than X – rays. These radiations ionized air and other gases, discharged electroscopes, and causes fluorescence. Such minerals were named radioactive minerals and the phenomenon was called radioactivity. The radioactive minerals emitted these radiations continuously, sometimes even for months together. The emissions were not affected by changing physical and chemical conditions.

Marie curie became interested in becquerel's discovery. She was working on pitch blends. She found it to be for more radio active that it should be on the basis of its uranium content alone. She thought that some other more radio active element might be present in the mineral. She worked day and night with her husband and finally in 1898 obtained a new element which was million times more than uranium. She named it as radium. Earlier polonicem, another radio active element, more active than uranium, was also found by her. These discoveries led to the discovery of many other radio active elements.

Radioactive Emanations

The spontaneous disintegration of a substance resulting in the emission of radiations is called radioactivity. The emitted radiations were of three types (i) $\propto$ - rays or $\propto$ - particles (ii) β -rays or β - particles and (iii) δ – rays.

These radiations were sent through a magnetic field. β - rays were deflected in a magnetic field in the same directios as cathode rays, $\propto$ - rays were deflected in an opposite direction. δ -rays were not deflected. From this it was concluded the β - rays were negatively charged, $\propto$ - rays were positively charged and δ - rays were light rays comparable to x-rays.

Further researches led to the discovery of the properties of these radiations. They are summerised and are given below:

S. No.	Property	$\propto$ - rays	β - rays	δ - rays
1.	Nature	He $^{2+}$ ions	electrons	Light rays
2.	Velocity	10% of speed of light	33 to 99% of speed of light	Speed of light
3.	Penetrating Power	Not very nigh	More than $\propto$ - rays	Very high
4.	Ionising Capacity	Maximum	Small	Weak
5.	Action on Zns and Photographic plates	Affect	Affect Greater then $\propto$ - rays	No effect

Nuclear Changes that occur during the emission of various radiatiors.

i) $\propto$ - Particle :

When particle is emitted $\propto$ new element is formed with atomic number two units less and atomic weight four units more.

E.g. 9^2 U^{238} $\xrightarrow{\quad 90 \quad}$ Th ^{234} $+_2$ He^4.
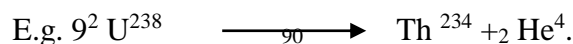
ii) β - Particle :

When particle is emitted a new element is formed with atomic number one units more and atomic weight four units more and with the same atomic weight.

E.g. $_{11}$Na^{24} $\xrightarrow{\quad 12 \quad}$ Mg^{24} $+_{-1}$ e^O.

iii) δ - rays :
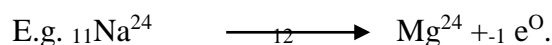
When a δ - rays is emitted no change to the parent atom occurs.

E.g. $*_4$Be^8 $\xrightarrow{\quad 4 \quad}$ Be^8 + δ
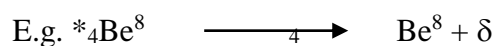
(* obtained by bombarding$_3$ Li^7 with a proton)

iv) Positron ($_{+1}$e^O) :

When a positron is emitted a new element is formed with atomic number one unit less and with the same atomic weight.

E.g. $*_7$N^{13} $\xrightarrow{\quad 6 \quad}$ C^{13} + $_{+1}$e^O
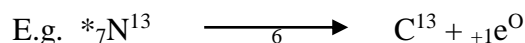
(* obtained by bombarding $_5$ B^{10} with $_2$ He^4)

Detection and measurement of Radioactivity

Radioactivity may be detected and measured by the ionisation of gases caused by $\propto$ and β - Particles and also indirectly by δ - rays. The following instruments are used for the purpose.

1. Geiger – Muller Counter :

It consists of a copper cylinder which acts as cathode. It is closed a thin mica plate at one end. A tungsten wire at the middle of the cylinder well insulated from cylinder acts as the anode. It is kept at a potential of about 1500 V. The cylinder is filled with an inert gas like argon and alcohol vapour at a pressure of about 10 mm of Hg. The radioactive substance is placed out side the tube closed to the mica plate. When ever an $\propto$, or β - particle or δ - ray is emitted by the radioactive substance, it enters the tube and causes ionization of the gaseous molecules. A momentary flow of current occurs which is amplified. It causes a flash of light in a neon tube and a mechanical register records it.

RR = Radioactive rays ; C = cathode ; A = Anode ;

A + Av = Argon + Alcohol Vapour; MP = Mica Plate ;

NT = Neon tubes; MR = Mechanical Register.

2. Wilson cloud chamber :

It consists of a chamber (A) (Fig -2) with a glass window (G). It is closed by a piston (B) which can be moved up or down. It is filled with dust free air and water vapour at saturation pressure. When the piston is moved down by means of values (V) the pressure is reduced. The air expands. This causes cooling. Minute water droplets are formed. If the $\propto$ and β particles from a radio active source enter the chamber now the water droplets condense on them and their path is illuminated by a light source (L) and the cloud tracks are photophaphed with camera (C). This leads to the detection and measurement of radioactivity.

The Disintegration Theory

It is be lived that the stability of an isotope depends upon the number of neutrons and protons present in its nucleus. If the number of protons (P) present in the nucleus is plotted against the number of neutrons (N) also present, we find that the stable nuclei lie within the dotted area shown in figure – 3 which is known as the " Zone of Stability " (ZS).

MODES OF DECAY
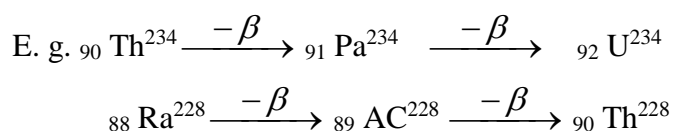
There are mainly two modes of decay.

1. ∝ Particle emission :

We known ∝ - particles are helium nuclei ie., $_2He^4$. So when an ∝ - particles is emitted, the resultant undeus has a mass less by four unit and charge less by two units as compared with the parent uncleus. The new element produced is called the daughter element. There, the daughter element will have atomic weight less by four units and atomic number less by two units.

E.g. $_{92}U^{234} \xrightarrow{-\alpha} {}_{90}Th^{230} \xrightarrow{-\alpha} {}_{88}Ra^{226} \xrightarrow{-\alpha} {}_{86}Rn^{222}$
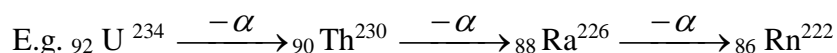
2. β - Particle emission :

We know β - particles are electrons ie., $_{-1}e^O$. So when a particle is emitted the resultant nucleus has the same mass and charge more by one unit as compared with the parent uncleus. Thus the daughter element will have the same atomic weights and atomic number more by one unit.

E. g. $_{90}Th^{234} \xrightarrow{-\beta} {}_{91}Pa^{234} \xrightarrow{-\beta} {}_{92}U^{234}$

$_{88}Ra^{228} \xrightarrow{-\beta} {}_{89}AC^{228} \xrightarrow{-\beta} {}_{90}Th^{228}$

It is interesting to note that during β emission, electron is emitted from the nucleus though there are no electrons in the nucleus. It is postulated that neutrons disintegrate as follows and produce electrons which are emitted as β - particles.

Neutron $\longrightarrow$ proton + Electron + Nutrino.
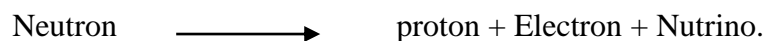
Group Displacement law (Fajan – Russel – Soddy)

We know that when an ∝ - Particle is emitted the daugher element has atomic number two units less than that of the parent element. So its position in the periodic table will be two places left to the parent element. Similarly when β - particle is emitted the daughter element has atomic number one unit more than that of the parent element. So its position in the periodic table will be one place right to the parent element. This is called group displacement low.

Use :

This law is helpful in predicting the nature of the daughter element if the mode of decay of a particular parent element is known.

E.g.

    I. $_{84}Po^{215}$ undergoes ∝ - emission. From this detail we can predict the nature of the daughter element. According to the group

displacement law the daughter element in this case will be two places left of Po in the periodic table i.e., it is Pb.

II. $_{82}Pb^{211}$ under goes β - emission. So the daughter element will be one place right of Pb in the periodic table. ie., it is Bi.

Rate of Disintegration – Half life period

The rate at which a parent element changes into its daughter element gives a measure of the activity of the parent radio active element. The rate of disintegration depends on the nature of the radio element and is independent of other external factors like temperature, pressure etc.

Law of radioactive decay :

The rate of disintegration (the quantity which disappears per unit time) of a radio element is directly proportional to the amount present.

Let us consider a radio element A which disintegrates to another element B.

$$A \longrightarrow B$$
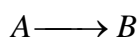
Let the number of atoms of A present initially be N. Let dN atoms decay in a time dt, then

Rate of disintegration $= \dfrac{-dN}{dt}$ $\longrightarrow$

According to the law of radioactive decay

$$\dfrac{-dN}{dt} \; \alpha \; N$$

or $\dfrac{-dN}{dt} = \lambda \, N$ $\longrightarrow$ (1)

Here λ is a proportionality constant known as decay constant or disintegration constant or radioactive constant.

Re arranging (1)

$$\dfrac{-dN}{N} = \lambda \, dt \qquad \longrightarrow \qquad (2)$$

(2) On integration gives

- In N $= \lambda t + C$ $\longrightarrow$ (3)

Where C is the integration constant.

The value of C is evaluated as follows ;

At the beginning of reaction t =o. Let N_o be the number of atoms of the radioactive element present at the beginning.

Substituting these values in (3) we have

$\quad$ - In N_o = O + C $\quad\longrightarrow\quad$ (4)

Substituting (4) in (3) we have

$\quad$ - $\quad$ In N = λt – In No

$\quad$ + In N_o – In N = λt

$\quad$ (or) In $\dfrac{No}{N}$ = λt $\quad\longrightarrow\quad$ (5)

$\quad$ ie., Lt = In $\dfrac{No}{N}$ $\quad\longrightarrow\quad$ (6)

$\quad$ or λ = $\dfrac{2.303}{t}$ log $\dfrac{No}{N}$ $\quad\longrightarrow\quad$ (7)

Unit of λ : time^{-1} ie., S^{-1} or min^{-1}.

Half life period : (t ½)

$\quad$ It is the time taken by 50% of any sample to disintegrate.

$\quad$ Half life period is a measure of the radioactivity the element. If it has a shorter half life period, it means that it will disintegrate faster.

$\quad$ When t = t½ $\quad\longrightarrow\quad$ (8)

$\quad$ The number of atoms present will be = $\dfrac{No}{2}$ $\quad\longrightarrow\quad$ (9)

Substituting (8) and (9) in (7)

$\quad$ λ = $\dfrac{2.303}{t\dfrac{1}{2}}$ log $\dfrac{No}{No/2}$ $\quad\longrightarrow$

$\quad$ λ = $\dfrac{2.303}{t\dfrac{1}{2}}$ log ^{2} .

$\quad$ t ½ = $\dfrac{2.303\ X\ Log^2}{\lambda}$ $\quad\longrightarrow\quad$ (10)

$\quad$ or t ½ = $\dfrac{0.693}{\lambda}$ $\quad\longrightarrow\quad$ (11)

$\quad$ Since λ is a constant t½ is a constant. This means that $\quad$ t½ of a partiauclar radioactive element is independent of the initial amount of the radioactive element.

$\quad$ From the above discussion it is clear that radioactive disintegration follows first order kinetics.

Radioactive disintegration series

Most of the natural radio – active elements of higher atomic numbers exist in nature as a number of radio – active isotopes. All the radio – active isotopes, which are about 40 in number, belong to definite chains of successive decays. These are called radio active series. They are uranium, thorium, actinium and neptunium series.

The first three radio active series have been named after a prominent member in each decay series. Uranium and thorium are having longest half – lives in their series. So the respective series are named after them. Long ago it was thought that the actinium series originated from actinium. But now it is known that U^{235} is the parent of that series with a longer half life than actinium. The thorium series is also referred to as 4n series because the mass numbers of its members are divisible by 4. The uranium series is known as 4n+2 series because its mass number is divisible by 4 with a remainder 2. The actinium series is known as 4n +3 because its mass number is divisible by four with a reminder of 3.

The first three series have close similarities. Their modes of decay are also similar the ultimate product in each of the three families is a stable, but different in each case, isotope of lead.

Although there is considerable similarity among the three radio active series, they are not specifically related. In other words, an isotope in one series will not decay to a particular isotope belonging to another series. This lack of inter change is to be expected, since mass change can take place only by the loss of α - particles of 4 mass units each and the charateristic mass of each family is either 4n, 4n+2 or 4n +3.

A radio – active chain is not always straight forwards. There are branded disintegrations in each series. In such cases an isotope breaks down in two different ways. This gives rise to branched products. Interestingly, the isotopes produced by a branched integration always decay into the same product.

The (4n+1) Series – The Neptunium Series:

We have seen that the three serious of natural radio elements contain members whose masses are divisible by 4 or by 4 with remainders of 2 and 3. But the series containing members whose masses are divisible by 4 with a remainder of 1, that is (4n+1) series could not be found. The most acceptable explanation for the absence of this series in nature was that no member of this series was sufficiently long lived.

The first five members of this series were discovered during the world war II. The other members have been discovered and studied later.

The (4n+1) series, derives its name from the longest lived member of the series, neptunium. Thus it is called neptunium series. The members of the series are man – made. It is an artificial series.

The series differs in several respects from the naturally occurring radioactive series. These are as follows:-

1. The end product in the series is the stable isotope of bismuth, $_{83}Bi^{209}$ where as the end products of the three natural radioactive series are stable isotopes of lead.

2. The only member of the series to be found in nature is the stable end product bismuth $_{83}Bi^{209}$.

3. The series contain no gaseous emition as in the case of the three natural series.

4. The series contain the isotopes of francium and astatine as direct and successive members of the decay chain. These elements appear only as minor branched disintegration products in the natural series.

5. Branched disintegration appears more frequently in the natural radioactive series than in the neptunium series.

Nuclear Binding Energies

Mass defects:

The mass of the proton has been determined accurately as 1.00758, the mass of the neutron as 1.00893 and that of the electron as 0.0005486 mass unit (on the physical atomic weight scale in which the mass of O^{16} atom is taken as the standard with mass exactly 16.00000 units). So we can calculate accurately the mass of an atom knowing the number of protons, Neutrons and electrons present in it. For example, the helium atom contains 2 electrons 2 protons and 2 neutrons. Therefore its mass should be

= (2 x 0.0005486) + (2 x 1.00758) + (2 x 1.00893)

= 4.03411.

But actually the mass of the helium atom is 4.00390 units. The difference between the expected mass and the actual mass is]

4.03411 – 4.00390 = 0.03021 mass unit and this difference is called the mass defect.

Thus the difference between expected mass of an atom of an element (calculated from the number of protons, neutrons and electrons and their respective accurate masses) and the actual mass is known as the mass defect.

Experimental mass of nucleus – (mass of proton + mass of neutron) = mass defect.

Binding Energies:

Thus when the helium atom is formed from its constituent particles 0.03021 mass unit of mass is converted into energy.

We know 1 mass unit = 1.661 x 10^{-24} g. Therefore 0.03021 x 1.661 x 10^{-24} g of mass has been converted into energy. This energy is the binding force which binds two protons and two neutrons together to form the helium nucleus.

From Einstein's mass energy equation

$$E = mc^2$$
$$E = 0.03021 \text{ x } 1.661 \text{ x } 10^{-24} \text{ x } (3 \text{ x } 10^{10})^2$$
$$E = 4.5119 \text{ x } 10^{-5} \text{ energy.}$$

We know 1.60 x 10^{-6} erg 1 Mev

$$4.5119 \text{ x } 10^{-5} \text{ erg} = \frac{4.5119 X 10^{-5}}{1.602 X 10^{-6}}$$
$$= 28.12 \text{ Mev}$$

Since the helium atom contains four particles, the binding energy per nucleon in He^4 is 28, 28/4. i.e, approximately 7.0 Mev.

[We can also calculate straight away using 1 mass unit = 931 Mev]

Thus the binding energy may be defined as the energy released when a given number of proton and neutrons combine to form a nucleus. It can also be defined as the energy required disrupting a nucleus into its constituent protons and neutrons.

This binding energy comes from the mass which has been lost during the formation of the nucleus. This mass has been converted into energy which is used to bind the nucleons together in nucleus.

Significance of Binding Energy:

Binding energies may be taken as a measure of the relative stability of the nucleus.

Binding energies increase progressively with atomic mass and are fairly constant expect for the very light elements. If we plot the binding energy per nucleon against the mass number we get a graph.

From this graph the following observation can be made

1. In the mass – number range between 25 and 140 the binding energy per particle is nearly constant and it is approximately equal to 8.5 Mev/ nucleon.

2. Nuclei with both small and large mass numbers have a smaller binding energy per particle. So these nuclei are less stable.

3. For nuclei with small mass numbers considerable irregularities occur i.e. the curve raise abruptly.

**Artificial Radioactivity (or) Induced Radioactivity:**

Definition:

Artificial radioactivity is a process by which a new radioactive isotope of a known element can be prepared.

Examples:

1. When magnesium is bombarded with α - particles we get an isotope of silicon which is radioactive. It disintegrates giving $_{13}Al^{27}$ and positron (+e).

$$_{15}Mg^{24} + {}_2He^4 \longrightarrow {}_{14}Si^{27} + {}_0n^1$$

Radioactive

$$_{14}Si^{27} \longrightarrow {}_{13}Al^{27} + {}_1e^0$$

2. When boron is bombarded with α - particles we get isotope of nitrogen which is radioactive. It disintegrates giving a stable isotope of carbon $_6C^{13}$, and a positron.

$$_5B^{10} + {}_2He^4 \longrightarrow {}_7N^{13} + {}_0n^1$$

Radioactive

$$_7N^{13} \longrightarrow {}_6C^{13} + {}_1e^0$$
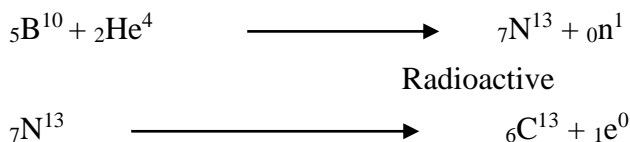
Artificial Transmutation of Element:

Conversion of one element into another is known as transmutation of elements. The conversion of one element into another by artificial means is known as artificial transmutation of element.

When elements are bombarded with some fundamental particles like alpha particle $({}_2He^4)$, proton $({}_1H^1)$, deuteron $({}_1H^2)$ and neutron $({}_0n^1)$, they are converted into other element. Artificial transmutation of elements depends upon the target nucleus, the projectile (bombarding particle) and its energy.

During artificial transmutation of elements, the daughter element emitted several particles such as protons and neutrons besides $\alpha, \beta \; and \; \gamma$−radiations. Other modes of artificial radioactive decay are,

i) Positron emission:

Positrons are produced during the transformation of protons into neutrons with in the nucleus. We know the stability of the nucleus depends upon n/p ratio. Emission of positron increases n/p ratio to a stable level.

ii) Orbital Electron Capture (or) K Capture:

The nucleus of the atom captures an electron from its K shell. This is called K – capture. To compensate this another electron from a higher energy level drops to the K – shell. When this happens energy is released in the form of radiation.
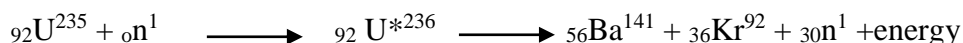
Nuclear Fission :

Definition:

Splitting of a nucleus into nearly equal parts with release of energy is called nuclear fission.

Explanation :

It is a type of disintegration. For example when uranium-235 is bombarded with slow moving neutrons, first a neutron is captured by the uranium nucleus. Then the whole nucleus splits into two nuclei, one of barium and other of Krypon. In this process 3 extra neutrons are released. Such a process is known as nuclear fission. Some of the liberated neutrons attact other uranium unclei and thus cause a chain reaction, which the others get annihilated and are converted into energy.

$$_{92}U^{235} + {_0}n^1 \longrightarrow {_{92}} U*^{236} \longrightarrow {_{56}}Ba^{141} + {_{36}}Kr^{92} + {_3}{_0}n^1 + energy$$

Importance of nuclear fission :

In fission reaction there is a loss of mass. This is converted into energy. The energy produced in nuclear fission is extremely large as compared to conventional sources. For example, when $_{92}U^{235}$ undergoes fission reaction on bombardment with slow moving neutrons about 0.2 units of mass per gram atom of uranium 235, is annihilated. It amounts $0.2 \times [3 \times 10^{10}]^2$ ergs according to einsteins equations $[E=MC^2]$ this equal to six million horse power hours.

The large amount of energy liberated in nuclear fission can be utilized in two important wags.

i. Preparation of the super explosive or atom bomb (destructive purpose)

ii. Super power plant (Constructive purpose)

The atom bomb works on fast neutron chain. It is accomplished bringing together two pieces of fissionable material (U^{235} or Pu^{239}) into

intimate contact. When these two pieces are kept separated they are stable. But when they are put together by a more mechanical operation they explode violently.

Controlled Fission Reaction:

Definition :

Atom bomb explosion is due to an uncontrolled chain reaction. If this chain reaction is put under control, after some time, a steady state is established. When such a steady state is established the number of neutrons produced and the number of neutrons consumed becomes nearly equal. The energy produced attains a constant level. Such a reaction is known as controlled fission reaction.

Controlled fission reactions are brought about in nuclear reactors. In nuclear reactions the fissionable material also called nuclear fuels like U^{235} or Pu^{239} is staked with heavy water (or) graphite called moderators. The neutrons produced in the fission pass through the moderators and they lose some of their energies. So they start moving slowly. Thus fission reactions are controlled.

Applications:

It is used for preparing radioisotopes (or) generating electricity.

Nuclear Fusion:

Definition :

It is the process of combining or fusing two lighter unclei into a stable and heavier nuclide with release of energy is called nuclear fusion.
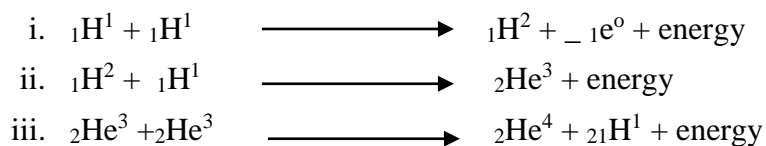
Explanation :

We may consider the formation of helium uncleus it is formed by the combination of two hydrogen atoms (i.o.2 protons and 2 electrons) and two neutrons. In this case also an enormous amount of energy is released by the formation of a heavier uncleus from those of lighter elements on account of loss of mass.

Importance of nuclear fusion :

Nuclear fusion can takes place by allowing highly accelerated protons and deutrons etc. to fall on nuclei of lighter elements. Such processes occur at reasonable rates only at very high temperatures of the order of a million degree centigrade which exist only in the interior of stars. Therefore, such processes are called therounclear reaction, once a fission reaction is initiated, the energy released is sufficient to maintain the temperature and to keep the process going.

The energy of the sun is supposed to arised from the following thermo – nuclear reactions.

i. $_1H^1 + _1H^1 \longrightarrow _1H^2 + \__{-1}e^o + energy$

ii. $_1H^2 + _1H^1 \longrightarrow _2He^3 + energy$

iii. $_2He^3 + _2He^3 \longrightarrow _2He^4 + _{21}H^1 + energy$

In the above reaction 26.7 Me V of energy is released. This is a tremendous quantity.

Comparison of nuclear fission and nuclear fussion:

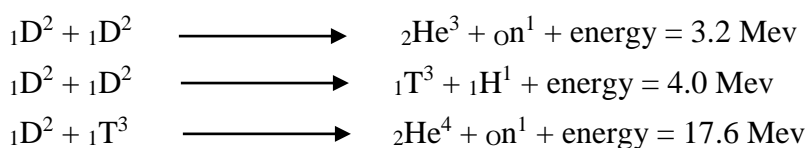**a. Similarities:**

Both release very large amount of energy

b. Difference:

i. Fission involves the breaking up of a heavy uncleus into lighter unclei. Fusion involves combining of two lighter nudei into one heavy nucleus.

ii. The links of the fission process are neutrons. The links of a fusion process are protons.

iii. Fission proceed with thermal neutrons where thermal means room temperature. Fusion proceeds with thermal particles where thermal means millions of degrees in Kelvin scale.

Hydrogen Bomb:

The thermo nuclear reactions among nuclei of hydrogen isotopes, deuterium and tritium, can serve as possible sources of energy on earth as these can occur more rapidly, provided the temperature is very high such an energy obtained from thermonuclear reactions is called thermonuclear energy.

These reactions may be represented as.

$_1D^2 + _1D^2 \longrightarrow _2He^3 + _0n^1 + energy = 3.2 \, Mev$

$_1D^2 + _1D^2 \longrightarrow _1T^3 + _1H^1 + energy = 4.0 \, Mev$

$_1D^2 + _1T^3 \longrightarrow _2He^4 + _0n^1 + energy = 17.6 \, Mev$

These fusion processes are responsible for the release of a tremendous amount of energy in the form popularly known as a hydrogen bomb. But the above nuclear reactions can take place only at very high temperatures. Therefore an external sources of energy to provide an atmosphere with required high temperatures is necessary. In the preparation of a hydrogen bomb, a suitable quantity of deuterium or tritium or a mixture of both is combined with an atom bomb. The atom bomb provides an

atmosphere of required high temperature. A hydrogen is for more powerful than an atom bomb.

Now man is capable of controlling nuclear fission and obtaining energy in a controlled manner in a nuclear reactor and using it for peaceful purposes. Similarly, man in future, probably will be able to conbrol nuclear fusion processes and to obtain an abundance of energy for the benefit of mankind.

Application of Radioactivity:

Rock – dating age of earth:

Knowledge of the rate of decay of certain radioactive isotopes helps us to determine the age of various rock deposits. Let us consider rock containing U^{238} formed many years ago. The age of this rock determined using the following equation.

$$t = \frac{2.303\,T}{0.693}\ \ \log\left(1 + \frac{Pb^{206}}{U^{238}}\right)$$

Where,

t – The age of the rock

T – Half life period of U^{238}

(Known: 4.5 x 10^9 years)

Pb^{206} – Amount of Pb^{206} present in the sample in moles.

U^{238} – Amount of U^{238} present in the sample in moles.

Problem:

The ratio of the mass of Pb^{206} in a certain rock specimen is found to be 0.5. Assuming that rock originally contained no lead, estimate it's age.

Half life period of U^{238} = 4.5 x 10^2 years

Solution:

The age of the rock is given by

$$t = \frac{2.303\,T}{0.693}\ \ \log\left(1 + \frac{Pb^{206}}{U^{238}}\right)$$

T = 4.5 x 10^9 years

$$\frac{Pb^{206}}{U^{238}} = 0.5$$

$$= \frac{2.303\ x\ 4.5\ x\,10^9\ years}{0.693}\ \ \log\left(1 + 0.5\right)\ years$$

$$= \frac{2.303 \times 4.5 \times 10^9 \; years}{0.693} \; \log(1.5) \; years$$

$$= \frac{2.303 \times 4.5 \times 10^9 \; years}{0.693} \times 0.1761 \; years$$

$$= 2.63 \times 10^9 \; years$$

Exercise:

A sample of Uranium ore is found to contain 11.6 g U^{238} and 10.3 g of Pb^{206}. Calculate the age of the ore. Half life period of Uranium is 4.5 x 10^9 years.

Answer:

4.5 x 10^9 years; Clue: The amounts of U^{238} and Pb^{206} have been given in grams. Convert them into moles by dividing their weights by their respective mass number and calculate Pb^{206}/U^{238}. This is given calculate using the formula is

$$t = \frac{2.303 \, T}{0.693} \; \log\left(1 + \frac{Pb^{206}}{U^{238}}\right)$$

Isotopic Dilution Method:

It is an example of radio – metric method of trace analysis. It is used to determine the quantity of constituent (radioactive or non - radioactive) a mixture of closely related components which are difficult to separate and to estimate quantitatively by the used of conventional method.

The Method Involved the Following Steps:

Let the mass of a given non – radioactive element, which is to be determined to be m. An amount of m of the same compound, isotopically labeled is added to it. Let the isotopic compound have an activity of 'S'. The two are mixed thoroughly to obtain a uniform mixture. Now by some suitable method compound is isolated in a pure form. Now the active of the compound is measured. Let it be 'S'.

Sine the total activity is constant m can be calculated as follows.

$$m = m' \left[\frac{S'}{S} - 1 \right]$$

Thus knowing m, S and S' we can calculate m.

Uses:

1. Zn, Cu, Hg and other cations have been determined by this method.

2. This method is used to analyse the mixture of amino acids obtained by hydrolysing proteins outside the body using labeled amino acids containing N^{15} to act as a tracer.

C – 14 Dating:

The age of a piece of a wood or animal fossil can be determined by C – 14 dating technique. This technique is based on the determination of C^{14}/C^{12} ratio.

Plants take up the CO_2 from the atmosphere. The CO_2 in the atmosphere contains a small amount of radioactive C^{14} also. When the plant is alive $_6C^{14}$ decays as follows.

$$_6C^{14} \longrightarrow _7N^{14} + _1n^0$$
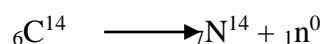
(T = 5760 years). But the loss is compensated by taking C^{14} form the atmosphere. So the ratio C^{14}/C^{12} remains always constant. But when the plant dies the ratio C^{14} continues to disintegrate. But the loss is not compensated. So C^{14}/C^{12} continuously decreases. Thus by measuring C^{14}/C^{12} and knowing. T, the age of the plant and t can be determined using the formula.

$$t = \frac{2.303\,T}{0.693}\ \log\left(1 + \frac{Amount\ of\ C^{14}\ in\ fresh\ wood}{Amount\ of\ C^{14}\ in\ dead\ wood}\right)$$

Problem:

The beta activity from 1 gram specimen of carbon obtained from an old wood showed a count of 10.66/ min while the activity from 1 gram of carbon from the wood of recently cut tree showed a count rate of 12.24/ min. What is the age of the old specimen of wood?

[For C^{14}, $t_{1/2}$ = 5600 years]

Several Times

Solution:

The age of the old specimen t is given by

$$t = \frac{2.303\,T}{0.693}\ \log\left(1 + \frac{Amount\ of\ C^{14}\ in\ fresh\ wood}{Amount\ of\ C^{14}\ in\ dead\ wood}\right)$$

β activity of fresh wood α Amount of C^{14} in it

12.24 α Amount of C^{14} in fresh wood.

β activity of old wood α Amount of C^{14} in it

10.66 α Amount of C^{14} in old wood.

$$\frac{\text{Amount of } C^{14} \text{ in fresh wood}}{\text{Amount of } C^{14} \text{ in old wood}} = \frac{12.24}{10.66}$$

$$t = \frac{2.303 \times 5.600}{0.693} \times \log \frac{12.24}{10.66}$$

$$t = \frac{2.303 \times 5.600}{0.693} \times 0.06$$

$$t = 1,117 \text{ years}$$

Exercise:

The amount of $_6C^{14}$ isotope in a piece of wood is found to be one sixth present in fresh piece of wood. Calculate the age of wood. Half life period of $C^{14} = 5577$ years.

Answer:

20,170 years. Clue: Put amount of C^{14} in fresh wood $= 1$ and amount of C^{14} in old wood $= 1/6$.

Isotopes as tracers:

Each radioactive isotope has specific property and by which the isotope can be easily detected and estimated quantitatively. Since the radioactive isotope possesses identical chemical properties, by mixing a small quantity of radioactive isotope with non radioactive elements, the course of a chemical reaction can be studied. Thus the radioactive isotope is acting as a tracer element. The presence of radioactive tracer in the product can be detected and estimated quantitatively using sensitive instruments. Some of the examples are given below.

**Application in the determination of the mechanism of reactions:**

a) Photosynthesis Reaction:

In photosynthesis the green plants, when exposed to sunlight take up CO_2 and H_2O which are converted into sugars and starch. However at the same time plants give out oxygen, whatever the oxygen produced by plants originates from CO_2 or from H_2O both had been answered by the use of radioactive O^{18}. So it is clear that the evolved oxygen comes from the water and not from CO_2^{18}. Thus the reaction that takes place in photosynthesis is as follows.

$$6CO_2^{18} + 12H_2O \longrightarrow C_6H_{12}O_6^{18} + O_2 + 6H_2O^{18}.$$

b) Ester Hydrolysis Reaction:

The course of Ester hydrolysis can be studied by using stable O^{18} isotopes as the labeled atom. The hydrolysis of an atom by water enriched with heavy oxygen is indicated as:

$$R-\underset{\underset{O}{\parallel}}{C}-OR' + HO^*H \rightleftharpoons R-\underset{\underset{O}{\parallel}}{C}-O^*H + R'OH$$
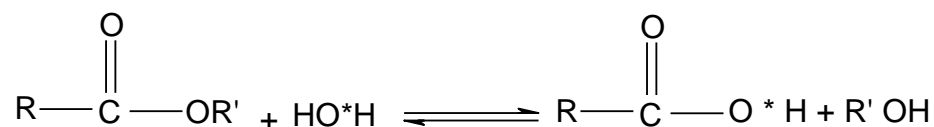
This clearly indicates that the labeled oxygen is present in the acid which proves that the OR' group has been substituted by the OH group in the hydrolytic reaction.

Uses of radio isotopes in the treatment of disease: (Radiotherapy).

The treatment of a disease using radioisotope is called radiotherapy. Some of the examples of radiotherapy are given below.

Treatment of Cancer growth:

Radio Cobalt (Co^{60}) and radio gold (Au^{198}) are used in the treatment of cancer.

Treatment of Hyperthyroidism:

Radioactive Iodine (I^{131}) is used in the treatment of hyperthyroidism and cancer of the thyroid.

Treatment of Skin Disorder:

Radio phosphorus (P^{30}) is used in the treatment of skin disease.

Treatment of Leukemia: (Blood Cancer)

Radioisotope of phosphorus is being used in the treatment of Leukemia.

Nuclear Reactors in India :

Important nuclear fules which are used for the production of nuclear energy in nuclear reactors are U^{235} in its natural concentration of 0.715% or in an enriched proportion and Th^{232} and U^{238} which can be converted party into U^{235} and Pu^{239} obtained form U^{238}

Uranium is extracted form pitch plende which is not available in India. But carnotite is another mineral containing uraium mineral have been recently found in Bhatin (Bihar) and in Lalipur (UP). Monazite sands of travan core are major sources of U and Th. Plutonium does not occur in nature ; It is produced form U. A big plutonium plant is in Trombay, Mumbai, in Maharashtra state. India produces about 90kg of plutonium anually.

NOTES

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Unit II

Alkynes

Alkynes are unsaturated hydrocarbons which contains a carbon – carbon trible bond (c≡c). The general formula of this class of compounds is C_nH_{2n-2}

| Structure	IUPAC Name
H-C ≡ C-H	Ethylene
CH_3 ≡ C- H	Propyne
CH_3-C≡C-CH_3	2-Butyne

Alkynes like alkenes are reactive compounds and hence they never occur in the free state in nature. They are present to a sizeable extent in the gases obtained by crocking of petroleum.

Methods of preparation:-

1. Dehydrohalogenation of 1,2- dihalides:-

1,2 dihalides (vinyl dihalides) when treated with alcoholic KOH eliminate two molecule of hydrogen halide from adjacent carbons to yield an alkyne.

$$R-C\equiv C-H \quad \text{Alkyne}$$

$$\xrightarrow[\text{-2HX}]{\text{KOH}}$$
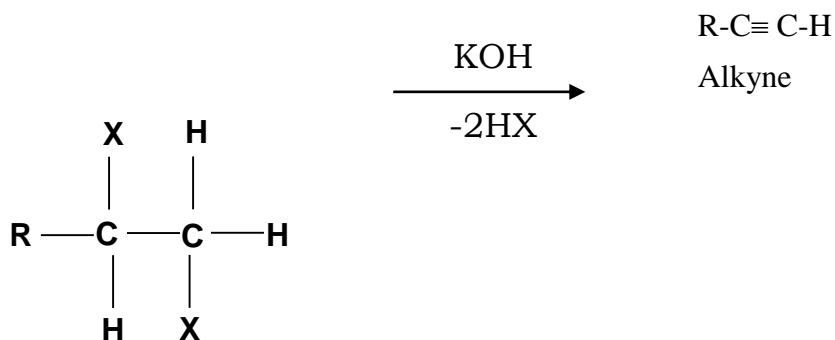
1,2 dihalides

2. Dehydrohalogenation of 1,1- dihalides:-

1,1- dihalides (vinyl dihalides) when treated with alcoholic KOH elimate two molecule of hydrogen halide from adjacent carbons to yield to alkyne.
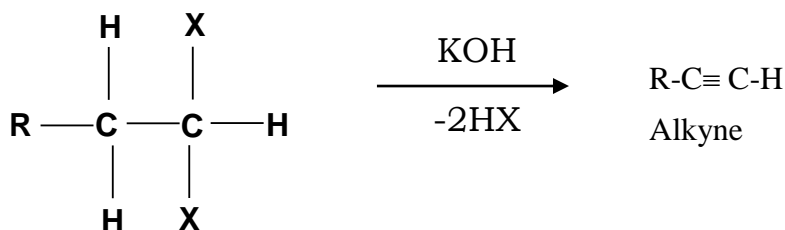
1,1,-dihalides

3. Dehalogenation of tetrahalide:-

Tetrahalide in which the halogen atoms are attached to adjacent carbon atoms (two on each carban) when heated with zinc dust in alcohol yields alkynes.

$$+2Zn \xrightarrow{alcohol} R - C \equiv C - H + 2ZnX_2$$
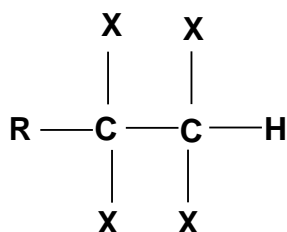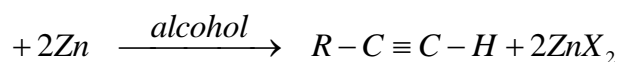
1,1,22-Tetra

halide alkane

Acidity of alkynes:-

A very importance feature of acetylene and other alkynes having a hydrogen attached to the triply bonded carbon atom is the acidic nature of such a hydrogen. There fore unlike alkanes and alkenes, alkynes behave as weak acids.

Acidic nature of Acetylene:-

The acidic nature of hydrogen in acetylence is characteristic of hydrogen in the group $\equiv CH$. The $\equiv$ C-H bond has considerable ionic character due to resonance.

$$H - C \equiv C - H \leftrightarrow H - C \equiv C^- H^+ \underset{H^+}{\longleftarrow} H^+ C^- \equiv C - H \leftrightarrow H^+ C^- \equiv C^-$$
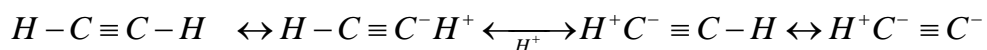
We know that the electronegativity of a carbon atom depends on the number of bonds by which it is joined to its neighbouring carbon atom π electrons are more weakly bond that electrons.

So the electron density around a carbon atom with π bonds is less than that with only σ bonds. So carbon atom having one π bond has a slight positive

charge campared with a carbon atom which has only. σ - bonds. Hence the electronegativity of an sp^3 hybridized. carbon is greater than that of an sp^3 hybridsed carbon similarly a carbon atom with two π bonds carries slightly more positive charge when compared to the carbon with one π bond. Thus the electronegativity of an sp hybridized carbon is greater than an sp^2 hybridized carbon.

There fore the more 's' character bond has, the more electronegative carbon. Thus the electronegativity of carbon is in the order $sp>sp^2>sp^3$, just as that characters decrease from 50 to 33:3 to 25% respectively.

Hence the proton of acetylene is more easily released, than ethylene or ethane. Thus acetylene is acidic. However, the acidic nature of acetylene and other terminal alkynes is very weak. The acidic nature is even weaker than water.

Acetylene and other terminal alkynes undergo following reactions due to the presence of acidic hydrogen in them.

 i. Acetylene forms a number of metalic derivatives by the subtitution of the hydrogen atoms of acetylence by alkali metals.

 ii. Heavy metal acetylide are also formed when acetylene reacts with Ag^+ and Cu^+ solutions

Formation of Acetylides :

1. Alkali metal acetylides:

Acetylene and higher the terminal alkynes react with alkali metals to form salts and liberated hydrogen. For example, acetylene reacts with sodium to produce disodium acetylides and evolve hydrogen.

$$\text{H-C} \equiv \text{C-H} + 2\text{Na} \xrightarrow[-H_2]{} Na^+C^- \equiv C^-Na^+$$
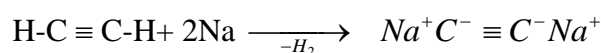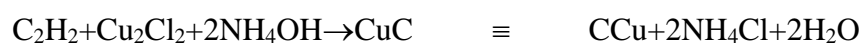
acetylene   disodium acetylide

By using large excess of acetylene mono sodium acetylide is got as the main product. When ocetylene is passed through a solution of sodium in liquid ammonia mono sodium acetylide is formed.

2. Heavy metal acetylides:

Alkynes react with heavy metal ions particularly Ag^+ and Cu^+ ions to form metal acetylides. when acetylene is passed into ammoniacal Curprous chloride solution, a chocolate brown precipitate of copper acetylide is formed.
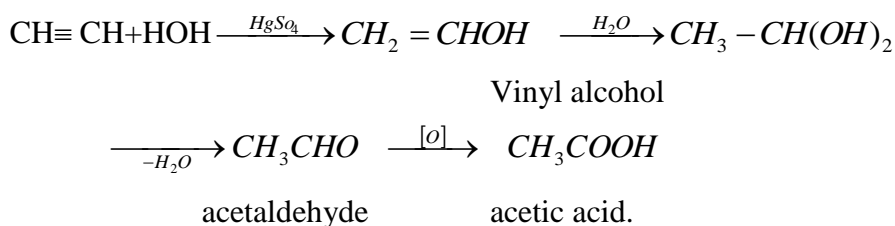
$$\text{C}_2\text{H}_2 + \text{Cu}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{CuC} \equiv \text{CCu} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$$

Copper acetylide

with ammoniacal silver nitrate solution a while solution precipitate of silver acetylide is formed.

$$C_2H_2 + 2AgNO_3 + 2NH_4OH \rightarrow AgC \equiv C\ Ag + 2NH_4NO_3 + 2H_2O$$

Silvers acetylide.
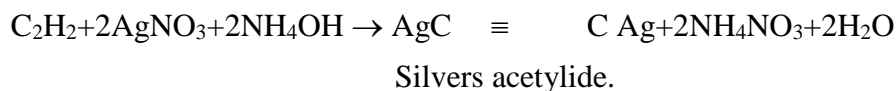
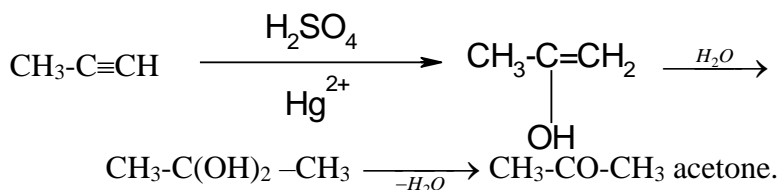## 3. Addition of water with HgSo₄ catalyst:

A characteristic property of alkynes is the direct addition of water. This reaction is not shown by the alkenes. When acetylence is passed into water containing (40% sulphuric acid and mercuric oxide). Mercuric sulphate, acetaldehyde is formed.
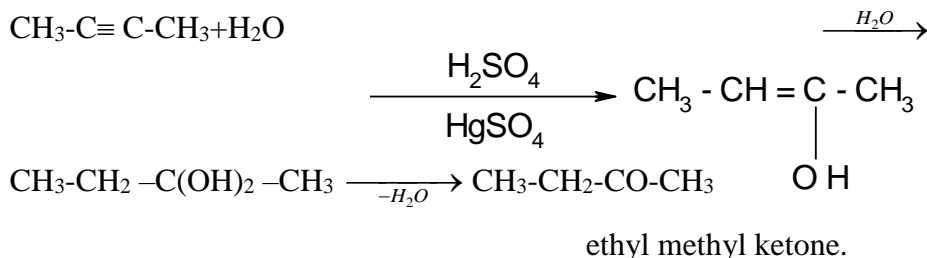
$$CH \equiv CH + HOH \xrightarrow{HgSo_4} CH_2 = CHOH \xrightarrow{H_2O} CH_3 - CH(OH)_2$$

Vinyl alcohol

$$\xrightarrow[-H_2O]{} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

acetaldehyde   acetic acid.

The reaction is of great industrial importance since acetaldehyde can be converted into acetic acid and various other compounds.

The addition of water to vinyl alcohol in the second step follows Markownikoff's rule.

When propyne is passed into water containing H_2So_4 and $HgSo_4$ acetone is formed.

$$CH_3\text{-}C\equiv CH \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3\text{-}\underset{\underset{OH}{|}}{C}=CH_2 \xrightarrow{H_2O}$$

$$CH_3\text{-}C(OH)_2 - CH_3 \xrightarrow[-H_2O]{} CH_3\text{-}CO\text{-}CH_3 \text{ acetone.}$$

When 2-butane reacts with dilute H_2So_4 and $HgSo_4$ we get ethyl methyl ketone.

$$CH_3\text{-}C \equiv C\text{-}CH_3 + H_2O \xrightarrow{H_2O}$$

$$\xrightarrow[HgSO_4]{H_2SO_4} CH_3 - CH = \underset{\underset{OH}{|}}{C} - CH_3$$

$$CH_3\text{-}CH_2 - C(OH)_2 - CH_3 \xrightarrow[-H_2O]{} CH_3\text{-}CH_2\text{-}CO\text{-}CH_3$$

ethyl methyl ketone.

4. Addition of hydrogen halide:

Alkynes and hydrogen halides add according to markowni koff's rule.

Markownikoff's rule states that the negative part of the addendum attaches itself to the carbon atoms containing less number of hydrogen atom. Eg.
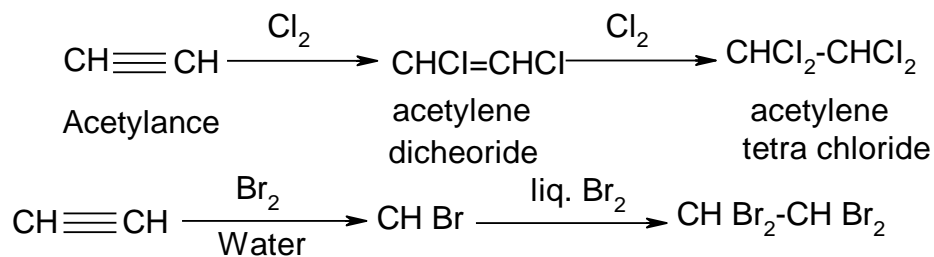
$$CH\equiv CH \xrightarrow[\text{M-rule}]{\text{HI}} CH_2=CHI \xrightarrow[\text{M-rule}]{\text{HI}} CH_3\text{-}CHI_2$$

acetylene   Vinyliodide   ethyliodene Iodide

$$CH\equiv CH \xrightarrow[\text{M-rule}]{\text{HBr}} CH_2=CH\,Br \xrightarrow[\text{M-rule}]{\text{HBr}} CH_3\text{-}CH\,Br_2$$

     Vinyl Bromide   ethyliden bromide

$$CH_3\text{-}C\equiv CH \xrightarrow[\text{M-rule}]{\text{HBr}} CH_3\text{-}CBr=CH_2 \xrightarrow[\text{M-rule}]{\text{HBr}} CH_3\text{-}CBr_2=CH_2$$

Propyne $_2$-bromo poop-I-ene $_{2'2}$-dibromo propane
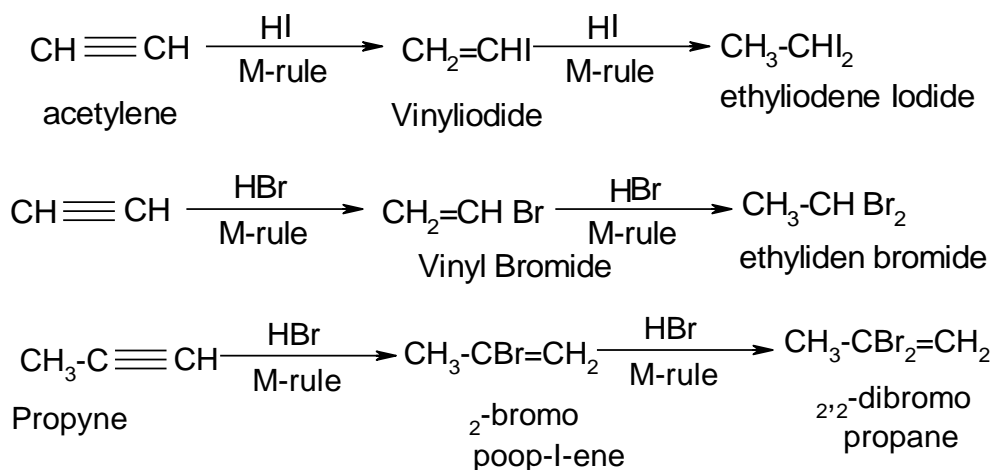
The presence of peroxide anti-Markownikoff'srule products are got (This is called peroxide effect).
Eg:

$$CH\equiv CH \xrightarrow[\text{Peroxide}]{\text{HI}} CH_2=CHI \xrightarrow{\text{HI}} CH_2I\text{-}CH_2I$$

ethylene Iodide
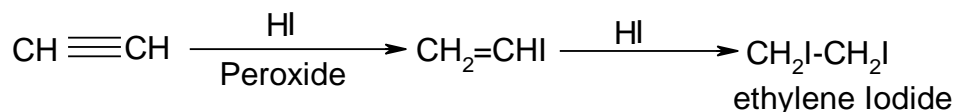
5. Addition of Halogens :

Alkynes add halogens and give dihalides first and then tetrahalides.

$$CH\equiv CH \xrightarrow{Cl_2} CHCl=CHCl \xrightarrow{Cl_2} CHCl_2\text{-}CHCl_2$$

Acetylance   acetylene dicheoride   acetylene tetra chloride

$$CH\equiv CH \xrightarrow[\text{Water}]{Br_2} CH\,Br \xrightarrow{\text{liq. } Br_2} CH\,Br_2\text{-}CH\,Br_2$$

6. Oxidations :

a) When accetylene is oxidised with chromic acid we get acetic acid.

$$CH\equiv CH \xrightarrow[\text{[O]}]{Cr_2O_3} CH_3\,COOH$$

acetylene   acetic acid
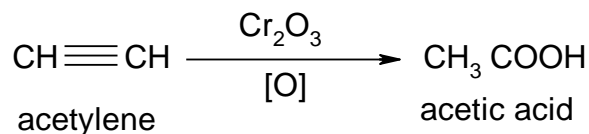
b) When acetylene is oxidised with alkaline $KMnO_4$ we get oxalic acid

$$CH \equiv CH \longrightarrow COOH - COOH$$

acetylene   oxalic acid
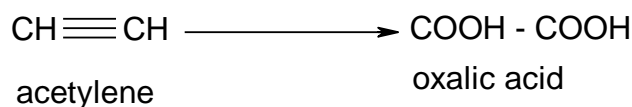
c) Higher alkynes are broken where the triple bond is present on treatment with strong alkaline $KMnO_4$ gives a mixture of acids. From the nature of the products we can locate the position of the triple.

$$R-C \equiv C-R' \xrightarrow[\text{[O]}]{\text{AlK.KMno}_4} R-COOH + R' \, COOH$$

Eg:

$$CH_3-C \equiv C-CH_3 \longrightarrow _2CH_3 \, COOH$$
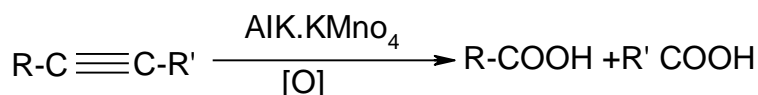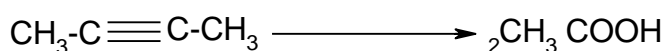
2- Butune   Acetic Acid

7. Ozonolysis:

Definition :

When an unsaturated compound is treated with ozone an ozonide is formed. This ozonide on hydrolysis gives various products. This reaction is known as ozonolysis.

E.g.

a) With ozone, acetylene first forms the ozoide. This on hydrolysis gives glyoxal, which gives formic acid in turn.

Ozonide   glyoxal   Formicacid
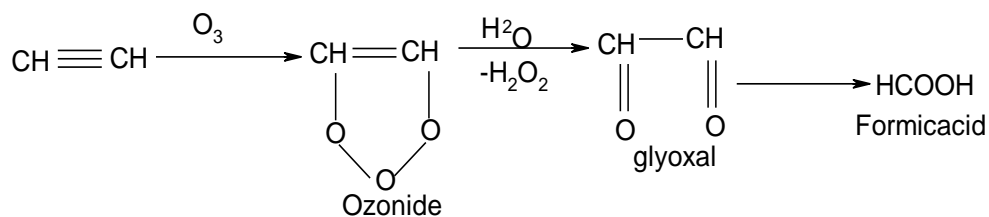
b) Higher alkynes give diketones (I) which are further oxidised to a mixture of corresponding acids.

$$\longrightarrow RCOOH + R' \, COOH$$

53

(i) $CH_3 - C \equiv CH$ ⟶ $CH_3-C = C\text{-}H$

Propyne

(with ozonide ring: two C's connected to O, O joining at O below)

Ozonide

$\xrightarrow[-H_2O]{H_2O}$ $CH_3\text{-}C\text{-}CHO$ ⟶ $CH_3 COOH + HCOOH$

(CH_3-C-CHO with $\parallel$ O below)

acetic acid   Formic acid

ii) $CH_3\text{-}CH_2\text{-}C \equiv CH$ $\xrightarrow[\text{ii) } H_2O]{\text{i) } O_3}$ $CH_3\text{-}CH_2\text{-}COOH + HCOOH$

Propinoic acid

Impotance :

As in the case of alkenes, ozonolysis of alkynes helps to locate the poistion of the triple bonds.

8. Hydroboration :

Addition of boron hydride to Unsaturated compound is known as hydroboration.

Alkynes under go mono hydroboration and protolysis to give pure alkene. The addition is its in nature.

$HC \equiv CH$ $\xrightarrow{B_2H_6}$ $(CH_2=CH)_3 B$ $\xrightarrow[HOAC]{H^+}$ $CH_2=CH_2$

acetylene   ethylene

$RC \equiv CH$ $\xrightarrow{BH_3}$ $(R\,CH = CH)_3 B$ $\xrightarrow[HOAC]{H^+}$ $R\,CH = CH_2$

alkene

Terminal and non-terminal higher alkynes and boron hydride (BH_3) is in a –manner to give vinyl boranes. These can be oxidised with alkaline hydragen peroxide to form aldehydes and ketones respectively.

$CH_3CH_2\,CH{=}CH\,OH$ ⟶ $CH_3\,CH_2\,CH_2\,CHO$

butyl aldehyde

i) $CH_3CH_2C \equiv CH$ $\xrightarrow{BH_3}$ $CH_3\,CH_2\,CH = CH\,BH_2$ $\xrightarrow{H_2O_2\,/\,OH\text{-}}$

l-butyne

terminal alkyne   vinye borane

ii) $CH_3-C \equiv CX-CH_3$ $\xrightarrow{BH_3}$ $CH_3-CH = C-CH_3$ $\xrightarrow{H_2O_2/OH^-}$

2 - butyne non

terminal alkyne

$CH_3-CH=C(OH)-CH_3$ $\xrightarrow{\hspace{3cm}}$ $CH_3-CH_2-COCH_3$

Ketones   butan-2-one

(with BH_2 group on the middle carbon)

Mechanism:

The π-bond in acetylene is electron rich and boron is electrons deficients BH_3 coordinates itself with ten π eletrons of the triple bond and froms –a π- complex (I)

(1)   (2)   (3)
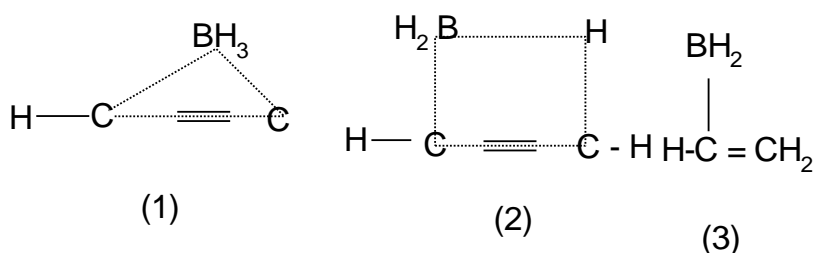
This is follows by the formation of C-H bond as show in figure via a four centered transition of sate (2). As a result of this the new C-Bond C-H bonds are formed from the same side of the triple bond. i.e, syn addition (3) takes place. The addition is controlled by steric considerations. So hydroborations is regioselective unlike electrophilic additon.

Steric factors control regioselectivity and not electronic factors. The boron goes to the carbon which is less conjugated.

Example :

$CH_3-C \equiv CH$ $\xrightarrow{BH_3}$ $CH_3-CH = CHBH_2$
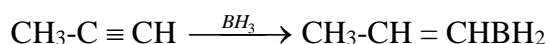
The allyl boranes are not isolated normally. They are either hydrolysed to get alkynes or oxidised to alconhols, aldehydes, or ketones as required.

Importance:

Hydroboration of alkynes is important in organic synthes is as the method provides a way to synthesis of alkenes and carbonyl compounds such as aldehydes and ketones.

Reaction Mechanism II

Aliphatic Nucleophilic Substitutions:

The reaction which involve direct replacement of an atom or group by some other atom or group are called substitutions reactions.

Consider the reaction R–L+ $\bar{A}$ $\rightarrow$ R –A + I

Here R-L is the compound undergoing substitution. It is called the substrate. I is the leaving group and $\overline{A}$ is the attacking group.

When the attacking group is electron rich attacking carbocations are positively charged centers or prints of low electron density, it is called a nucleophile.

E.g   Halide ion X- (X^- Cl, Br or I) Hydronide ion $-OH^-$ alkoxide ion RO^- Cyanide ion CN^- etc.,

A nucleophilic substitution reaction involves the displacement of a leaving group, from the carbon atom and formation of a new bond with attacking nucleophile.

Two steps may be considered in nucleophilic substitutions.

  i.   Breaking of an old bond and

 ii.   Formation of a new bond. The time lag between the two steps.

iii.   They can give rise to three types of reaction namely SN^1, SN^2 and SNi reactions.

  a.   In SN^1 reaction, an old bond is first broken and then the new bond is formed.

  b.   In SN^2 reaction, an old bond is broken and the new bond is formed simultaneously.

  c.   In SNi reaction, a new bond is first formed and then the old bond is broken.

Mechanism of SN^1 Reaction :

This is called substitution nucleophilic unimolecular reaction. The hydrolysis of t-butyl chloride in alkali is found kinetically to follow the equation.

$$Rate \propto [R – Halide]$$

That is, the rate is independent of the concertration of OH^-, OH^- can play no part in the rate determining step. The mechamism of the reaction is interpreted as follows. The halide under goes shows ionization. This step is the rate determining step. An intermidiate planer carbonium ion is formed. This followed by fast OH^- attack. The energy necessary for the initial ionication is largely recovered in the energy of solvation of ions. In the planer intermediate the three methyl groups are as far apart as they can. The attack by OH^- can take place from either side. Tertiary butyl bromide shows SN^1 mechanim.
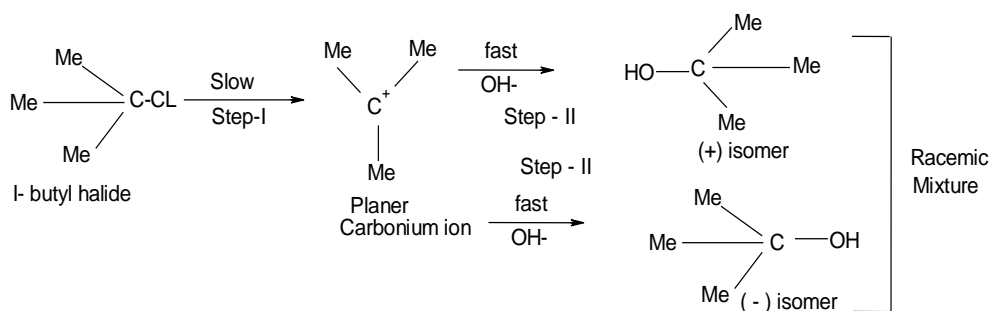
As the carbonium ion formed in the show rate determining step of the reaction is planer, it is to be expected that the subsequent attack by the nucleophilic reagent such as OH^- will take place with equal readiness from either side of the planer ion. Thus 50:50 mintures of species having the same and oppsite configuration of the starting material will be obtained. That is racemisation will take place yielding an optically inactive produced. That is a racemic (±) mixture will be obtained.

Mechanism of SN^2 Reaction :

This is called substitution bi molecular reaction. Here bi refers to the molecularity and not to the order of reaction. The hydrolysis of methyl bromide in aqueous alkali bas been shown to proceed according the equation.

Rate α [R – Halide] [OH^-]

The rate of the reaction depends on the concentration of alkyl halide and alkali. That is, in the rate determining slowers step both akyl halide and alkali participate. Ingold suggested the following mechanism for this reaction. The hydroxide ion approaches the molecule from the opposite side of the halogen atom. The hydroxide ion gets partially attached to the methyl group before the halogen atom is removed. The breaking of C-X bond and the formation of C-OH bond takes place simultaneously. The energy required for breaking C-X bond is supplied by the formation of C-OH bond. This may be represented as.

The rate of this reaction is dependent on the case of formation of transition state. In the transition state we have groups attached to the carbon atom. Methyl and ethyl bromides follow SN^2 mechanism.

Methyl bromide
(+) isomer

transition state

(-) isomer
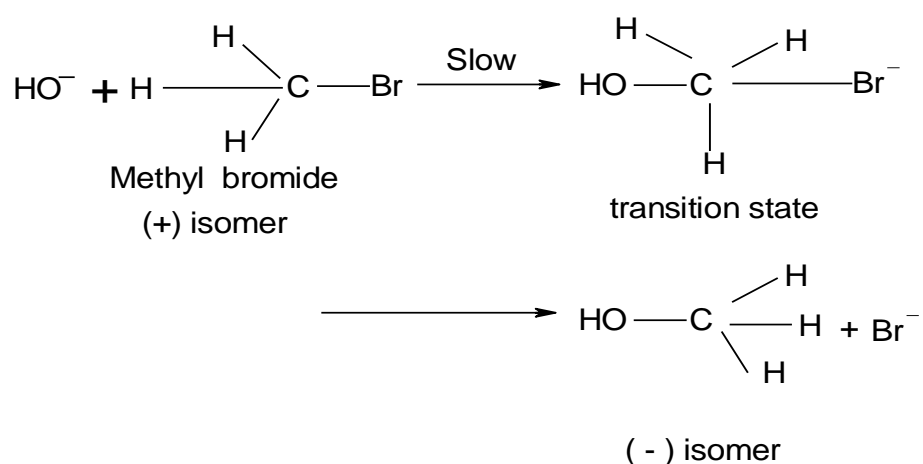
The transition of, the hydrohysis of an optically active halide presents some interesting stereo chemical features. In the SN^2 mechanism, the three groups attached to carbon and effectively turned inside, out. The carbon is said to have inversion of configuration. If the optically active halide is dextro rotatory, the alcohol formed may be leavo – rotatory. We should bear in mind that while the formation of a new compound, if the configuration is reversed there need not necessarily be a different rotation. Suppose that the compound formed is also a halide definitely it will have opposite rotation. So we can conclude that SN^2 mechanism which brings out reversal of configuration may give a compound of opposite rotation.

Mechanism of SN^i Reaction :

In the above two mechanisms the replacement of groups led to inversion of configuration or racemisation. In certain cases the reaction proceeds with retention of configuration. This is SNi reaction. In the SN1 reaction, an old bond is first broken and a new bond is formed. In the SN2 reaction an old bond is broken and a new bond is formed simultaneously. In the SNi reaction a new bond is first formed and then the old bond is broken. In this case the starting material and the product have the same configuration i.e, retention. Example for such type of reaction is the chlorination of alcohol by the chloride. This reaction follows second order kinetics.

Rate $\propto$ [ROH] [SoCl$_2$]

The mechanism of the reaction is follows;

58
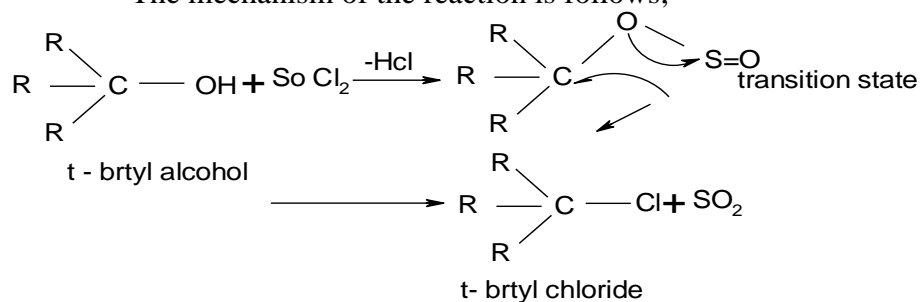
1. Effect of solvents :

        The nature of the solvent plays a very important role in determining the mechanism by which a reaction occurs. This is because polarity of the solvent becomes important in the case of formation of Carboninm ions from alkyl halides. In the case of SN^1 reactions, Ionisation of an alkyl halide takes place. The energy requried for ionisation is supplied by the formation of dipole bonds between the solvent and the polar transistion state. It is obvious that the higher the polarity of the solvent the stronger the solvent forces and faster than.

        In the case of SN^2 reaction, there is no transition state which is more polar than the reactions. In fact polar solvent can solvent the reactants more stronglly than the transistion state. This shows down the rate if SN^2 reaction to a small extent.

2. Effect of living groups:

        The nature of the halogen atom does not have much influence on reaction mechanisms. However it alters the rate of the reaction which follows the order.

        R-I > R-Br > R- Cl

        This order is applicable for both SN^1 and Sn^2 reaction

3. Effect of nucleophiles:

        The nature of the nucleophilic reagent is an important factor in determining the actual mechanism of a reaction. The nucleophile does not enter into the rate determining step in SN^1 mechanism. But it is involved in the SN^2 mechamism. Generally speaking, strong nucleopilic reagents favour SN^2 mechanism. It is because they can push halogen away from the molecule of alkyl halide. On the other hand weak nucleophilic reagents such as C_2H_5OH. H_2O tend to favour SN1 mechanism. The following is the order of nucleophilicity.

$$HS^- > CN^- > I^- > CN^- NH_3 > OH^- N_3^- > Br^- > CI^- > F^- > No_3^- > H^2O.$$
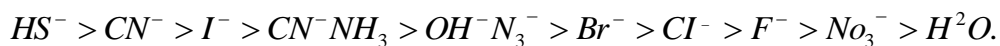
        The structure of the substrate products two types of effects namely

    i.   Steric effects namely

    ii.   Polar effect

(i) Steric effects of substrate :

        In the case of SN^2 mechanism the transition state has five groups attached to the carbon atom. The large the size of the groups is the greater is the over crowding or strain at central carbon atom. So the reaction will be

sterically more indered. The steric strain will be relieved in the ionisation step of SN^1 mechanism. Thus steric hindrance favours SN^1 mechanism. Such an effect of bulky groups on SN^1 mechanism is termed sterical acceleration. Thus the rate of SN^2 reaction goes on decreasing as the steric hindrance increase. E.g.

Methyl chloride undergoes hydrolysis by SN^2 mechanism where as t-butyl chloride undergoes hydrolysis by SN^1 mechanism.

(ii) Polar effects of substrate :

In the alkyl halides greater than electron density will be expected on the carbon atom of the X.X group of t-butyl halide because of the greater +I effect of the effect methyl groups.

$$CH_3CH_3X \qquad \begin{matrix} H_3C \\ \quad \diagdown \\ H_3C \quad CHX \\ \quad \diagup \\ H_3C \end{matrix} \qquad \begin{matrix} H_3C \\ \quad \diagdown \\ H_3C \quad\text{—}\quad C\text{-}X \\ \quad \diagup \\ H_3C \end{matrix}$$

As the negative charge on the central carbon atom increase, the attack by a negatively charge nucleophilic reagent is opposed. Thus the formation of transistion state by SN^2 mechanism is very less. So this favour SN^1 mechanism because the ionisation will be easier. Thus primary halides react by SN^2 mechanism while tertiary halides react by SN^1 mechaism due to both steric and polar effects.

Secondary alkyl halides follow either SN^1 or SN^2 mechanism depending upon other factors.

When hydrogen atom in methyl chloride is replaced by phenyl group the mechanism is shifted from SN^2 to SN^1.

$$\text{C}_6\text{H}_5\text{—CH}_2\text{Cl} \longrightarrow \text{Cl}^- + \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2 \longleftrightarrow \text{etc.,}$$
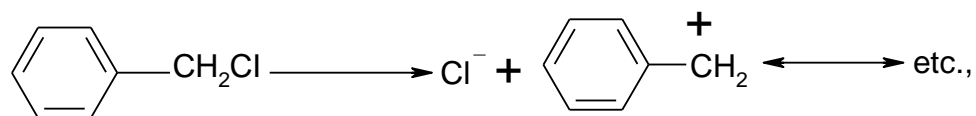
The carbonium ion got during ionisation is stabiliced by resonance and so SN^1 mechanism is favoured.

The presence of the electron with drawing group in the P-posision retards the ionisation. So the reaction of P-nitro bezyl chloride is low when compared to benzyl chloride.

$$O_2N\text{—C}_6\text{H}_4\text{—CH}_2\text{Cl}$$
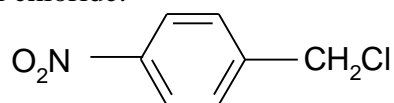
Vinyl chloride and chloro benzene are not reactive due to the double bond character between chlorine and the next carbon. So it is not ionsed.
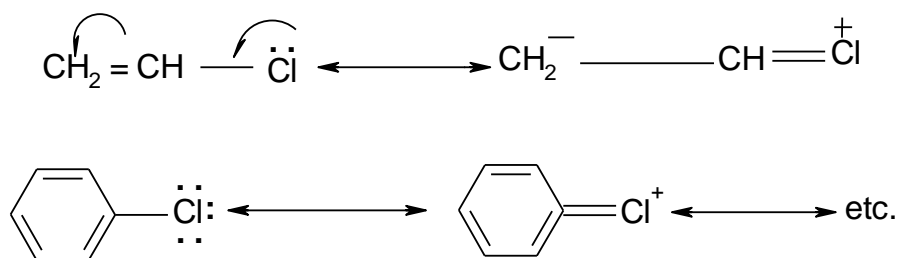
Elimination Reactions:

Elimination reactions are those reactions in which two groups are removed from the substrate molecule without replacement by other groups. Eg:-

$$RCH_2CH_2 X \xrightarrow{OH^-} RCH = CH_2 + HX + H_2O$$

Elimination reaction can be clasified under two general headings.

 i. α - Elimination reaction, and

 ii. β - Elimination reaction

α - Elimination reactions:-

In these reactions the group eliminated are from the same carbon atom.

$$CHCl_3 \xrightarrow{-HCl} CCl_2$$
Dichlorocarbene
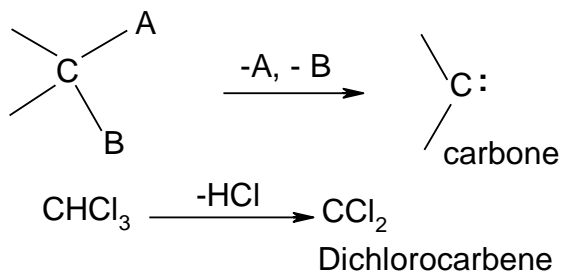
β - Elimination reactions:-

These are reactions in which groups on adjacent atoms are eliminated with the formation of an unsaturated bonds like.
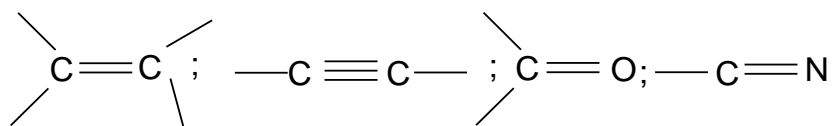
β - Elimination reactions are so common that the prefix β - is generally dropped. The β - elimination reactions can be further sub – divided into.

 i. Those, which occur by a biomolecular mechanism called E_2 reactions analogous to SN^2, and

ii. Those which occur by a unimolecular mechanism called E_1, reactions analogous to SN^1.

E1 Elimination Reaction :

Elimination reactions, which take place irresective of the concentration of hydronyl ions or of other basic reagents are called unimolecular or E_1 elimination reations. The elimination of HBr from t-butyl bromide is an example for this type of reaction.

t- butyl bromide   alkene
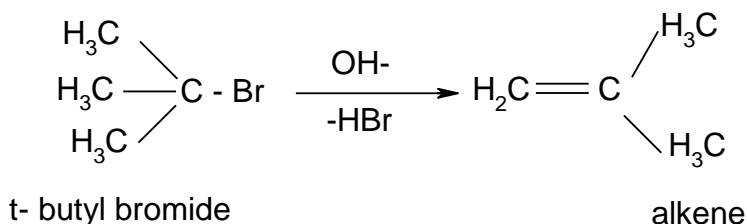
The rate equation of this reaction is

Rate α [R – Halide]

Mechanism of E_1 Reaction :

A mechanism analogous to SN^1 has been proposed for each elimination reactions.

As in the case SN1 mechanism. Solvation plays an important role in E_1 mechanism. Primary and secondary alkyl halides generally react E_2 mechanism. Where as tertiary halides reacts according to E_1 mechanism.

alkyl halide
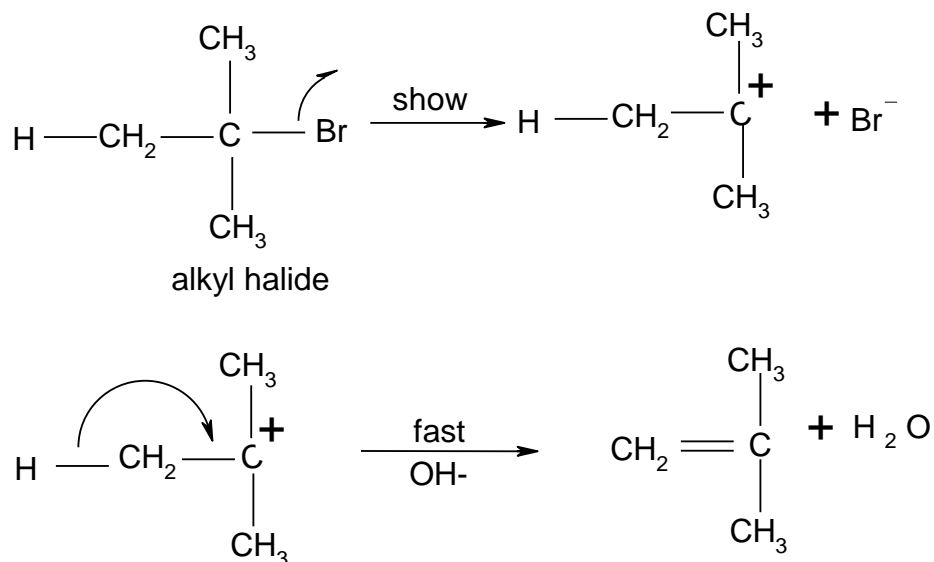
The rate determining step is ionisation of the substrate to give a carbonation. This rapidly loses a β - proton to give the product. The E_1

mechanism normally operates without an added base. The first step in E_1 is exactly the same as that of the SN_1 reaction.

E_2 Elimination Reaction :

The rate of reaction following this mechanism is dependent upon the concentration of both the substrate and the attacking base since both are involved simultaneously in the rate determining step. For example, the rate of elimination of hydrogen halide from an alkyl halide by alcholic KOH is given by.

Rate ∞ [R – Halide] [OH⁻]

alkyl alide   alkene
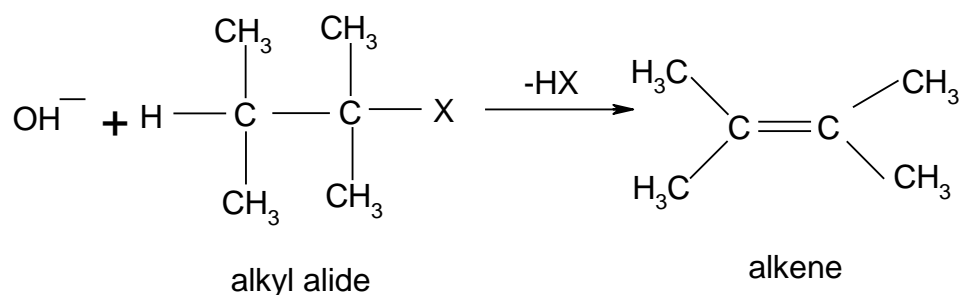
Mechanism of E_2 reaction :

The reaction takes splace in one step. The removal of a proton from the β - carbon atom by a base occurs with a simultaneous loss of halide ion from the carbon atom along with the electrons which formed the C – X bond.

Alkyl halide   alkene
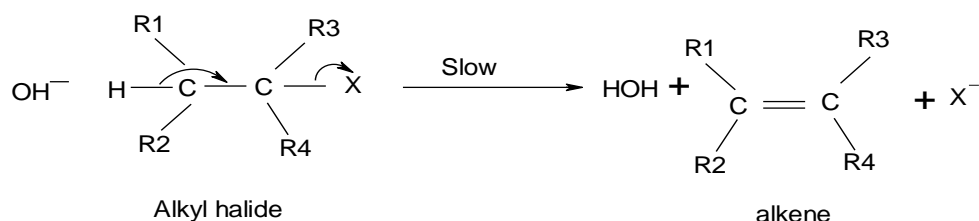
The transition state of E_2 reaction may be represented as,
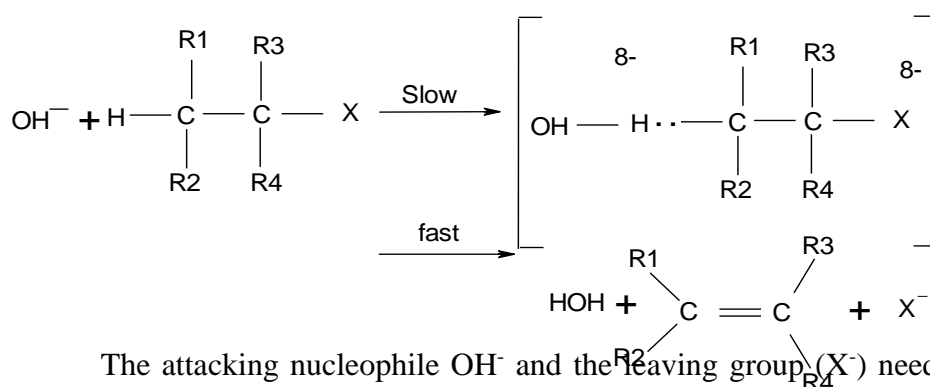
The attacking nucleophile OH⁻ and the leaving group (X⁻) need not necessarily be negatively charged. They should have a shared pair of

electrons (Like H_2O). Thus in E_2 reaction removal of proton formation of double bond and elimination of halide ion normally occur simultaneously.

The factors which favours bi molecular substitution reactions SN^2 usually promote bi molecular eleminations. E_2 also, that is, any factor that serves to stabilize the tranistion state will promote the E_2 reaction.

Hofmann elimination :

Eliminations following hofmann rule are called hofmann eleminations.

Hofmann's rule :

When quarternary ammonium bases are decomposed the olefin formed is that whose unsaturated carbon atoms are linked to the least number of alkyl groups. That is the least conjgated olefins is formed. For example in the following reaction A and B are two possible products.
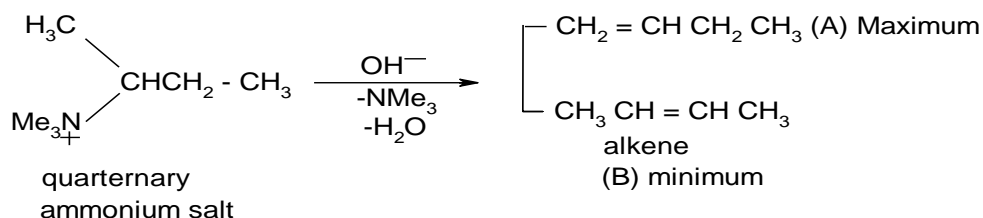
A has the minimum alkyl group attached to the olefine carbon where as B has two alkyl groups attached to olefinie carbon. Therefore A is the predominant product according to Hofmann's rule.

Saytzeff's Elimination:

Eliminations following Saytzeff's rule are called Saytzeff's Elimination.

Saytzeff's Rule:

Need for the rule: We have to seen that an alcohol on dehydration gives an alkyl and an alkyl halide on dehydrohalogenation gives an alkene.

If the alcohol or the alkyl halide can eliminate in two different ways to gives two different olefins, which will be formed with much case E.g.,
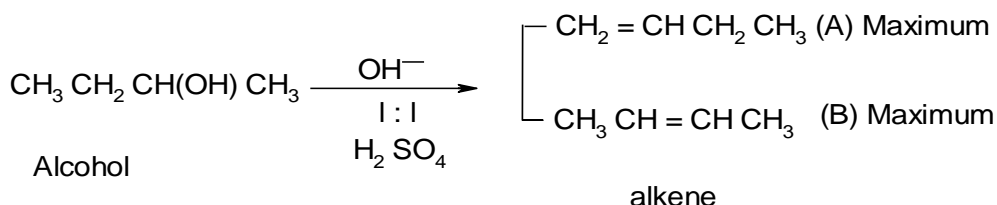

which alkene will be formed? A or B?

64
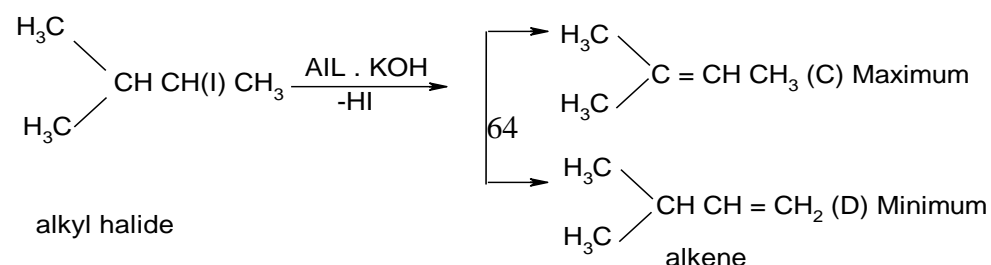
Saytzeff's rule helps us to predict the product in such cases.

Reaction Mechanism:

Electrophilic Substitution Reactions:

Benzene undergoes electrophilic substitution reactions. The benzene ring with its delocalized π electrons in an electron rich system. It is attacked by electrophiles, giving substitution products. These reactions can be represented as,
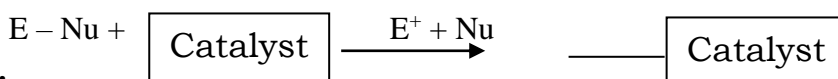

Substitution
Product
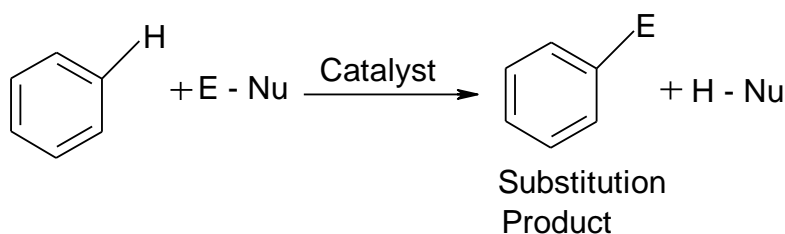
Where E^+ is any electrophile and Nu;⁻ is a nucleophile. Such reaction in which hydrogen atom of the aromatic ring is replaced by an electrophile is called electrophilic aromatic substitution reactions.

General Mechanism:

All electrophilic aromatic substitution reactions follows the same three step mechanism.

Step 1:

Formation of an electrophile.

$$E - Nu + \boxed{Catalyst} \xrightarrow{E^+ + Nu} \underline{\qquad} \boxed{Catalyst}$$

Step 2:

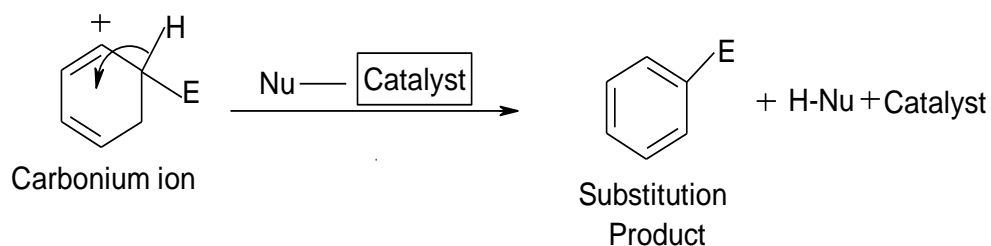The electrophile attacks the aromatic ring to form a carbonium ion.
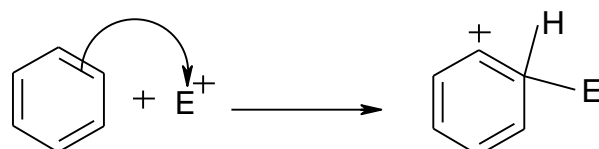
The intermediate ion is resonance – stabilized. It is a hybrid of the following three structures.
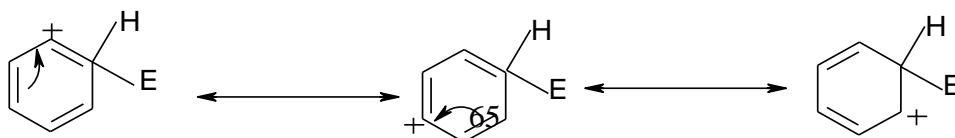
Step 3:

Loss of proton gives the substitution product.

Carbonium ion

Substitution Product

1. Halogenation:
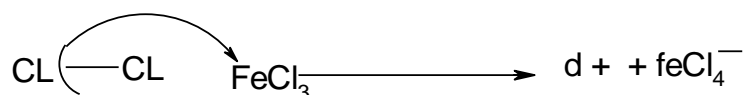
Benzene reacts with chlorine in the presence of FeCl$_3$ (or) AlCl$_3$ at room temperature to form chlorobenzene. Iron powder can be used in place of ferric chloride (2 Fe + 3 Cl$_2$ = 2 FeCl$_3$).

Benzene
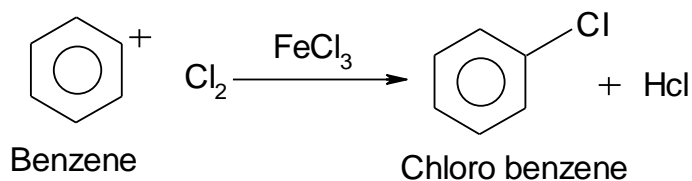
Chloro benzene

Mechanism:

Following steps are involved:

Step 1:

Formation of the electrophile (d$^+$)

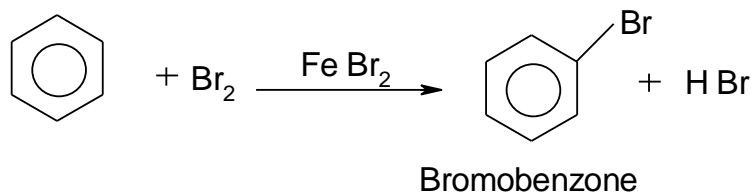$$CL\!-\!CL \quad FeCl_3 \longrightarrow d+ \; + feCl_4^-$$

Step 2:

The electrophile attacks the benzene ring to form a carbonium ion.
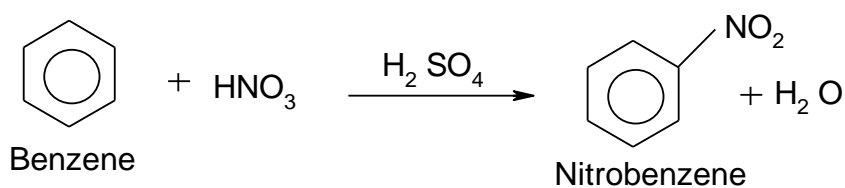
Step 3:

Loss of proton yields the chlorobenzene.

Benzene

Carborium ion

Chloro benzene

66
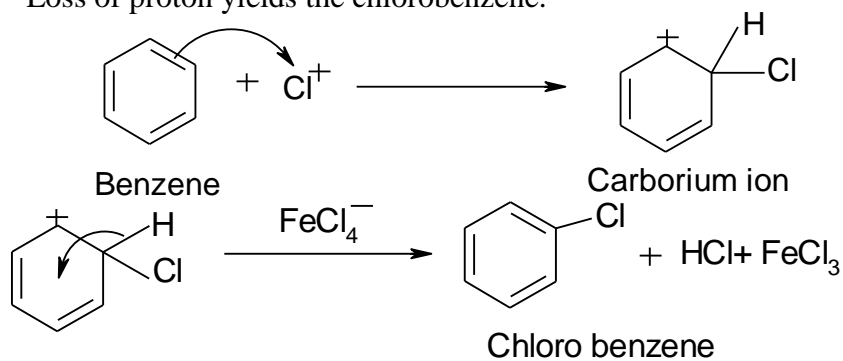
Bromine reacts with benzene similarly.

$$\text{Benzene} + Br_2 \xrightarrow{Fe\ Br_2} \text{Bromobenzone} + H\ Br$$

Bromobenzone

2. Nitration:

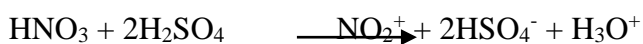Benzene reacts with conc. HNO_3 in the presence of con. H_2SO_4 at 60° to form nitrobenzene.

$$\text{Benzene} + HNO_3 \xrightarrow{H_2\ SO_4} \text{Nitrobenzene} + H_2\ O$$

Benzene   Nitrobenzene

Mechanism:

Following steps are involved.

Step 1:

Formation of the electrophile (NO_2^+)

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$
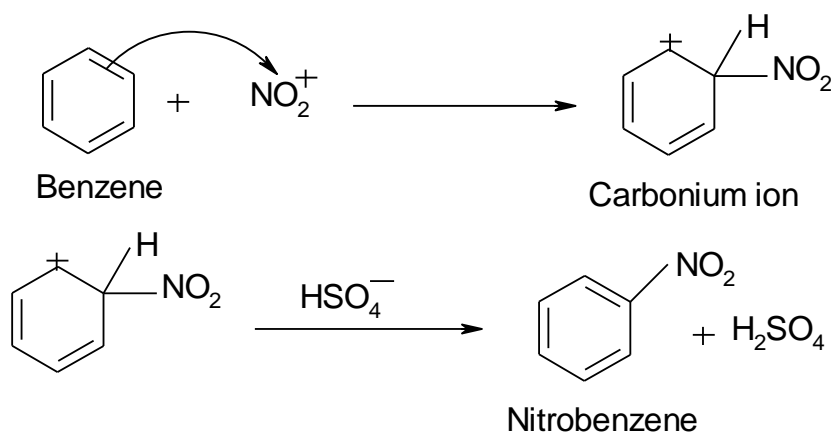
Step 2:

The electrophile attacks the benzene ring to form a carbonium ion.

Step 3:

Loss of proton yields the nitrobenzene.

Benzene NO_2^+ Carbonium ion

$$\xrightarrow{HSO_4^-}$$

Nitrobenzene
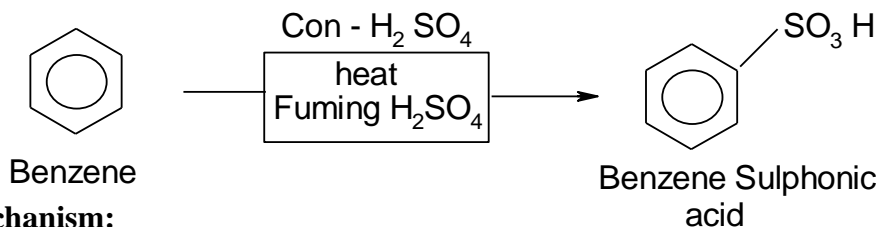
Sulphonation:

Benzene reacts with concentrated sulphuric acid at $120^\circ C$ or fuming sulphuric acid at room temperature to give benzene sulphonic acid.

Note:

Fuming sulphuric acid is concentrated sulphuric acid that contains added sulphur trioxide.

Benzene   Benzene Sulphonic acid
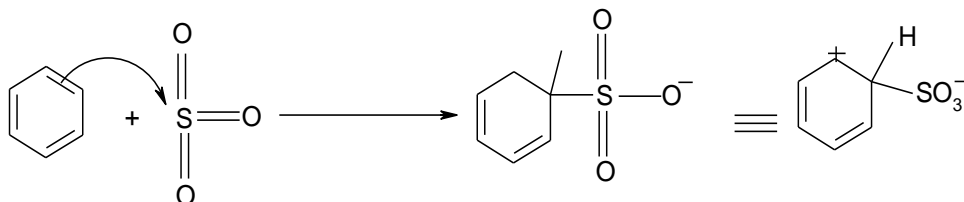
Mechanism:
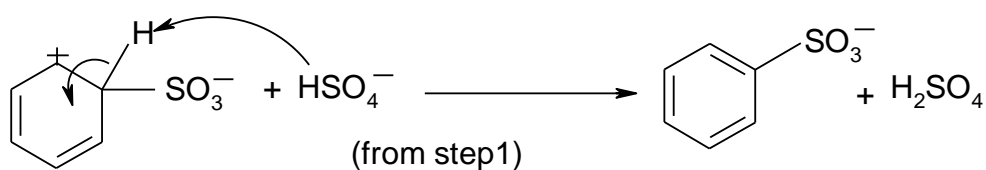
Following steps are involved.

Step 1:

Electrophile is formed. In this reaction the electrophile is sulphur trioxide (SO_3). In concentrated sulphuric acid, SO_3 is produced as follows. In fuming sulphuric acid, this step is unimportant because the dissolved SO_3 reacts directly.
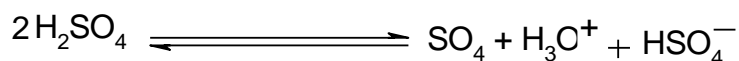
$$2\,H_2SO_4 \rightleftharpoons SO_4 + H_3O^+ + HSO_4^-$$

Step 2:

The electrophile attacks the benzene ring to form a carbonium ion.

Step 3:

Loss of proton.

Step 4:

Addition of proton gives benzene sulphonic acid.

$$\underset{\text{(from step1)}}{C_6H_5-SO_3^-} + H_3O+ \longrightarrow \underset{\substack{\text{Benzene Sulphonic} \\ \text{acid}}}{C_6H_5-SO_3H} + H_2O$$
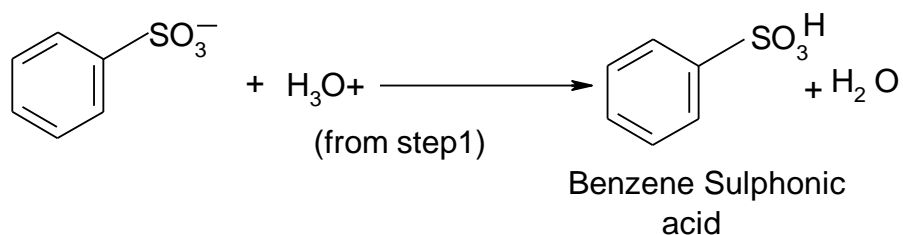
4. Friedel Craft's Alkylation:

Benzene reacts with alkyl halides in the presence of aluminium chloride to form alkyl benzenes.

For example,
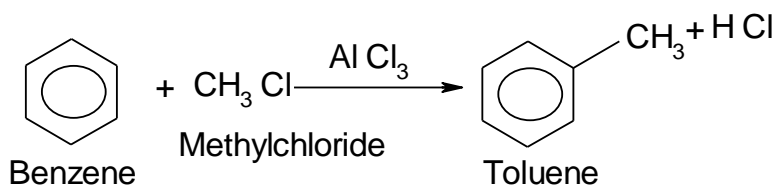
$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Methylchloride}}{CH_3 Cl} \xrightarrow{Al Cl_3} \underset{\text{Toluene}}{C_6H_5-CH_3} + HCl$$

Mechanism:

Following steps are involved.

Step 1:

Formation of the electrophile (CH_3^+)

$$CH_3-Cl + \overset{\frown}{Al Cl_3} \longrightarrow C^+H_3 + Al Cl_4^-$$

Step 2:

The electrophile attacks the benzene ring to form a carbonium ion.

Step 3:

Loss of proton gives alkyl benzene.

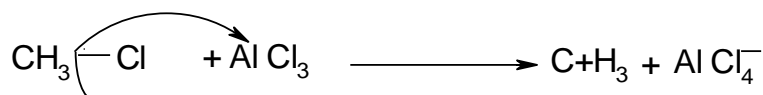$$\underset{\text{Benzene}}{C_6H_6} + \overset{+}{CH_3} \longrightarrow \underset{\text{Carbonium ion}}{[C_6H_6(H)CH_3]^+}$$

$$[C_6H_6(H)CH_3]^+ \xrightarrow{Al d_4^-} \underset{\text{Toluene}}{C_6H_5-CH_3} + Hd + Al d_3$$
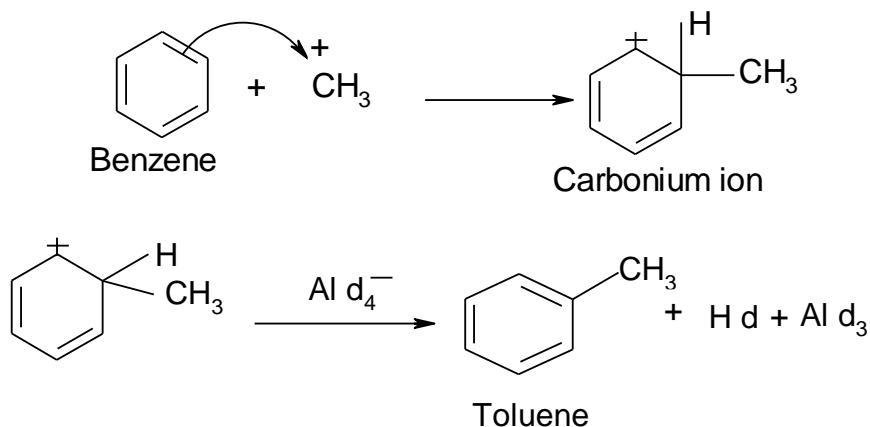
5. Friedel Craft's Acylation:

Benzene reacts with acid chlorides (or anhydrides) in the presence of aluminium chloride to give aromatic ketones. For example.,

Ben zene   Aceto Phenone

Mechanism:

Following steps are involved.

Step 1:

Formation of the electrophile $(CH_3 - C^+ = O)$

Step 2:

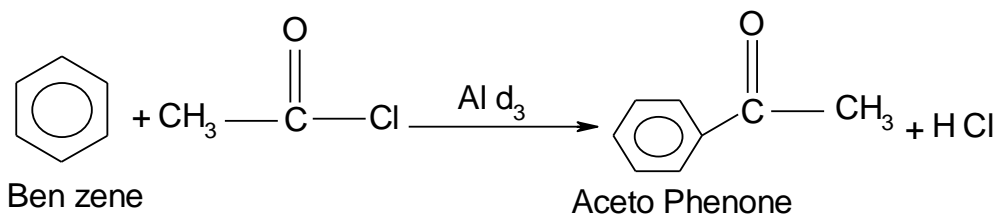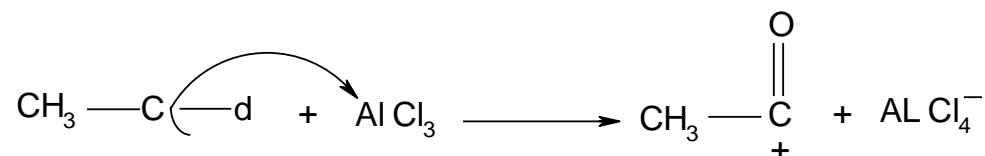The electrophile attacks the benzene ring to form a carbonium ion.

Carbonium ion
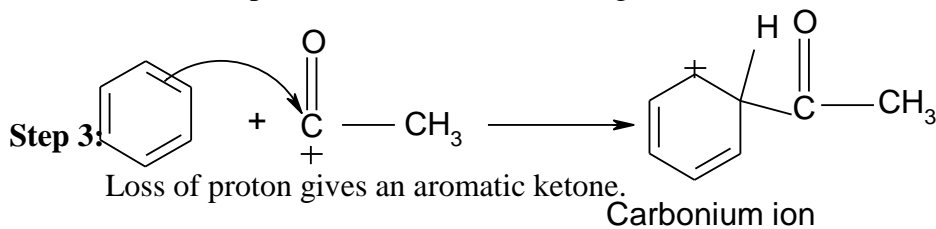
Step 3: Loss of proton gives an aromatic ketone.
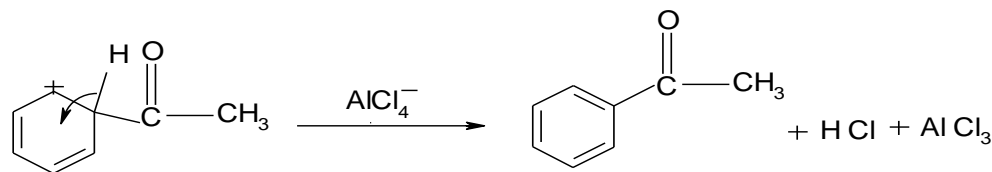
Since alkyl benzenes other than methyl, ethyl or t – alkyl cannot be prepared from alkyl halides with rearrangement, they are best prepared by Friedel Craft's Acylation – Clemmensen Reduction Sequence. For example.,

Ben zene   n-Propyl Ben zene
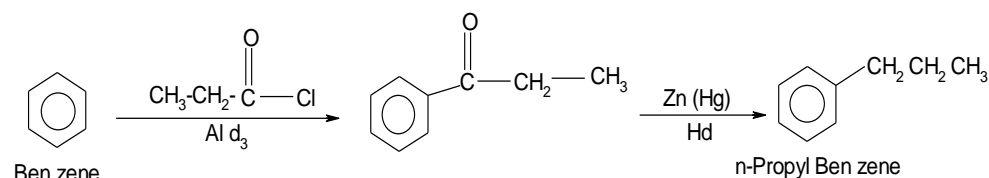
Alkyl benzenes can also be prepared by treatment of benzene with alcohol or an alkene in the presence of an acid catalyst. In each case the initial step involves the formation of stable carbonium ion.
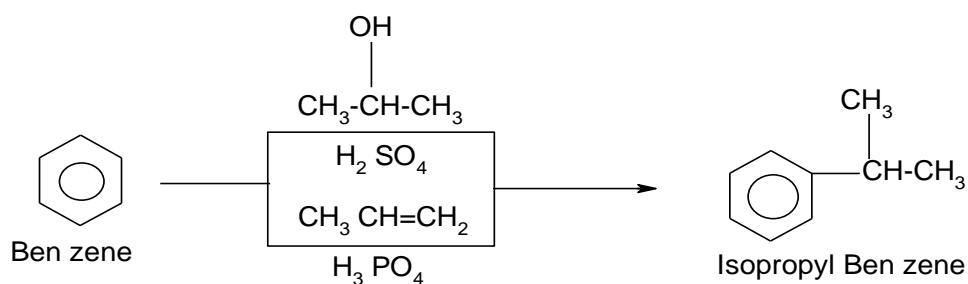
Directive or Orientation Effect:

The first substituent (S) may direct the next incoming substituent (E) (or) Ortho, Meta, or Para position depending on the nature of the first substituent. This is called the Directive or the Orientation (orient = to arrange) Effect.

Electron Contiguration
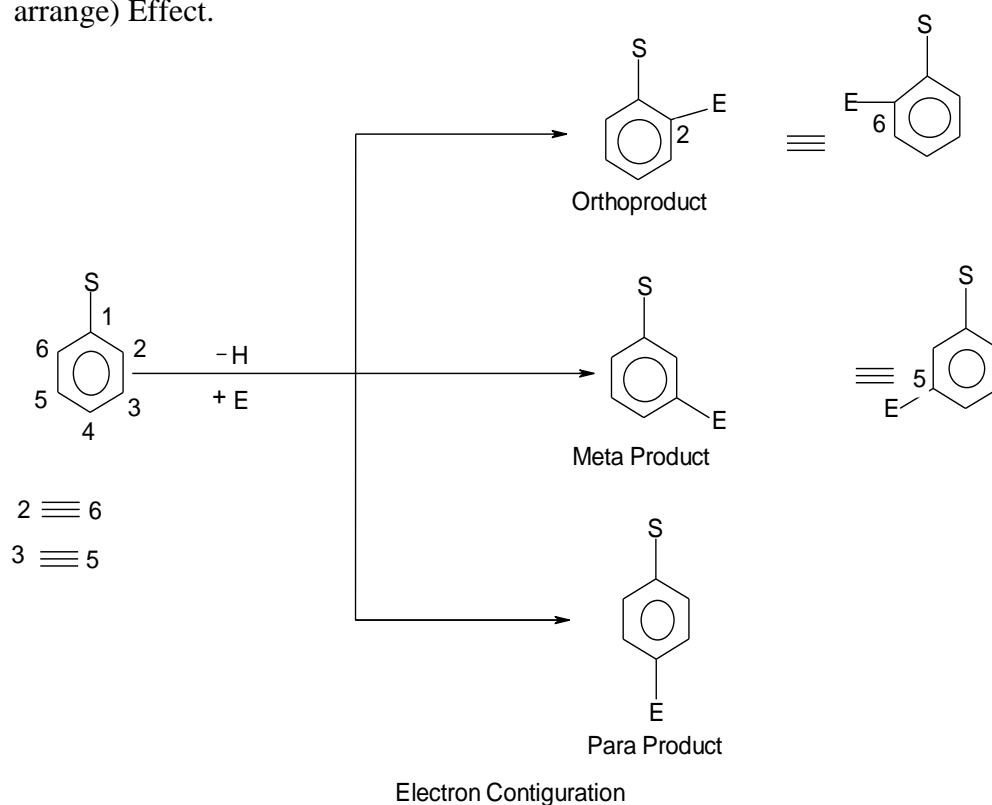
2) Activity Effects:

The substituent already present may activate or deactivate the benzene ring toward further substitution. These effects are called the 'Activity Effects'.

Ortho – Para Directing Effects:

Certain substituents direct the second substituent to the Ortho and Para positions simultaneously. These are called Ortho – Para Directors. For

example, when phenol is nitrated, the only products obtained are O – nitro phenol (53%) and p – nitro phenol (47%) and no Meta isomer is produced.
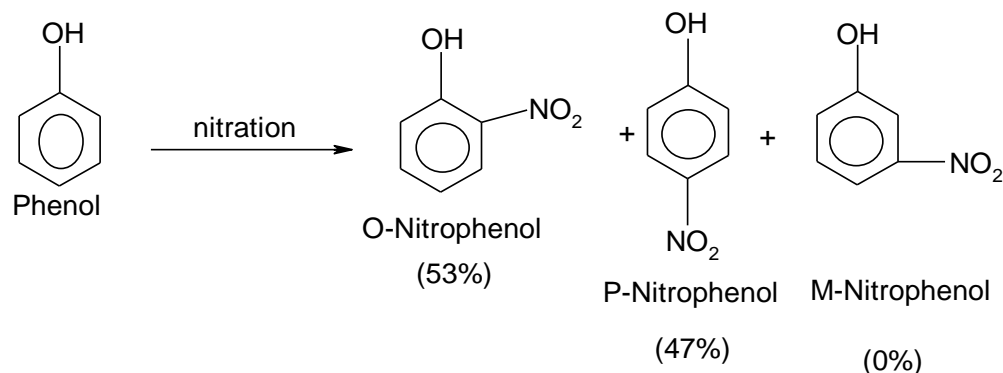
The substituent -OH is said to have directed the –NO$_2$ group to Ortho and Para positions on the ring. Therefore, -OH is designated as Ortho – Para Directors.

2.2.2. Polynuclear Aromatic Hydrocarbons:

Definition:

Fused or condensed aromatic hydrocarbons contain more than one ring and have two carbons shared by two (or three) aromatic rings.

Eg:
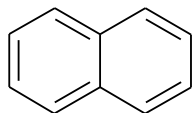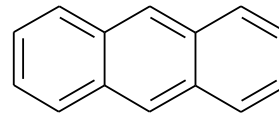
Naphthalene   Anthracene

Naphthalene:

Synthesis of Naphthalene:

1, Haworth Synthesis:

This involves the following five steps.

Step 1:

Benzene and Succinic anhydride are heated in the presence of aluminium chloride to form β -benzoylpropionic acid.

72
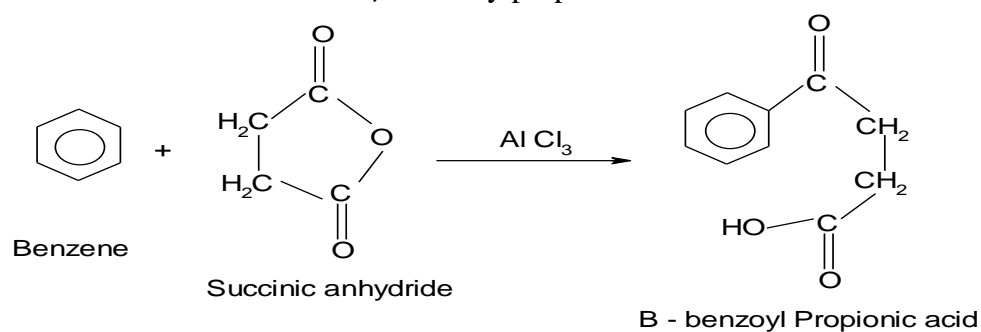
Step 2:

β - Benzoylpropionic acid is treated with amalgamated zinc in the presence of hydrochloric acid to give γ - Phenyl butyric acid.

B - benzoyl Propionic acid δ - benzoyl Propionic acid
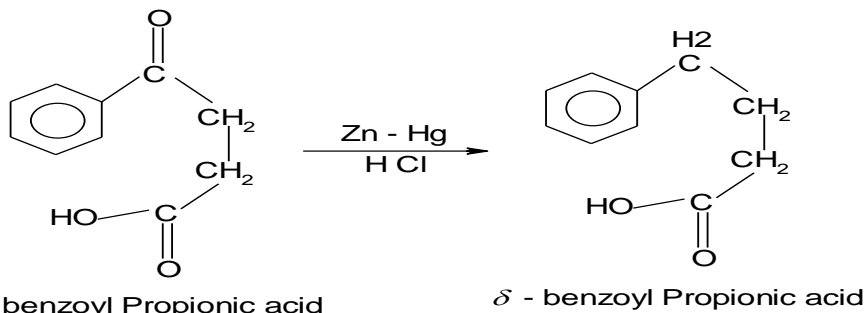
Step 3:

γ - Phenyl butyric acid is heated with concentrated sulphuric acid or polyphosphoric acid to form α - tetra lone.

δ - Plenyl butyric acid   Tetralone
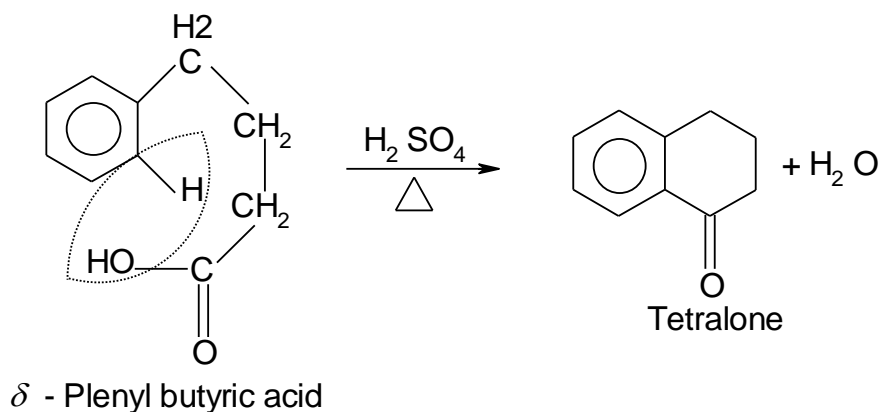
Step 4:

α - tetralone is heated with amalgamated zinc and hydrochloric acid to give tetralin.

Tetralone   Tetralic
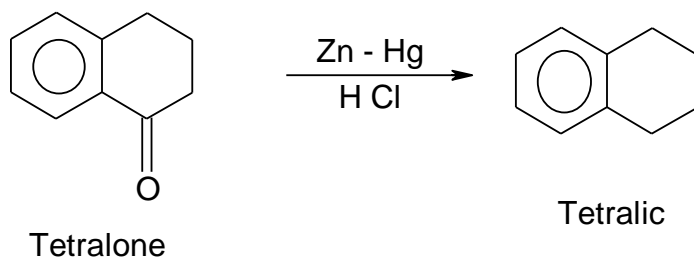
Step 5:

Tetralin is heated with Selenium or Palladium to yield Naphthalene.

Tetralin   Naphthalene
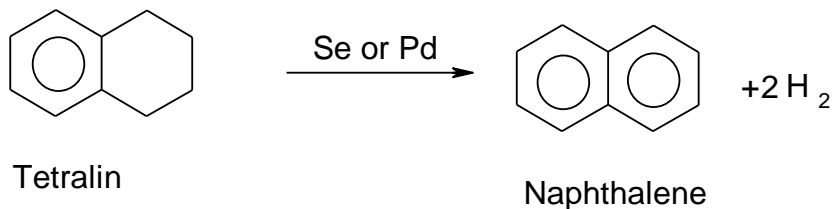
2, From Petroleum:

When petroleum fractions are passed over copper catalyst at 690°C, naphthalene and methylnaphthalenes are formed. Methylnaphthalenes are separated and converted into naphthalene by heating with hydrogen under pressure.
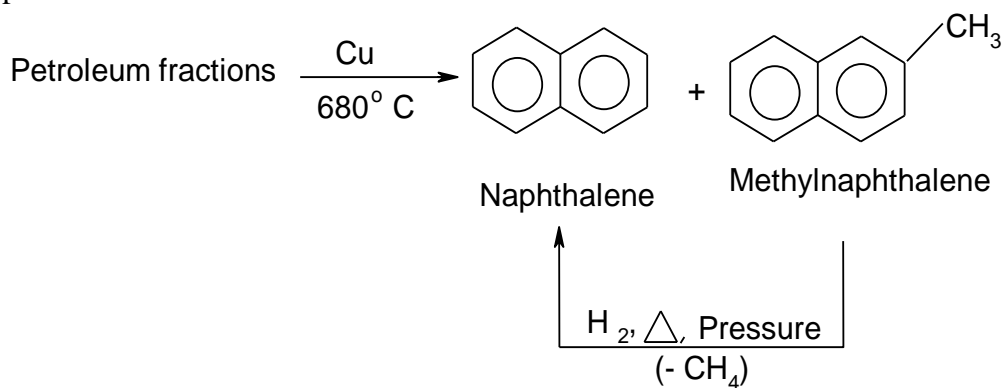
Physical Properties:

1. Naphthalene is a colourless crystalline solid. It melts at 82°C and boils at 218°C.
2. Naphthalene is insoluble in water, but dissolves in ether, benzene and hot ethanol.
3. It sublimes readily when warmed and is volatile with stream. It has a characteristic 'moth ball' odour.

Chemical Properties:

Electrophilic Substitution Reaction:

1, Nitration:

Naphthalene undergoes nitration with concentrated nitric acid in the presence of sulphuric acid at 60°C to produce 1 - nitro naphthalene.
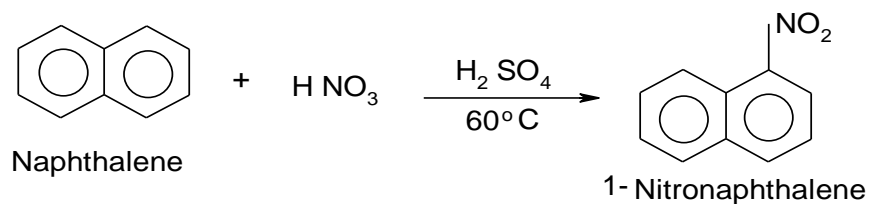
2, Sulphonation:

Naphthalene undergoes Sulphonation with concentrated sulphuric acid at 60°C to form 1 – Naphthalenesulphonic acid. If the reaction is carried at 165°C, 2 - Naphthalenesulphonic acid is obtained.

1- Naphthalene Sulphonic acid   Naphthalene   2- Naphthalene Sulphonic acid
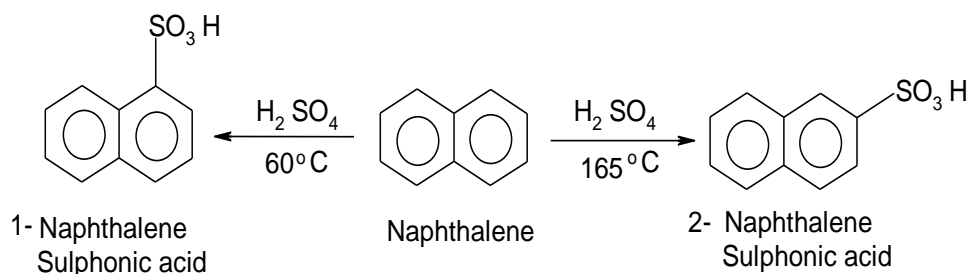
3, Halogenation:

Naphthalene undergoes chlorination or bromination in boiling carbon tetrachloride to give 1 – chloronaphthalene. Unlike benzene, no Lewis acid catalyst is required.

Naphthalene   1- Chloronaphthalene
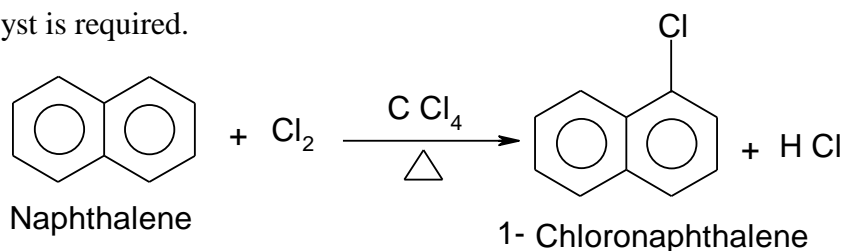
4, Friedel Craft's Acylation:

Naphthalene undergoes Acylation with acetyl chloride and aluminium chloride in carbon disulphide to give 1 - acetyl naphthalene. When nitrobenzene is used as a solvent, 2 - acetyl naphthalene is obtained.

1- Acetylnaphthalene   Naphthalene   2- Acetylnaphthalene
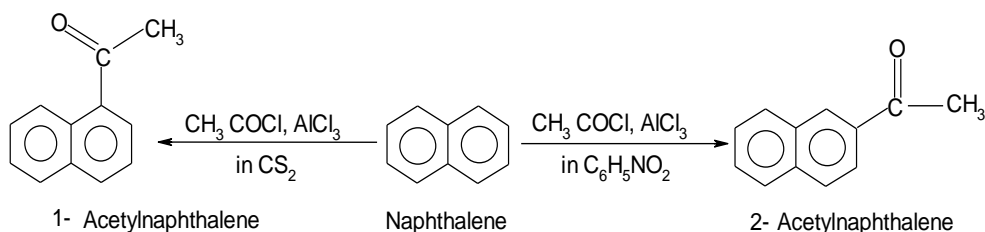
5, Friedel Craft's Alkylation:

Naphthalene undergoes Alkylation with alkyl halides in the presence of aluminium chloride to give 2-alkyl naphthalenes

Naphthalene   2- Ethyl Naphthalene
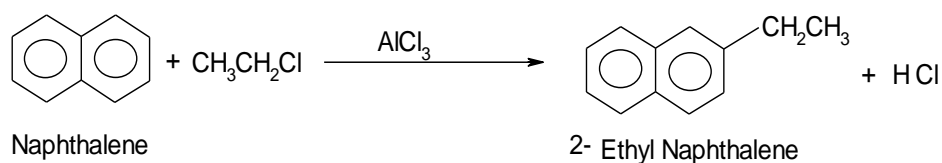
6, Chloromethylation:

Naphthalene reacts with formaldehyde and HCl in the presence of Zinc chloride to form 1 – chloromethyl naphthalene.

Naphthalene   Formaldehyde   1-Chloromethyl Naphthalene
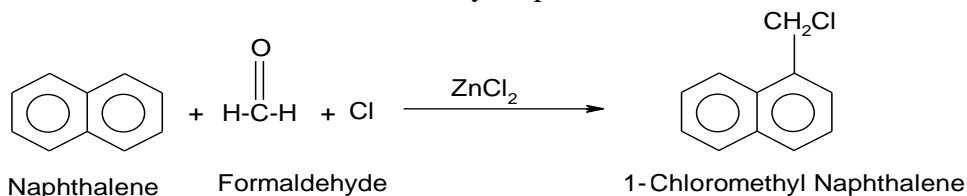
Other Reactions :

7, Reduction:

Naphthalene undergoes reduction more readily than benzene. With sodium and ethyl alcohol it gives 1,4 – dialin or 1,4 – dihydronaphthalene. With sodium and isopentanol it gives tetralin or 1,2,3,4 - tetra hydronaphthalene.

Tetralin   Naphthalene   1, 4 - Dialin
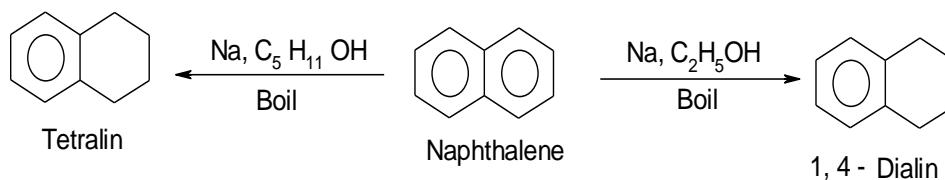
8, Oxidation:

Naphthalene is much more easily oxidised than benzene. With chromium trioxide in acetic acid at room temperature, it gives 1,4 – Naphthaquione.

Naphthalene   1,4 - Naphthaquinone
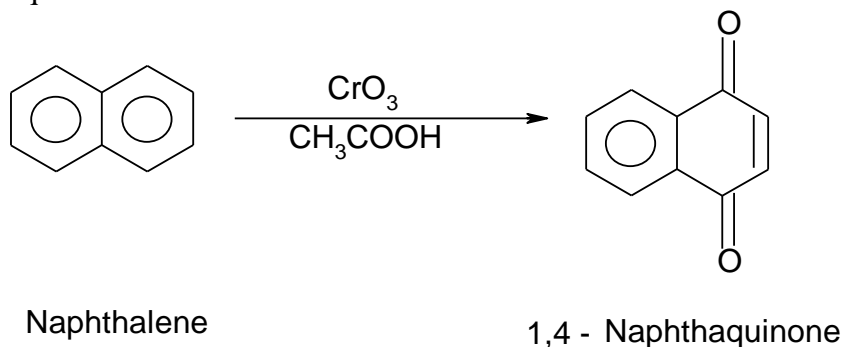
Uses:

1. Naphthalene as 'moth balls' has been used to protect woolen goods from moths from many years. Recently, p – dichlorobenzene has replaced naphthalene in the manufacture of moth balls, as it has a less abnoxious odour.

2. It is used for increasing the illuminating power of coal gas. Naphthalene is used in the manufacture of phthalic anhydride,

carbaryl for insecticides, 2 – Napthol, dyes and several medicinal products.

Anthracene:

Anthracene occurs in coal – tar and is obtained from the green oil fraction. On cooling this fraction crude anthracene crystallizes out. Crude anthracene contains phenanthrene and carbazole as impurities. It is purified by washing it successively with solvent naptha and pyridine. Finally the solid is sublimed to give pure anthracene.

Synthesis of Anthracene:

1, By Haworth Synthesis:

This involves the treatment of benzene with phthalic anhydride in the presence of aluminium chloride to form O – benzoylbenzonic acid. This is then heated with con. H_2SO_4 to give 9,10 – anthraquinone. Distillation of anthraquinone with Zinc dust yields anthracene.

phthalic anhydride

Benzene

O - Benzoyl benzoic acid

9,10- Anthraquinone
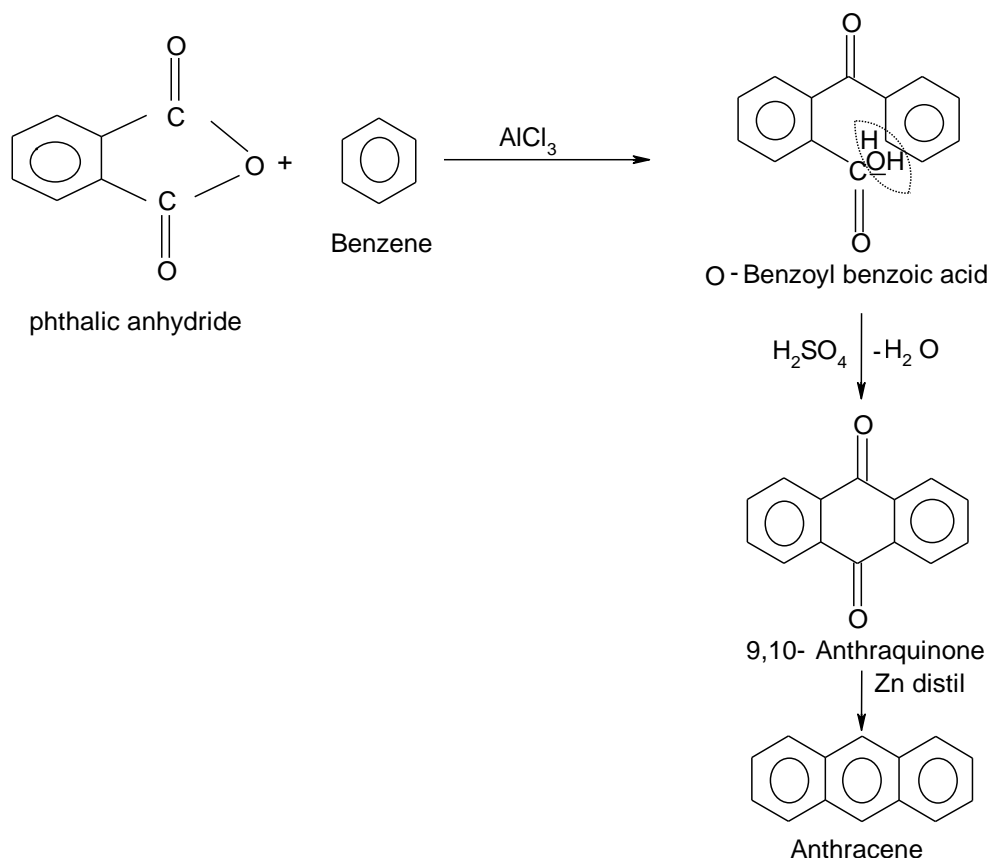
Anthracene

2, By Elbs Reaction:

The conversion of a diaryl ketone containing a methyl or methylene group Ortho to the carbonyl function is known as the Elbs reaction. For eg: When O – methylbenzophenone is heated at 450°C, anthracene is formed.
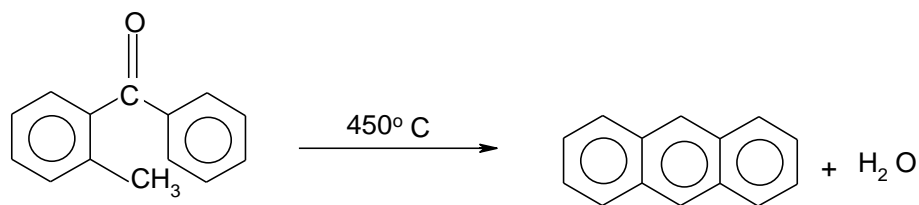
O - Methyl benzophenone

Anthracene

Physical Properties:

1. Anthracene is a colourless solid. It melts at 218°C and boils at 340°C. It is insoluble in water but dissolves in benzene.

2. It shows a strong blue fluorescence when exposed to ultraviolet light. This fluorescent property of anthracene is used in the criminal detection work, since a small amount of finely powdered anthracene on clothing, skin, money etc., is not detected under ordinary light but easily noticed when exposed to ultraviolet light.

Chemical Properties:

1, Reaction with Sodium:

Anthracene reacts with metallic sodium in liquid ammonia to form a deep blue 9,10 – disodioanthracene.

When the disodio derivative is heated with an alkyl halide, it gives the corresponding 9,10 – dialkylanthracene.

Anthracene

− disodia anthracene
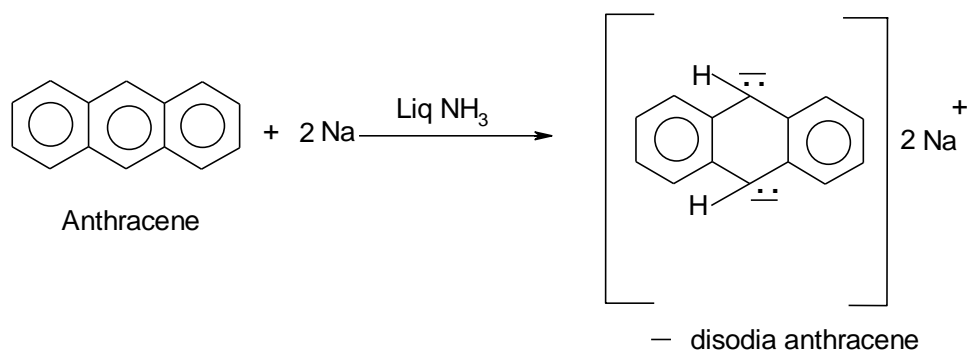
2, Reaction with Halogens:

Anthracene reacts with chlorine in carbon tetrachloride at room temperature to give 9,10 – dichloro – 9,10 – dihydroanthracene. On heating, this addition product loses a molecule of hydrogen chloride by 1,4 – elimination to form 9 – chloroanthracene.

9,10 - dichloro 9,10 - dihydro anthracene

9 - chloro anthracene
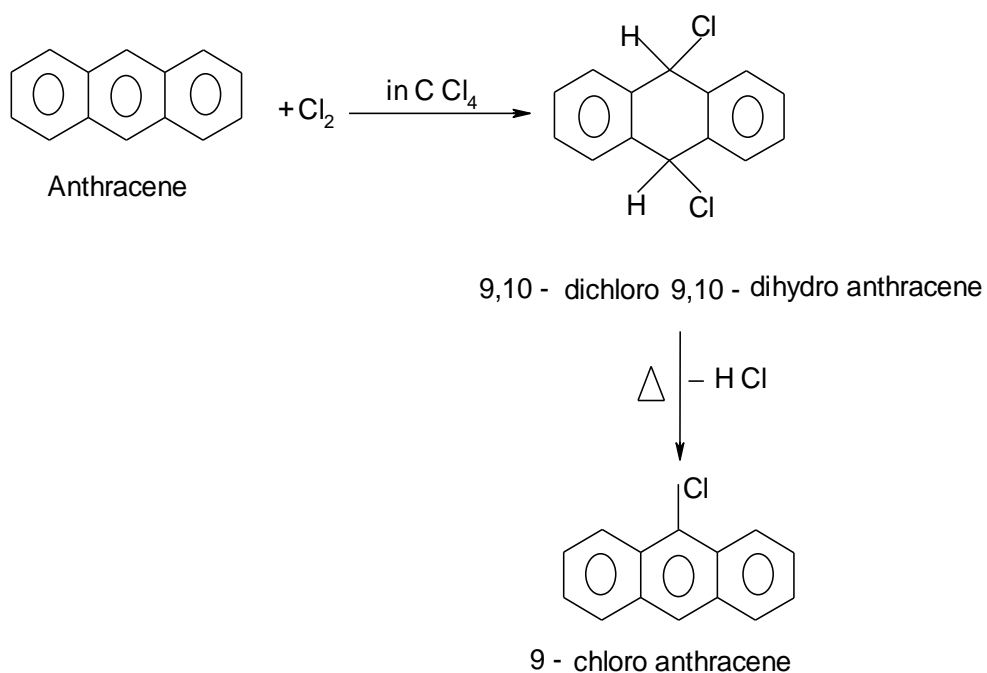
9 – chloroanthracene may also be obtained by chlorinating anthracene at 100°C, or by treating anthracene with cupric chloride in CCl₄.

3, Friedel Craft's Acylation:

Anthracene undergoes Acylation with acetyl chloride in benzene to form 9 – acetyl anthracene.

9 - acetyl anthracene
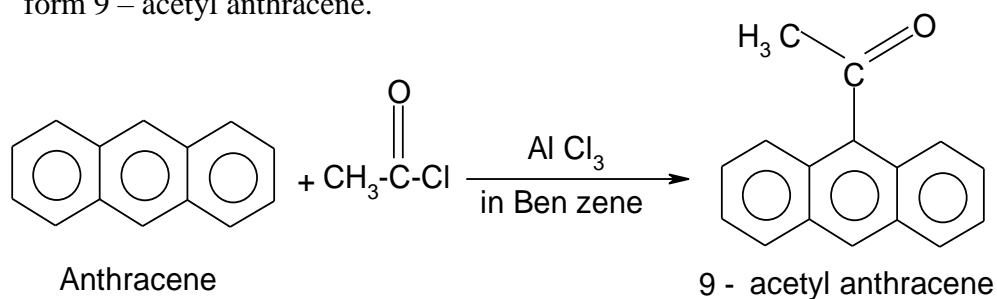
4, Nitration:

Anthracene undergoes nitration with concentrated nitric acid with acetic anhydride at room temperature to yield a mixture of 9 – nitro anthracene and 9,10 – dinitro anthracene. The usual nitrating mixture (HNO_3 + H_2SO_4) is not used because it leads to the formation of 9,10 – anthraquinone by oxidation.

Anthracene + HNO$_3$ $\xrightarrow[\triangle]{(CH_3CO)_2O}$ 9 - Nitroanthracene

+

9,10 - dinitranthracene
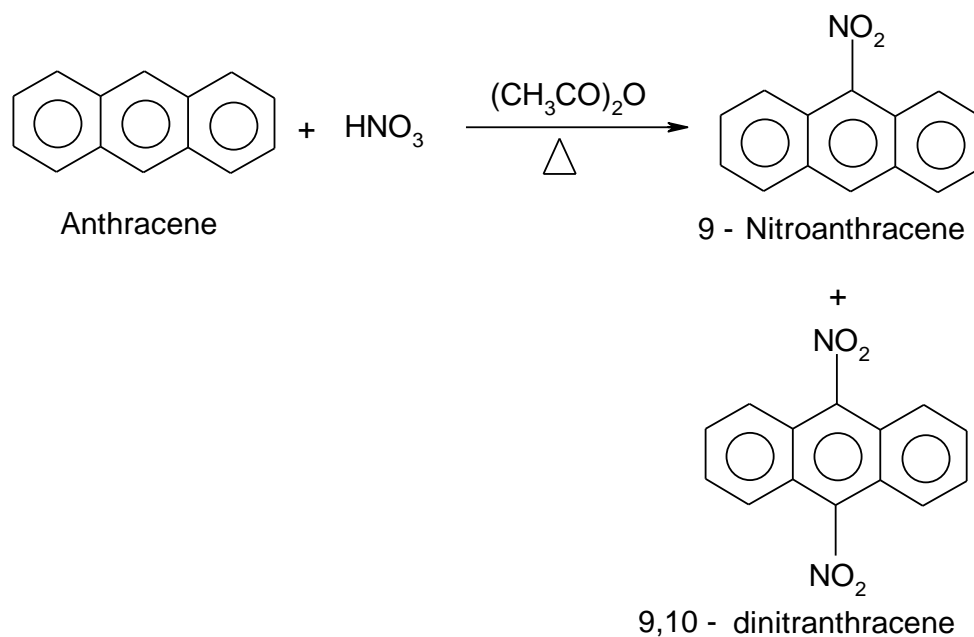
5. Sulphonation :

Anthracene undergoes sulphonation with concentrated sulphuric acid to yield a mixture of 1-anthracenesulphonic acid and 2-anthracene sulphonic acid. At lower temperature 1-anthracene sulphonic acid is the major product; where as at higher temperatures 2-anthracene sulphonic acid is the major product.

2 Anthracene $\xrightarrow{H_2SO_4}$ 1 - Anthracene Sulphonic acid + 2 - anthracene Sulphonic acid
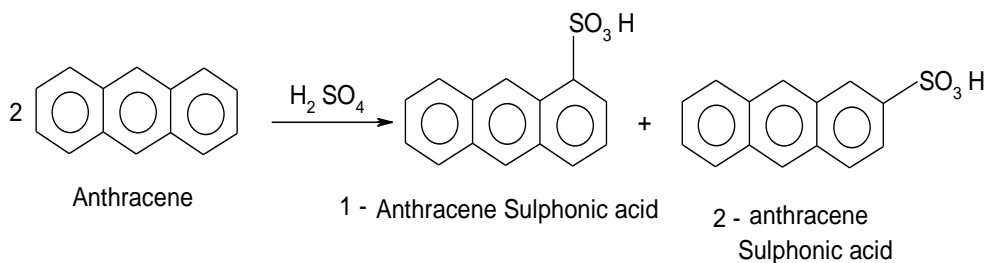
6. Reduction :

Anthracene undergoes reduction with sodium and ethyl alcohol to form 9,10-dihydro anthracene.

Anthracene $\xrightarrow[\triangle]{Na, C_2H_5OH}$ 9, 10 - Dihydro anthracene
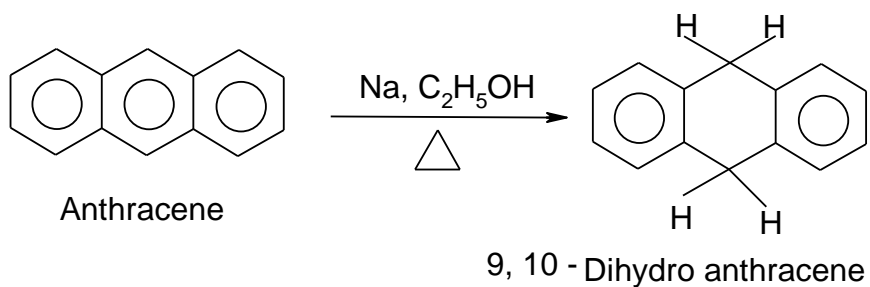
7. Oxidation :

Anthracene undergoes oxidation with sodium dichromate and sulphuric acid to form 9,10 – anthroquinone. Other oxidizing agents like nitric acid and air in the presence of V_2O_5 also lead to the formation of 9,10 – anthraquinone.

Anthracene $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ 9, 10 - Anthraquinone
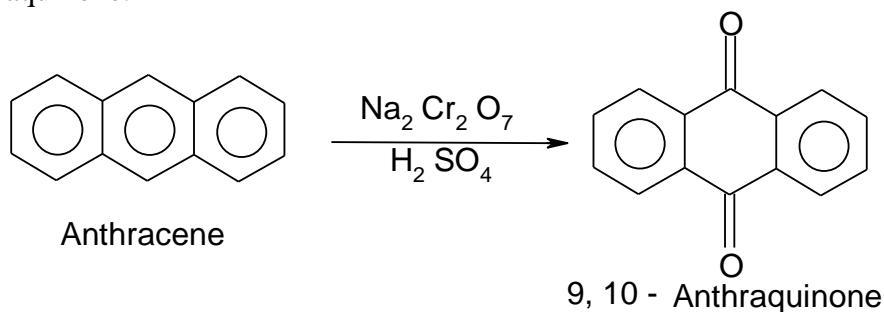
8. Diels - Alder Reaction :

Anthracene undergoes a diels – Alder reaction with maleic anhydride to yield the corresponding adduct.

Anthracene + Maleic anhydride → Diels - alder Adduct
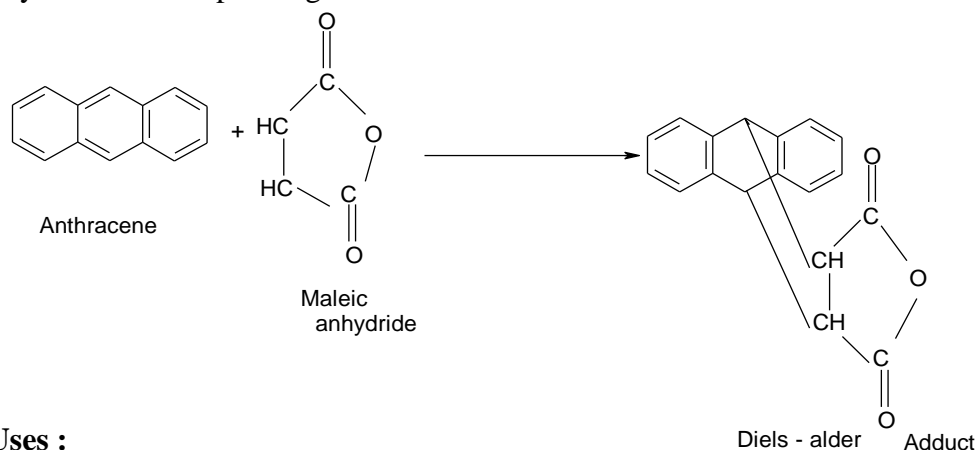
Uses :

Anthracene is used in the manufacture of anthraquinone.

2.3. Reaction Mechanism – IV

2.3.1

Mechanism of Kolb's reaction :

On paning carbon dioxide over sodium phenoxide at 125° COOH is directly introduced into the aromatic ring in ortho position to OH. Thus,

Sod - Phenoxide $+ CO_2 \xrightarrow{125^\circ}$ ... $\xrightarrow{HCl}$ O - hydrory benzoic acid (Salicylic acid)
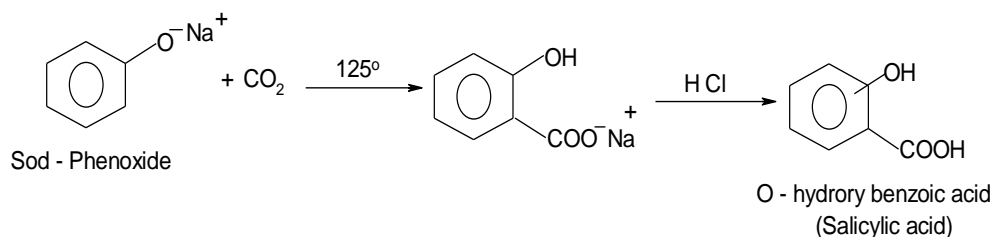
If the carbonation of sodium phenoxide is carried at $250 - 300^{\circ}C$, P-carbonylation product is obtained.
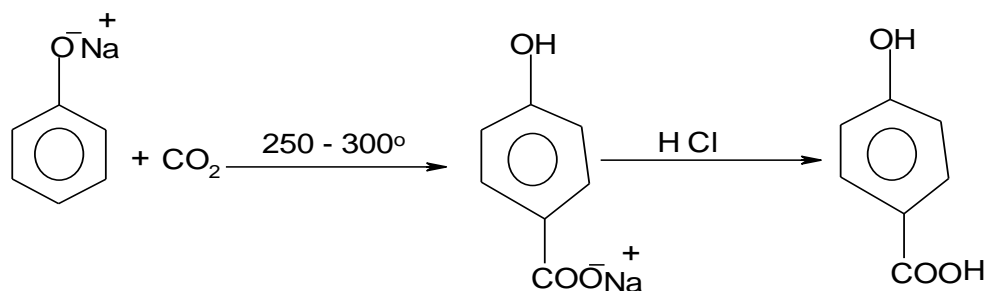
This reaction involving the carbonation of phenols to give phenolic acids is named as kolb's reaction.

Mechanism :

Carbon di oxide $(O = C = O)$ acts as a weak electrophile and brings about electrophilic substitution by usual mechanism.

Salicylic acid
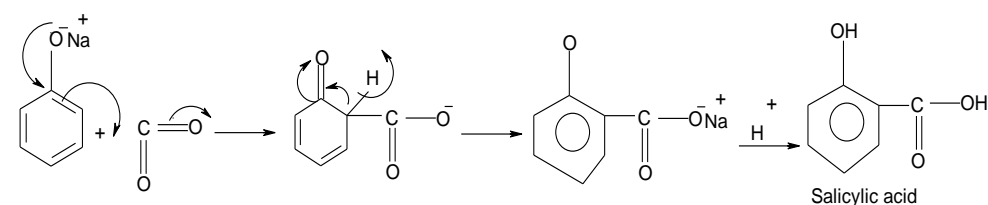
Reimer – Tiemann Reaction:

The treatment of a phenol with chloroform and aqueous NaOH at $60^{\circ}C$ followed by acidification, introduced a $-$ CHO group in the aromatic ring mainly in the ortho position to OH group. For example,

O - hydrory benzaldehyde

P - hydrory benzaldehyde
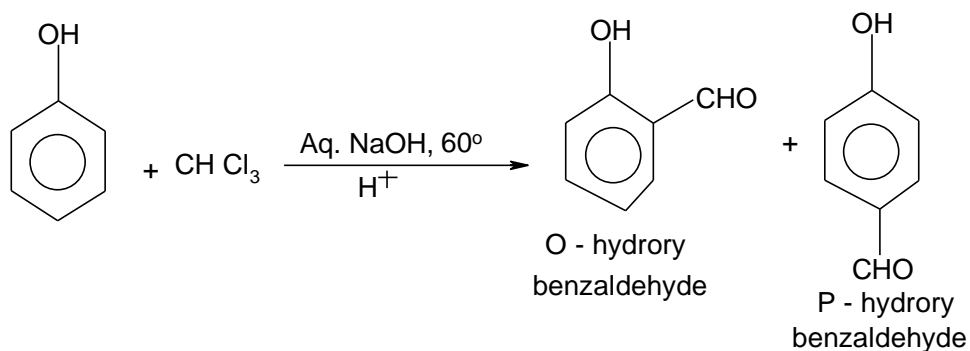
This reaction known as Reimer – Tiemann reaction is employed for preparing phenolic aldehydes.

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Mechanism:

The reaction is believed to proceed by the following steps.

(i)   Formation of dichloromethylene from chloroform.

$$H—C(Cl)_2—Cl + OH^- \longrightarrow H_2O + :C(Cl)_2—Cl \longrightarrow \bar{Cl} + :CCl_2$$

dichloro methyl
(electrophilic)
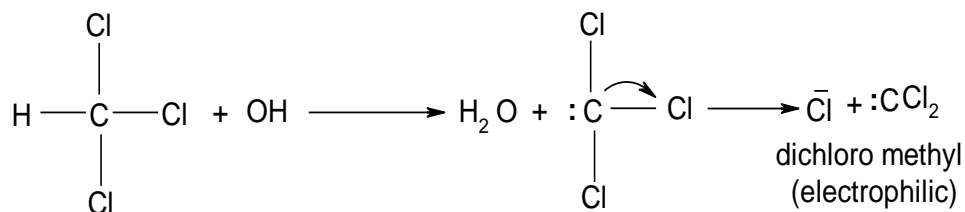
(ii)   Electrophilic substitution in the phenol ring.
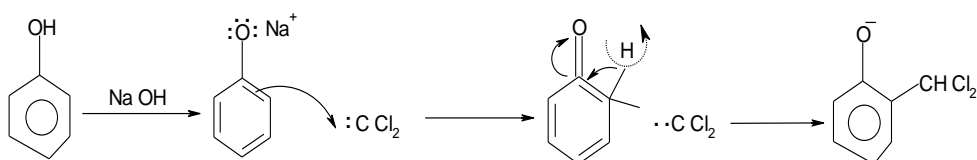
(iii)   Hydrolysis and acidification.

O - hydrory benzaldehyde
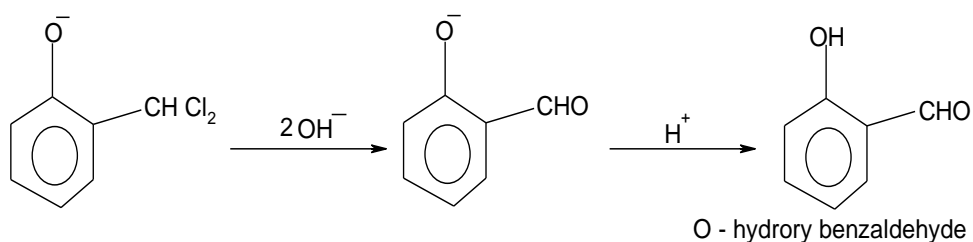
If CCl₄ is taken in place of CHCl3, salicyclic acid is obtained, ortho derivative being the main product.

O - hydrorybenzoic acid
(Main Product)

P - hydrorybenzoic acid
(Small Product)
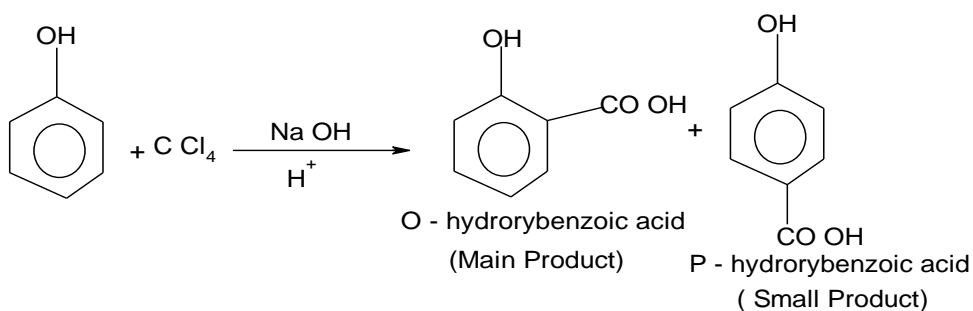
Gatterman Reaction:

When a phenol is treated with a mixture of hydrogen cyanide, hydrogen chloride and zinc chloride catalyst an aldehyde group is

introduced in the ortho position to OH. Thus phenol yields, O – hydroxybenzaldehyde.

O - hydroxy benezaldehyde
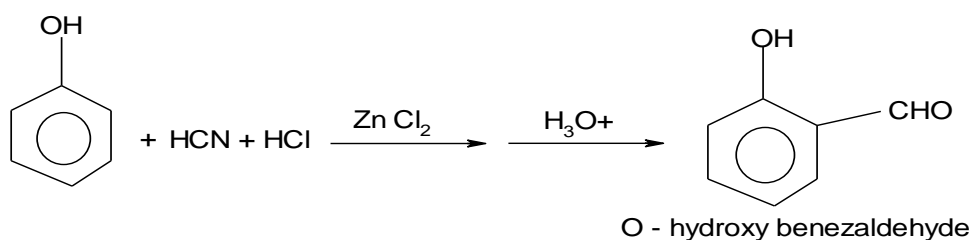
This reaction is known as Gattermann Reaction is a general one and is used for formylation of aromatic rings for which an electron withdrawing group (-OH, -OCH3, etc) is attached.

Mechanism:

The electrophile $HC^+ = NH$ is derived from formiminochloride, and the electrophilic substitution takes place by the usual mechanism.

formimino Chloride

Salicylaldehyde
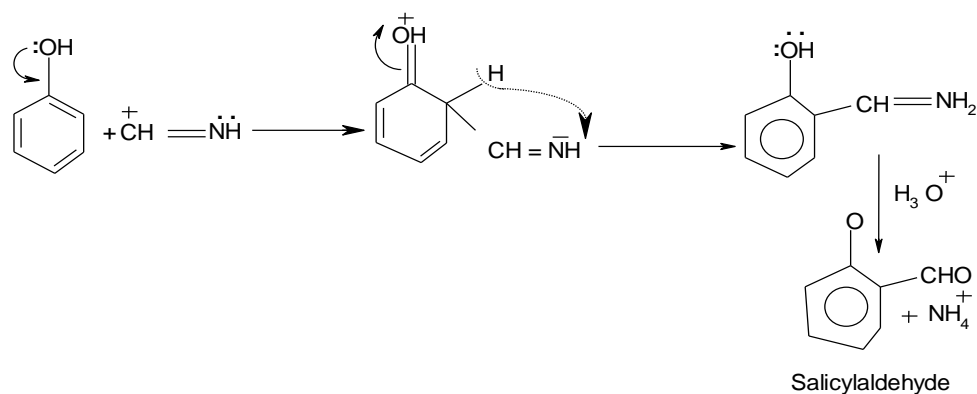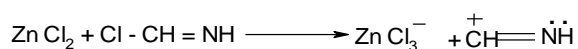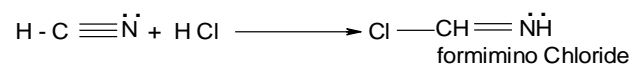
Laderer – Manasse Reaction:

Phenols undergo condensation with aldehydes by electrophilic substitution in ortho and para positions in presence of acids or alkalis as catalyst.

Phenol   electrophile

P - hydroxy - alkylbenzyl alcohol

O - hydroxy - alkybenzyl alcohol
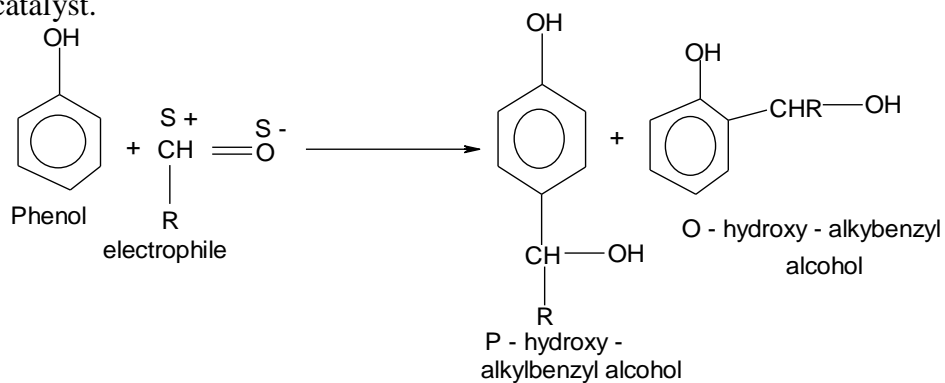
Formaldehyde undergoes such condensationto give O- and P-hydroxybenzyl alcholos.
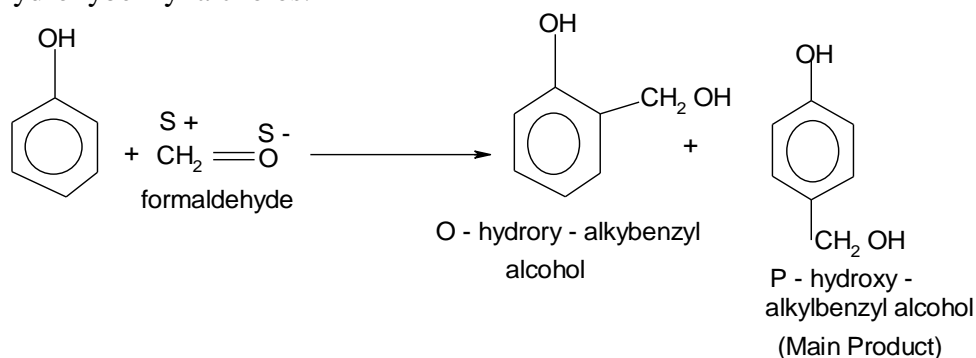
This reaction is known as Laderer – Manasee reaction. If the reaction mixture contains excess of formaldehyde disubstitution and trisubstitution occurs. Thus,

P - hydroxy benzyl alohol

2,4 - dihydroxy methyl phenol

2, 4, 6 - trihydroxy methyl phenol
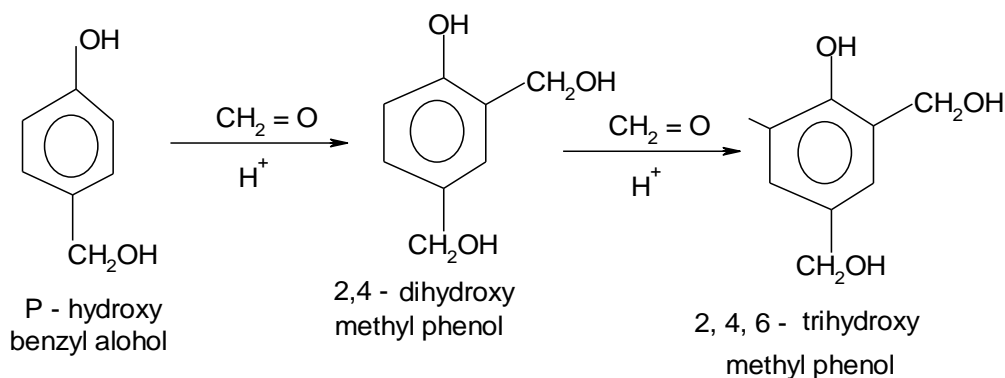
Houben – Hoesh Reaction:

Highly reactive polyhydric phenols in which OH groups are meta to one another, may be acylated when treated with alkyl cynaides in the presence of zinc chloride and hydrogen chloride. The product is a phenolic ketone.

resorcind for example

Phenolic ketone

Ketimine

resacetphenone $+ NH_3$
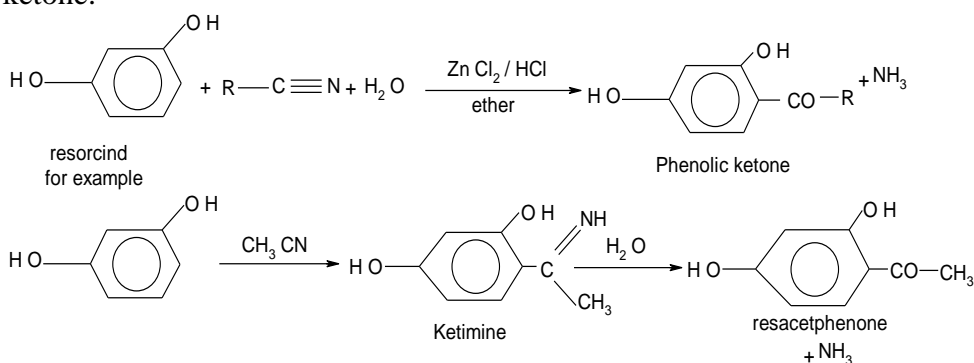
This reaction given by Houben and Hoesh in 1927, is named after them. Phenol does not respond to Houben – Hoesh Reaction.

Perkin reaction or Perkin condensation:

When an aromatic aldehyde is heated with the anhyride of an aliphatic acid in the presence of the sodium salt of the same acid. $\alpha, \beta -$ unsaturated acid results. Thus benzaldehyde on heating with acetic anhydride and sodium acetate for several hours at 180ºC, yields cinnamic acid.
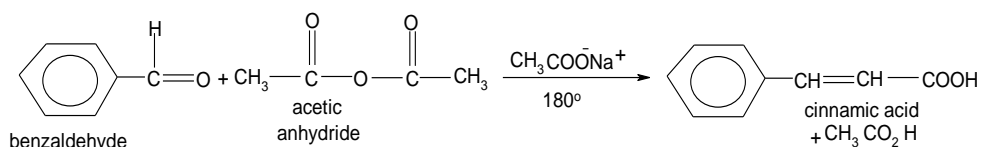
This condensation reaction between an aromatic aldehyde and aliphatic anhydride is named as perkin reaction. It is a useful synthetic method for the synthesis of $\alpha, \beta -$ unsaturated acids.

Mechanism:

(i)   In Perkin's reaction the CH_3COO- anion furnished by sodium acetate acts as a basic catalyst and helps in the abstraction of an α - hydrogen from the aliphatic anhydride to form carbanion(I).
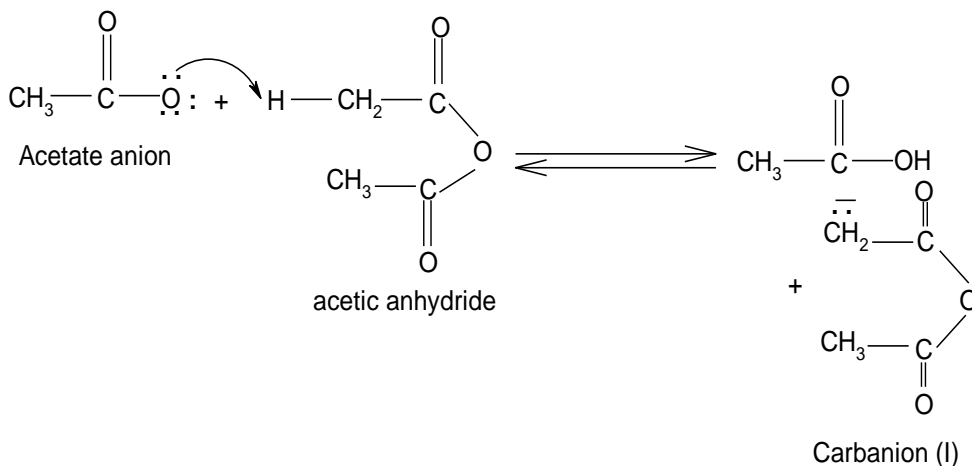
(ii)   Carbanion I adds to the carbonyl of aromatic aldehyde to form intermediate (II).

86
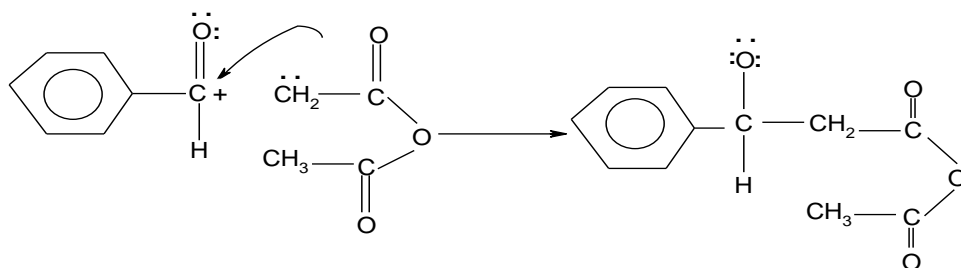
(iii)   Protonation of the intermediate II at the anionic oxygen produces hydroxy acid anhydride III.

Hydroxy acid anhydride (III)
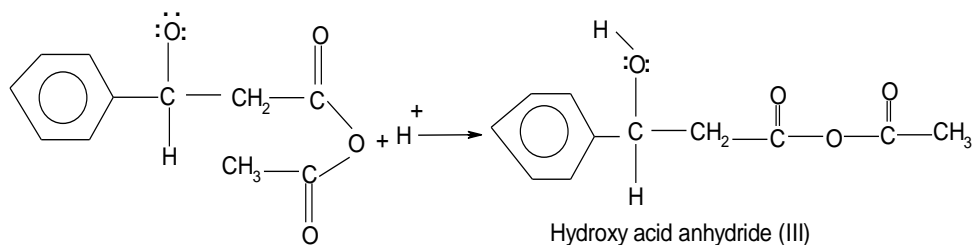
(iv)   Internal proton transfer leads to elimination of a water molecule to form $\alpha, \beta-$ unsaturated mixed anhydride (IV).

Unsaturated sminred
akhydride (IV)
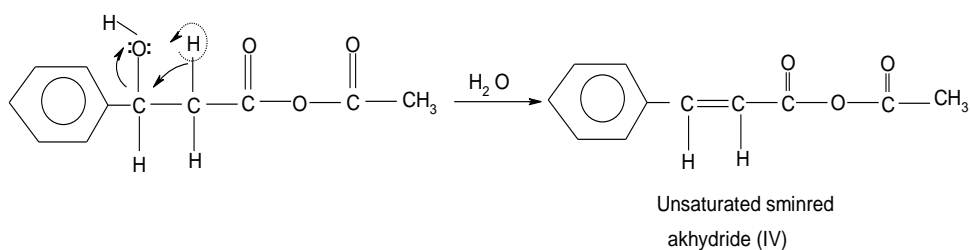
(v)   Hydrolysis of the unsaturated mixed anhydride.

(vi)   Finally yields cinnamic acid.

cinnamic acid
+ CH_3COOH
acetic acid
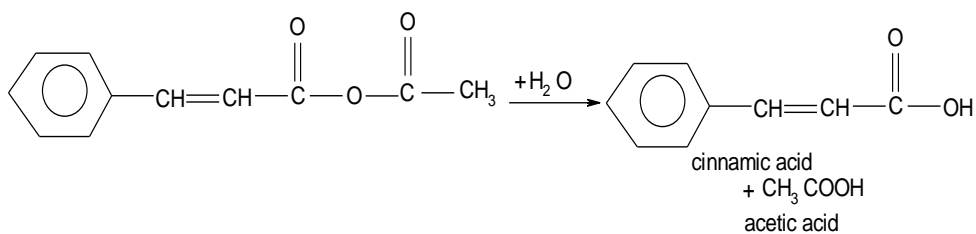
Haloform Reaction:

When a methyl ketone is treated with ahalogen in sodium hydroxide solution, it is oxidised to a carboxylic acid containing one carbon less than be original molecule with the simultaneous formation of trihalomethane. Thus,

$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3\,Br_2 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-\bar{O}Na^{+} + CH\,Br_3$$

bromo form

$+ 3\,H_2O + 2\,Na\,Br$
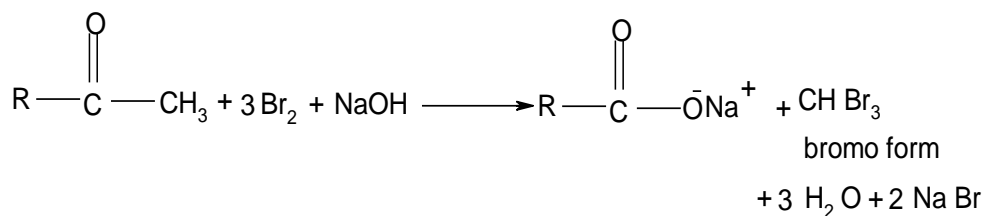
This reaction, infact takes place in two stages, First the three hydrogen atoms of methyl group are replaced by three halogen atoms and then the molecule is cleaved to give an acid and trihalomethane.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3\,Br_2 + 3\,NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-CBr_3 + 3\,NaBr$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CBr_3 + NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + CHBr_3$$
bromo form
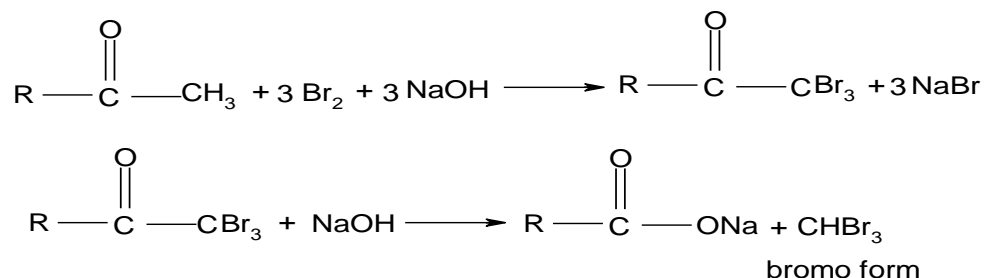
The reaction yields trihalomethanes – chloroform, bromoform or iodoform depending on the haolgen used. Since the common name for halomethanes is 'haloform', it is called Haloform reactions. Acetaldehyde is the only aldehyde which gives haloform reaction.

The haloform reaction is used as a diagnostic test for the presence of –COCH3 group. For this purpose, the reaction is carried with iodine and alkali because the iodoform produced being a yellow crystalline solid is then precipitated. This is known as Iodoform test and is given by methyl ketones, acetaldehyde and compounds such as CH_3CHOHR and CH_3CH_2OH which are oxidised to approprirate carbonyl compounds under conditions used for the reactions.

The haloform reaction is useful for distinguishing methyl ketones from other ketones. It is also used in synthesis for the preparation of the carboxylic acid with one carbon less than the original methyl ketone.

Mechanism:

It involves the following steps:

(i)   The hydrogen atoms of the –CH3 group are replaced by halogens in alkali solution. The methyl ketone enolises and the halogen reacts with the enolate ion.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-H + \bar{O}H \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{..}{CH_2} + H_2O$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{..}{CH_2} + Br-Br \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2Br + \bar{Br}$$
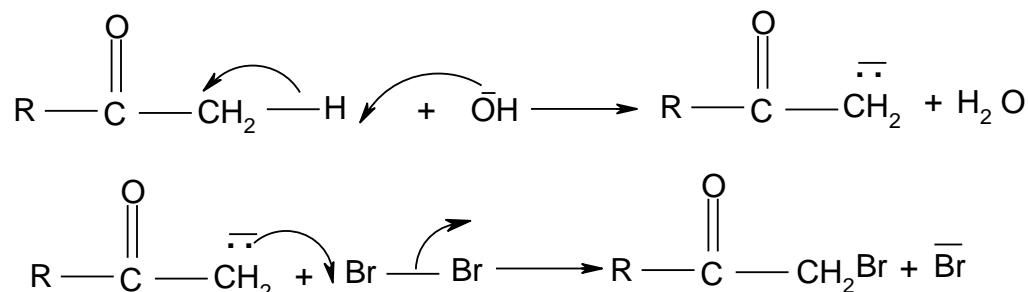
Due to the electron – withdrawing effect of the Br atom, the remaining two hydrogen atoms of the methyl group become even more acidic and the displacement continues till all the hydrogen atoms are successively replaced by the halogen atoms.
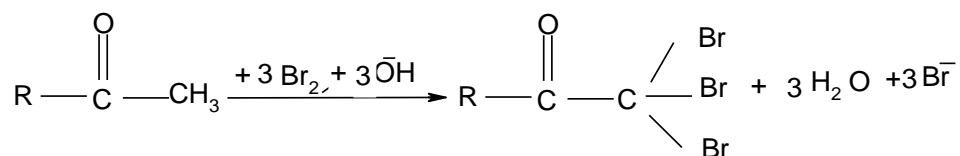
(ii) Due to the inductive effect of the halogen atoms, the positively of the carbonyl carbon increases and by a nucleophilic attack on it, anion(II) is formed. This then cleaves to give a molecule of iodoform and the carboxylate ion(III).
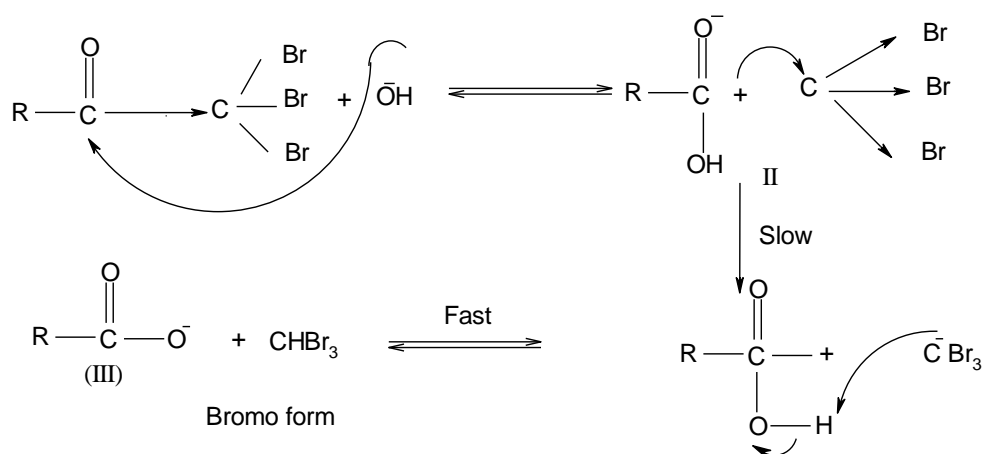
Cresols:

Hydroxytoluenes, $CH_3 – C_6H_4 – OH$

The mixture of O^-, m^- and p – cresols is called 'cresote' as these form major constituent of creosote oil – a coal, wood or petroleum tar fraction. The mixture is seperated into individual cresols by using a sophisticated fractioning column.

Preparation:

(i) Each of the isomeric cresols may be synthesised by diazotisation of the corresponding toludine and warming the resulting aqueous solution. For example.,

m - toluidine   diazonium Salt   m - cresol
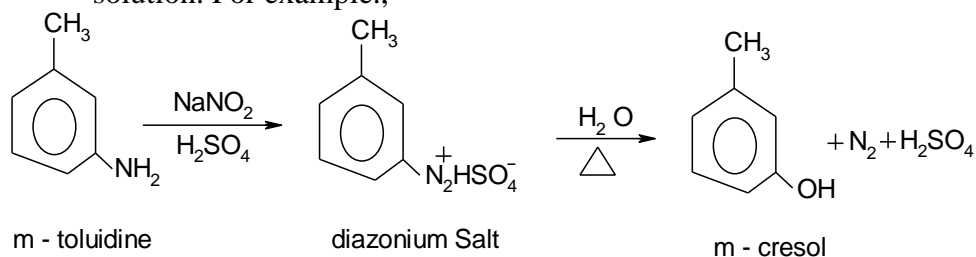
(ii)   Cresols may also be obtained by fusion of the corresponding toluenesulphonic acid with NaOH.

P - toluene sulponic acid
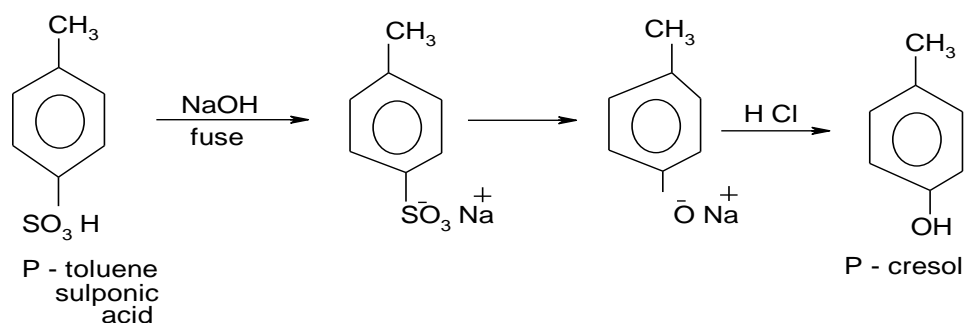
P - cresol

(iii)   When either – o or m – chlorotoluene is heated with aqueous NaOH at 300 – 320°C under pressure, m – cresol is produced.

m - chlorototuene   m - cresol
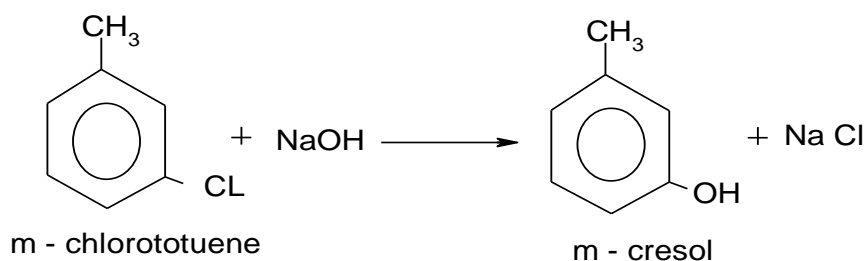
Uses:

Mixture of cresols is used:

1. As preservative for timber, railway sleepers, etc.,
2. for making liquid disinfectant lysol, a solution of cresol in soapy water.
3. for manufacture of synthetic regins, plasticicers, dyes and explosives.

Nitrophenols:

$$O_2N – C_6H_4 –OH \ (O, M, P)$$
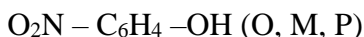
O and P – nitrophenols are prepared by direct nitration of phenol with dilute nitric acid at room temperature. The mixture is seperated by steam distillation, the o – isomer passing over leaving the p – isomer behind m – Nitrophenol is obtained by diazotization of m – nitroaniline and heating the resulting aqueous solution.

m - nitroaniline   diazonium Salt   m - nitrophenol
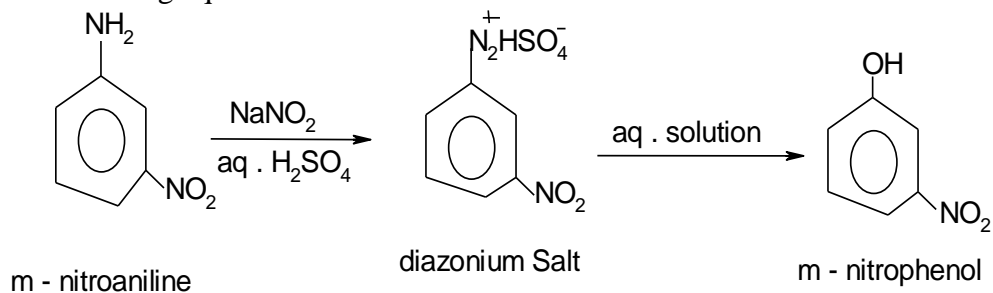
Aminophenols:

They may be prepared by the reduction of the corresponding nitro phenols with metal and acid (Sn or Fe/HCl) m – aminophenols are obtained commercially by reaction of resorcinol with ammonia and aqueous ammonium chloride under pressure at 200°C.
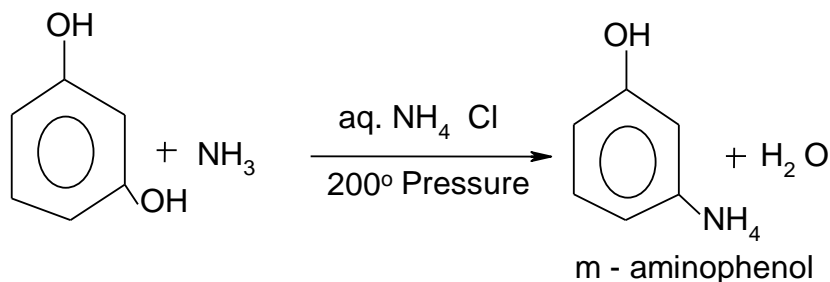
m - aminophenol

P – Aminophenols is prepared commercially by the electrolytic reduction of nitrobenzene in sulphuric acid solution. The nitrobenzene is reduced to N - hydroxyaniline C_6H_5–NH-OH which rearranges to yield phenol. It is also obtained from phenol by nitrosation, followed by reduction.

P - aminophenol
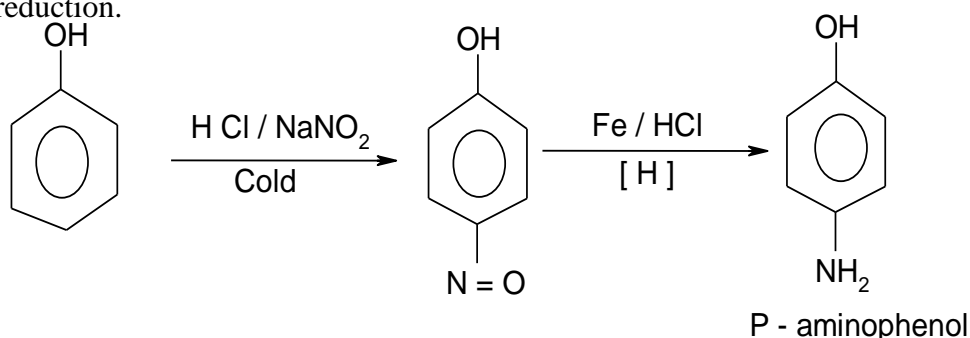
Naphthol (α - Naphthol):

Preparation: 1 – Naphthol may be obtained.

(1) From sodium 1 – Naphthalenesulphonate:

When sodium 1 – Naphthalenesulphonate is fused with sodium hydroxide at 300°Cit gives sodium 1 – napthoxide. Treatement of this with dilute sulphuic acid yields 1 – napthol.

Sodium 1 – Naphthalenesulphonate used in the above reaction may be obtained from naphthalene as shown below.

Sodium I - Naphthalene Sulphonate   Sodium I - Naphthoxide   I - Naphthol

Naphthalene → $con. H_2SO_4$, $60°C$ → 1 - Naphthalene Sulphonic acid (with SO_3H) → NaOH → Sodium 1 - Naphthalene alene Sulphonate (with $SO_3^- Na^+$)
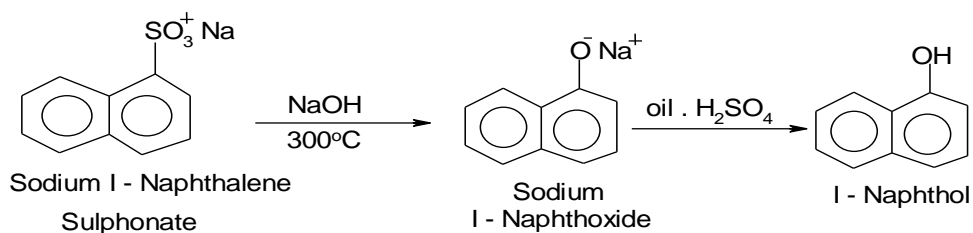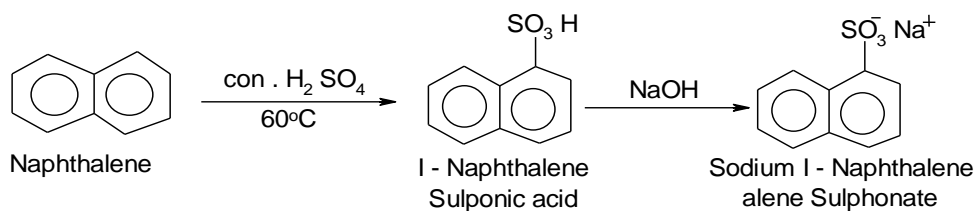
(2) From 1 – Naphthylamine:

When 1 – naphthylamine is heated with dilute sulphuric acid at 300°C under pressure, 1 – napthol is formed.

1 - Naphthylamine (NH_2) → oil . H_2SO_4, 300°C Poessure → 1 - Naphthol (OH)
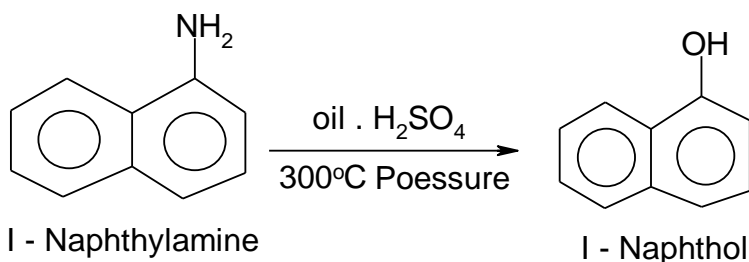
1 – naphthylamine used in the above reaction may be prepared from naphthalene as shown below.

Naphthalene → HNO_3, H_2SO_4 60°C → 1 - Nitro Naphthalene (NO_2) → Fe, HCl → 1 - Naphthly amine (NH_2)
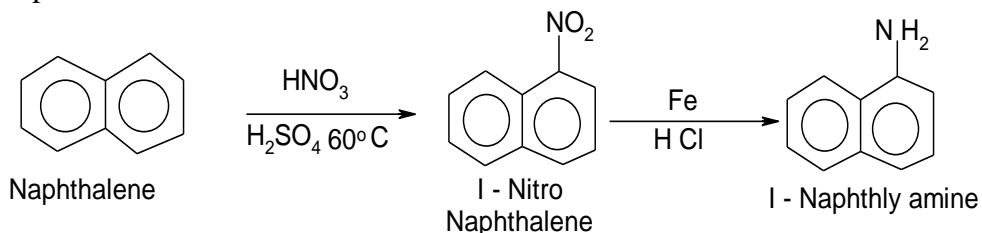
Uses:

1 – Napthol is used in the manufacture of insecticides and dyes.

Napthol (β - Napthol):

Preparation:

2 – Napthol is obtained by fusing sodium 2 – naphthalene sulphonate with sodium hydroxide at 300°C it gives sodium 2 – napthoxide is formed which on treatement with dilute sulphuic acid yields 2 – napthol.
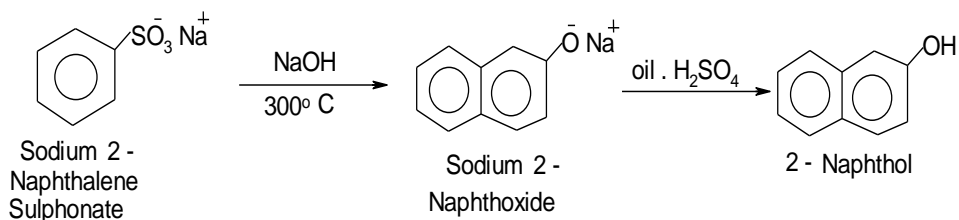
Sodium 2 - Naphthalene Sulphonate ($SO_3^- Na^+$) → NaOH, 300° C → Sodium 2 - Naphthoxide ($O^- Na^+$) → oil . H_2SO_4 → 2 - Naphthol (OH)

Sodium 2 – Naphthalenesulphonate used in the above reaction may be prepared from naphthalene as shown below.

Naphthalene $\xrightarrow[\text{165}^{\circ}\text{C}]{\text{Con. H}_2\text{SO}_4}$ 2 - Naphthalene Sulphonic acid $\xrightarrow{\text{Na OH}}$ Sodiam 2 - Naphthalene Sulpho nate
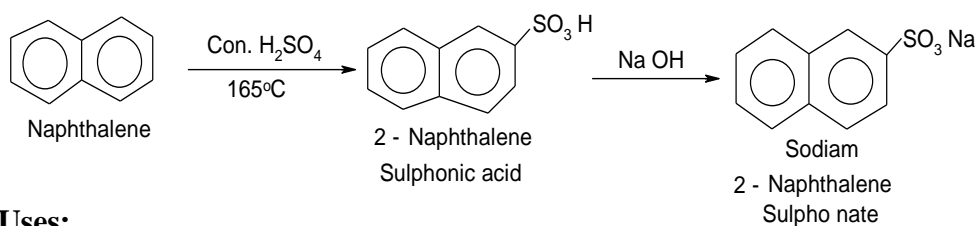
Uses:

1. For making dyes.

2. As an antioxidant in the manufacture of synthetic rubber.

3. As an antiseptic in the treatement of skin disease.

4. For preparing its methyl and ethyl ethers (nerolins) which are extensively used in perfumery.

NOTES

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3.1 Reaction Mechanism V

1. Hydrogen cyanide – HCN.

Hydrogen cyanide adds on to aldehydes and ketones to yield cyanohydrins, The reaction is carried with a basic crystal.

Aliphatic compound:

$$CH_3\ CH{=}O + HCN \longrightarrow CH_3\ CH\begin{smallmatrix} OH \\ CN \end{smallmatrix}$$

acetaldehyde   accetaldehyde cyanohydrin

$$\begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C{=}O + HCN \longrightarrow \begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C\begin{smallmatrix} OH \\ CN \end{smallmatrix}$$

acetone   aceto cyanohydrin
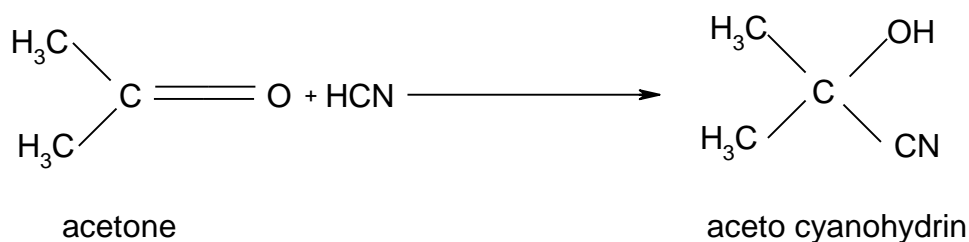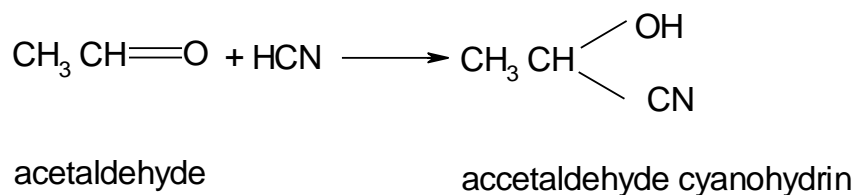
Hydrolysis of cyanohydrin to from hydroxy acid.

$$CH_3CH\begin{smallmatrix} OH \\ CN \end{smallmatrix} \xrightarrow{H_2O} CH_3 - \underset{OH}{CH} - COOH$$

acetaldehyde cyanohydrin   Lactic Acid

$$\begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C\begin{smallmatrix} OH \\ CN \end{smallmatrix} \longrightarrow \begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C\begin{smallmatrix} OH \\ COOH \end{smallmatrix}$$

aceto cyanohydrin   2, Methyl 2 - hydroxy propionic acid
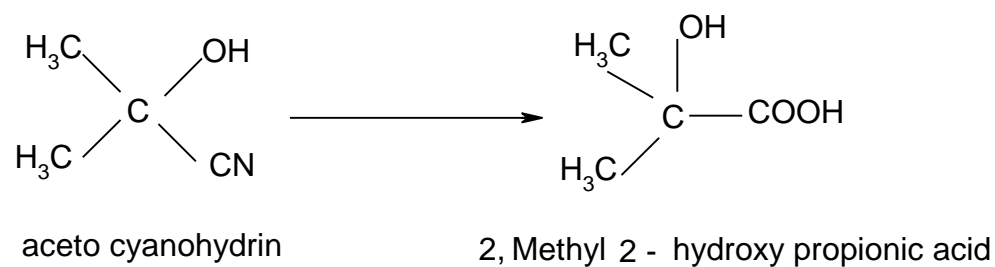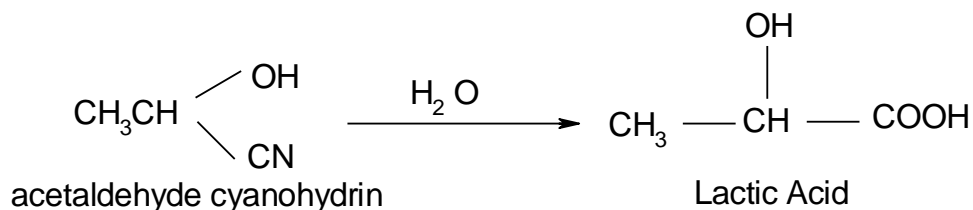
Mechanism :(Lapworth)

The presence of base OH promotes the ionization of HCN to give CN^- ions.

$$\begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C{=}O + CN^- \underset{}{\overset{fast}{\rightleftharpoons}} \begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C\begin{smallmatrix} O^- \\ CN \end{smallmatrix} \underset{Fast}{\rightleftharpoons} \begin{smallmatrix} H_3C \\ H_3C \end{smallmatrix} C\begin{smallmatrix} OH \\ CN \end{smallmatrix}$$

corbonyl compound   cyanohy drin
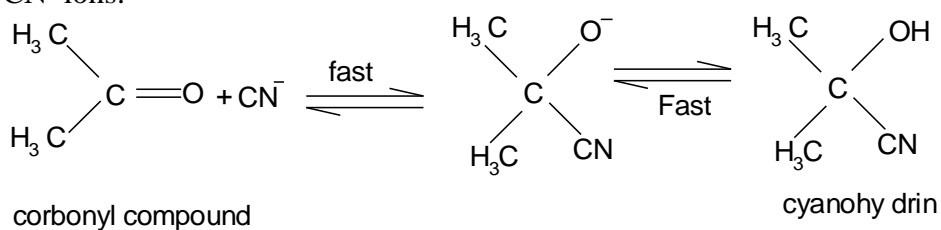
Aromatic compound:

Hydrolysis by Benzaldehyde with cyanohydrine gives bonzaldelyde.
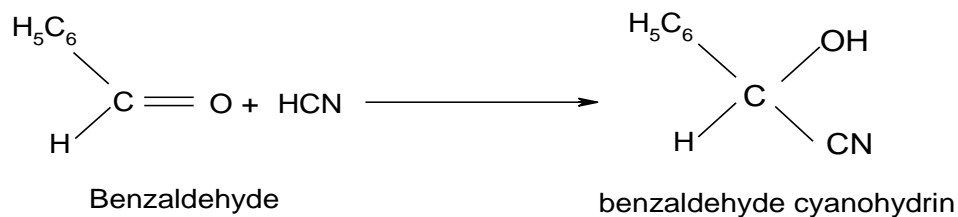
Benzaldehyde   benzaldehyde cyanohydrin

Benzaldehyde cyanohydoin react with HI and Red P to from phenyl acetic aid.

acetophenone   acetophenone cyanohydrin
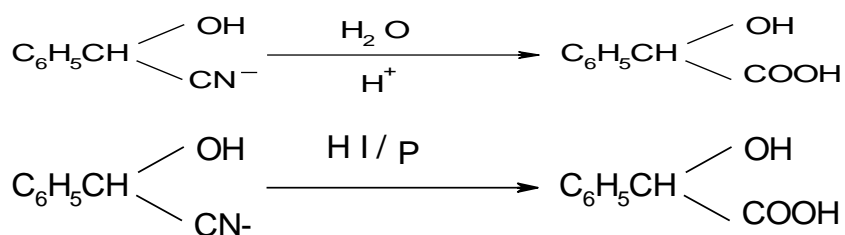
Mechanism:

The presence of base OH promotes the ionization of HCN to give CN ions It is cucleophilic addition reaction.

Acetophenone
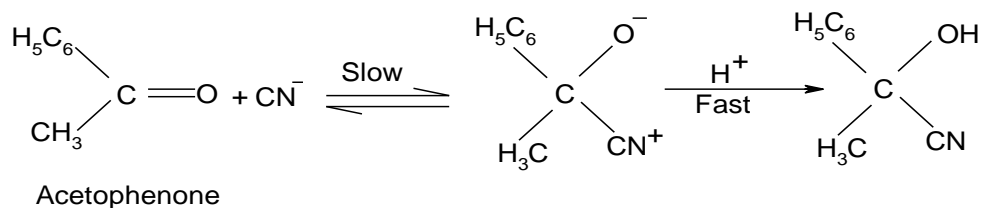
[Simialarly : C_6H_5 CHO – HCN]

2. Hydroxylamine – NH_2OH:

Aldehyde and ketone react with hydroxylamine to from oxime

Aliphatic compound:

$$CH_3CHO + H_2N - OH \xrightarrow{- H_2O} CH_3CH = N - OH$$

acetaldehyde   acetaoxime

acetone   aceto oxime
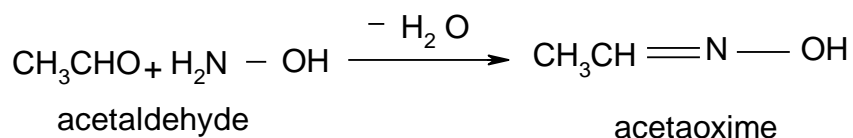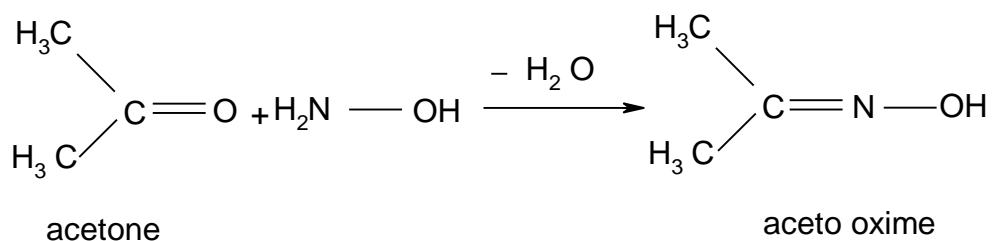
Mechanism:

The common derivative used for the reaction and the products obtained by following steps.

Aromatic compound:

$$C_6H_5 \, CHO + H_2N \, OH \longrightarrow C_6H_5 \, CH = NOH + H_2O$$

Benzaldehyde   Benzaldoxime

acetophenone   acetophenone oxime
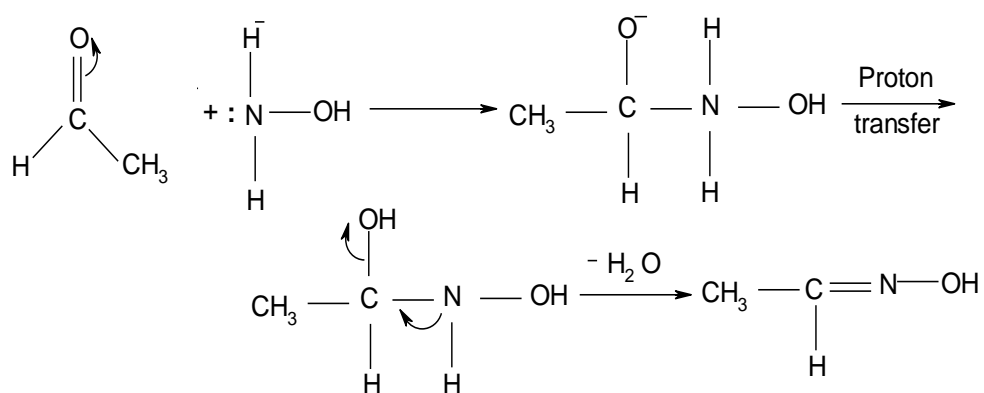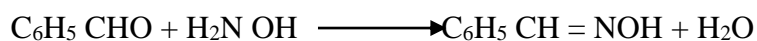
Benzophenone   Benzophenone oxime
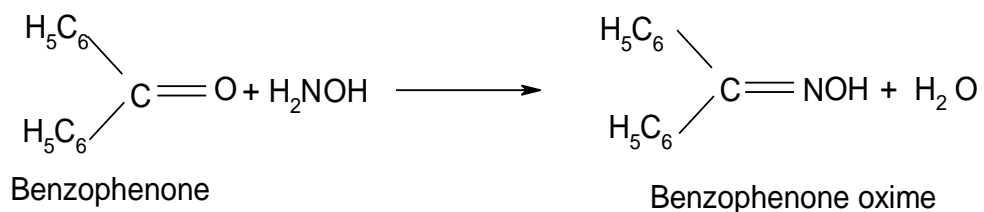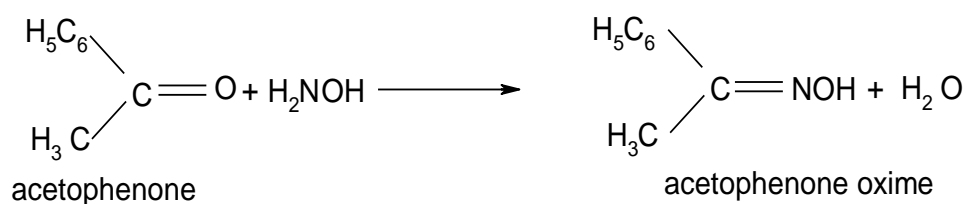
Mechanism:

It is similar to mechanism of aliphatic compound.
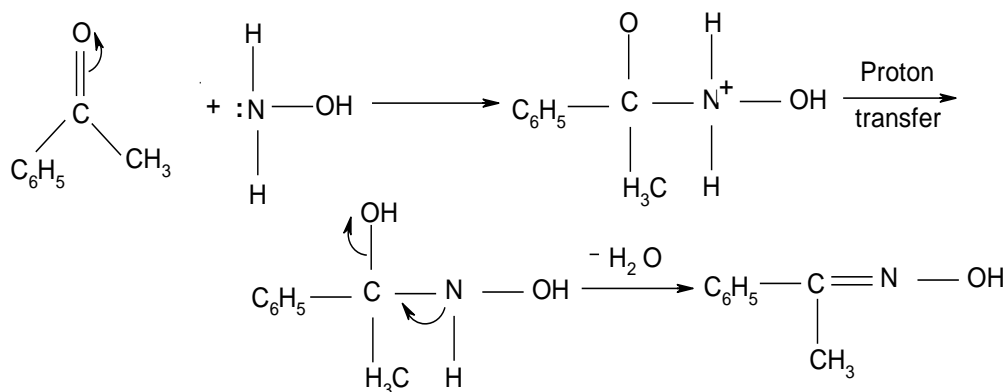
3) 2,4 – dinitro phenyl hydrazine:

Aldehyde and ketone react with 2,4 – dinitro phenyl hydrozine to form 2,4 – dinitro phenyl hydrozone (PNP).

Aliphatic compound:

A. CH_3CHO + H_2NNH— ... —NO_2 $\xrightarrow{-H_2O}$ CH_3C=NNH— ... —NO_2

acetaldehyde   2,4 dinitro phenylhydrazine   2,4 dinitro phenyl hydrazone (PNP)

B. acetone   2,4 dinitro phenylhydrazine   2,4 dinitro phenyl hydrazone (PNP)

Aromatic compound:

Aldehyde or Ketone   2,4 dinitro phenylhydrazine   aldehyde or ketone 2,4 dinitro phenyl hydrazone
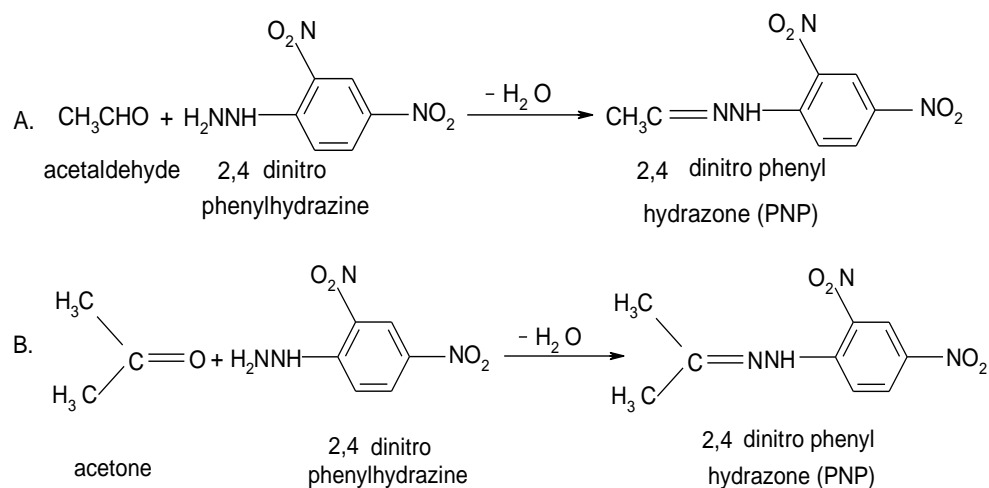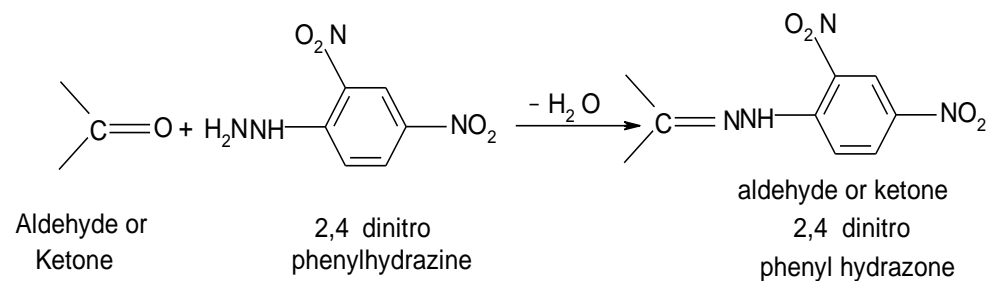
Benzaldehyde and ketone given 2,4 dinitro pheylhydrazone.

It is called Borsche reagent 2,4 – 2,4 dinitro pheylhy drazone yellow or orange colour solids. aldehyde and ketones gives this test.

Mechanism:
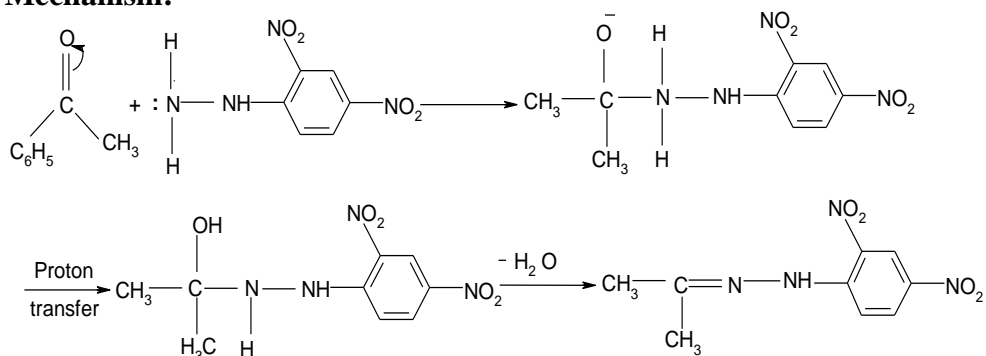
4. Semicarbazide:

Aldehyde and ketone react with semicarbazide to gives semicarbazone

Aliphatic compound:

$$CH_3CHO + H_2NNHCONH_2 \xrightarrow{-H2O} CH_3CH=NNHCONH_2$$

Aromatic compound:
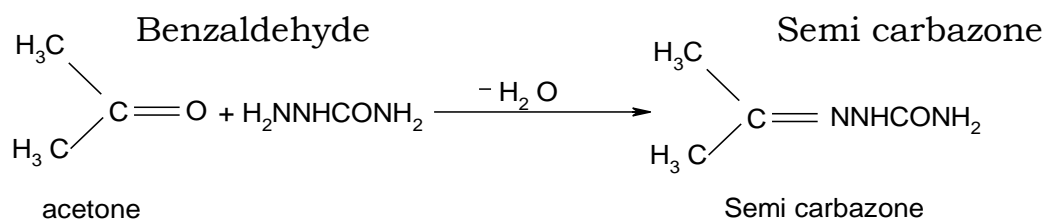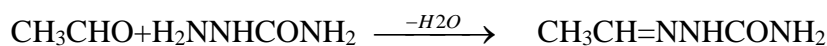
It is similar to aliphatic compound.
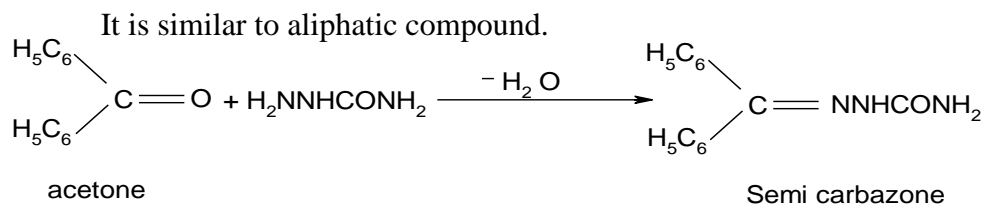
Mechanism:

Similar to NH_2OH.

[Note: Substitute $OH - NHCONH_2$]

99
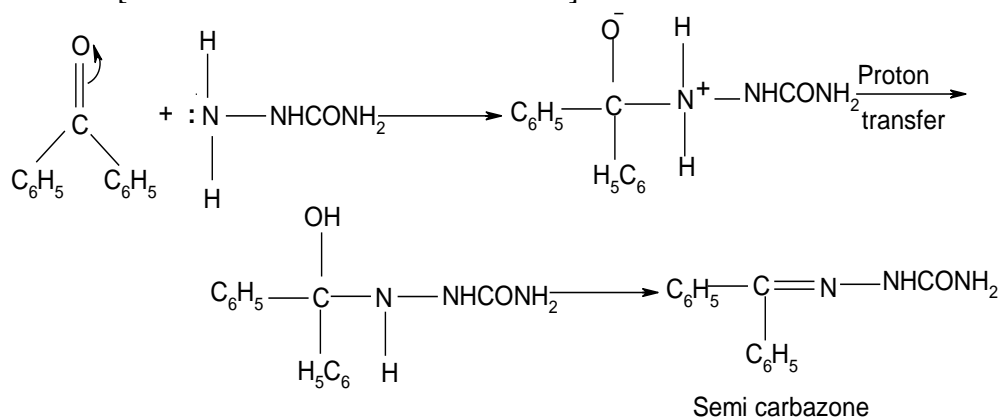
5. Grignard Reagent – R Mg X.

Alcohol:

Primary, secondary and tertiary alcohols are prepared by the reaction between a Grignard regent and a carbonyl Compound. The addition product is decomposed with water or dilute HCl.

(i) Primary alcohol:

Grignard reagent reacts with formaldehyde to given an addition product with on hydrolysis gives a primary alcohol.

Formaldehyde   Ethyl Alcohol
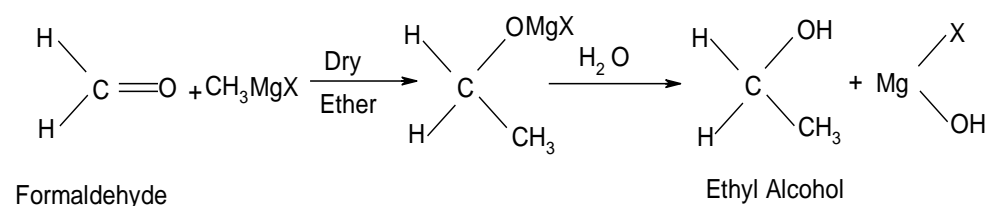
Primary alcohols can be prepared by the action of Grignard reagent on ethylene oxide

Ethylene oxide+phenyl Magnesium chloride $\longrightarrow$

Addition product $\xrightarrow{H2O}$ 2 Phenyl ethan – 1 – Ol.
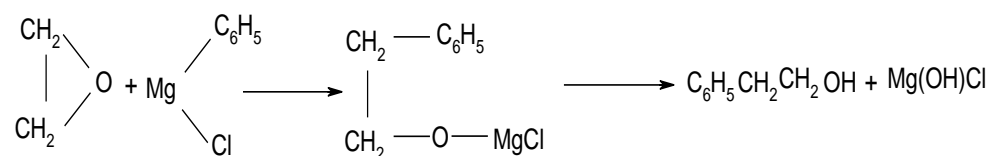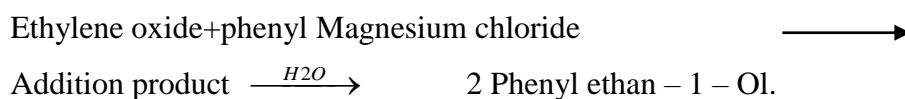
(ii.) Secondary alcohol:

Grignard reagent reacts with an aldehyde other than formaldehyde to give an addition product, which on hydrolysis gives a secondary alcohol.

Acetaldehyde   Isopropyl Alcohol
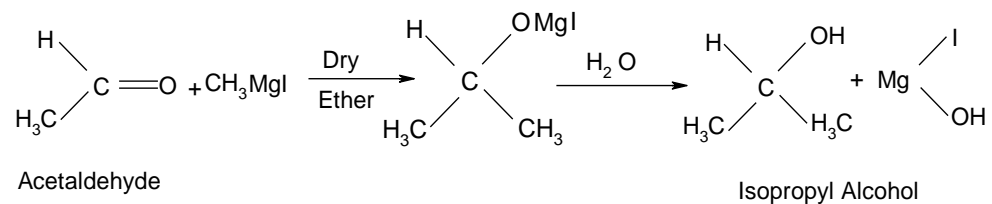
(iii.) Tertiary alcohol:

Grignard reagent reacts with a ketone to give an addition product which on hydrolysis gives a tertiary alcohol.

Acetone   1, Butyl Alcohol

100

Triphenyl Carbinol

Mechanism:

Intermediate

Teritary Alcohol
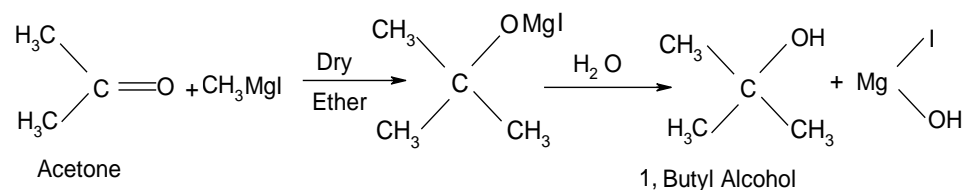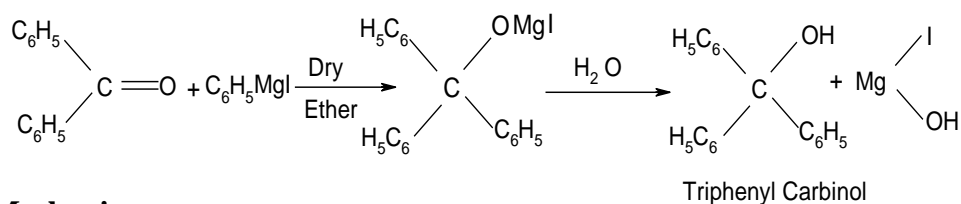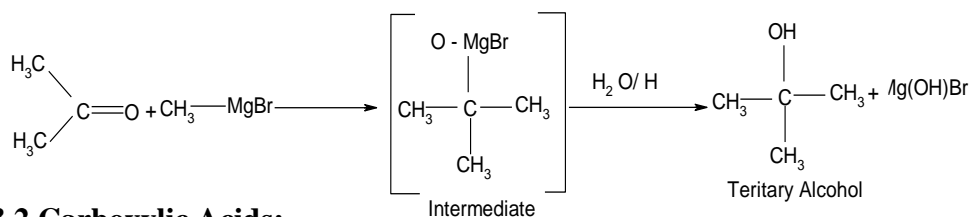
3.2 Carboxylic Acids:

3.2.1 Unsaturated Monocarboxylic Acids:

The unsaturated monocarboxylic acids having a single bond in their molecule are represented by the general formula $C_nH_{2n-1}COOH$.

Acrylic Acid:

$H_2C = CH – COOH$

Prop – 2 – enoic acid.

Preparation:

Acrylic acid derives its name from Acrolein, the corresponding aldehyde.

1. By oxidation of acrolein with ammoniacal silver nitrate.
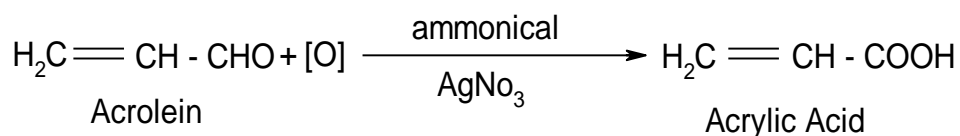
2. By acid hydrolysis of vinyl cyanide which can be obtained from acetylene.
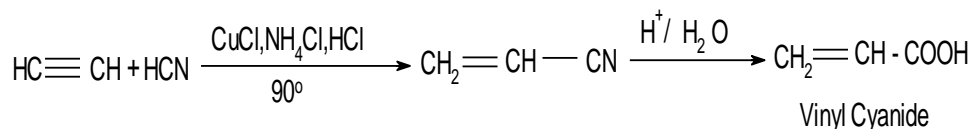
3. By refluxing $\alpha, \beta –$ dibromopropionic acid with Zinc in ethanol.
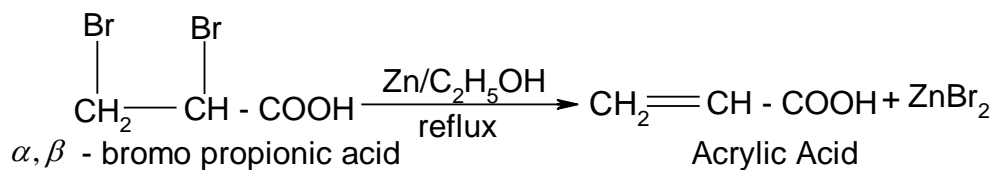
4. By distilling β - hydroxypropionic acid with Zinc chloride.

$$HO - CH_2 - CH_2 - COOH \xrightarrow[\triangle]{ZnCl_2} CH_2 = CH - CHOOH + H_2O$$

β -hydronxy propionic acid   Acrylic acid
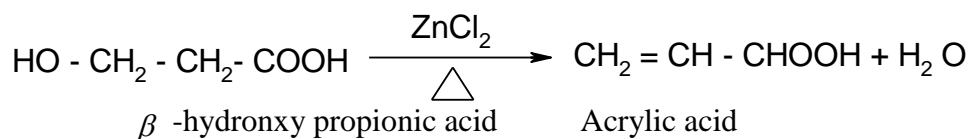
β - hydronxy propionic acid is obtained from ethyene in the folllowing manner.

$$H_2C = CH_2 \xrightarrow{\overset{+}{H}\overset{-}{O}\overset{+}{Cl}} HOCH_2 - CH_2Cl \xrightarrow{K\overset{-}{CN}} HOCH_2 - CH_2CN \xrightarrow{\overset{+}{H}/H_2O} HOCH_2 - CH_2 - COOH$$

ethyline chloro hydrine   ethylene cyanohydrin β – hydronypropionic acid
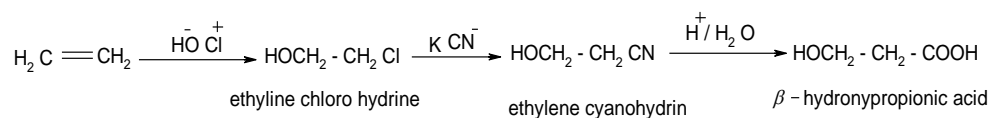
5. From propionic acid by the following sequence reactions.

$$CH_3CH_2COOH \xrightarrow[HYZ]{P + Br_2} CH_3\overset{\overset{\displaystyle Br}{|}}{CH_2}COOH \xrightarrow[C_2H_5OH]{KOH} CH_2 = CHCOOK \xrightarrow{\overset{+}{H}/H_2O} CH_2 = CHCOOK$$

propionic acid α – brormo propionic acid
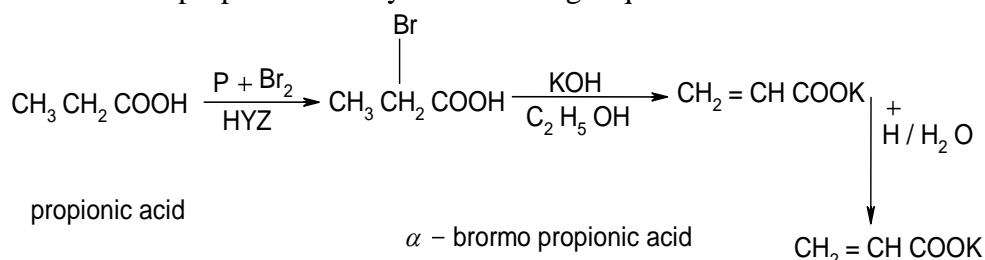
This is probably the best preparative method available for acrylic acid.

Manufacture:

1. From ethylene cyanohydrin in the following manner.

$$\underset{\substack{\displaystyle CH_2 \\ | \\ CH_2}}{\overset{}{\Big\rangle}} O \xrightarrow{HON} \underset{CH_2CN}{\overset{CH_2OH}{|}} \xrightarrow[-H_2O]{con. H_2SO_4} CH = CHCN \xrightarrow{H_2SO_4/H_2O} CH_2 = CHCOOK$$

ethylene cyanohydrin   acrylonitrite vinyl cyanide   Acrylic acid
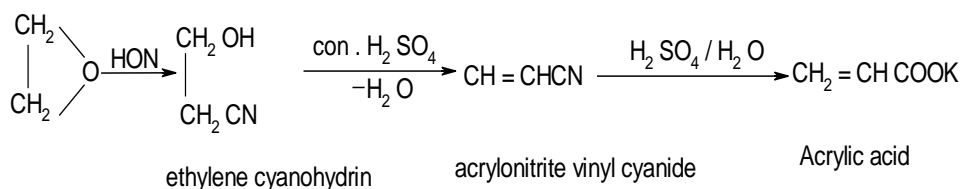
2. By hydrocarbonylation of acetylene in the presence of nickel carbonyl as catalyst.

$$HC \equiv CH + CO + H_2O \xrightarrow[HCl]{Ni(CO)_4} CH_2 = CHCOOK$$
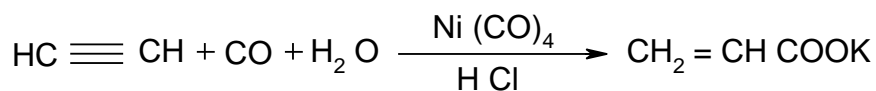
Properties: (Physical)

Acrylic acid is a colourless liquid, boiling point 142°, having a pungent odour like that of acetic acid. It is mixible with water in all proportions. It is a stronger acid than propionic acid and acetic acid, but is a weaker acid than formic acid.

Chemical Properties:

   Acrylic acid behaves both as an alkene and as a carboxylic acid.

A. Reactions of the double bond:

1. On catalytic hydrogenation it gives proponic acid.

$$H_2C = CH - COOH + H_2 \xrightarrow{\text{Ni}} CH_3 - CH_2 - COOH$$
$$\text{Propionic acid}$$
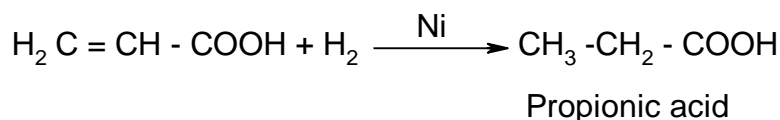
2. With chlorine and bromine it forms addition products.

$$CH_2 = CH - COOH + Br_2 \xrightarrow{\text{C Cl}_4} \overset{\overset{\displaystyle Br \quad Br}{|\quad\quad|}}{CH_2 - CH - COOH}$$
$$\alpha, \beta - \text{dibromo propionic acid}$$
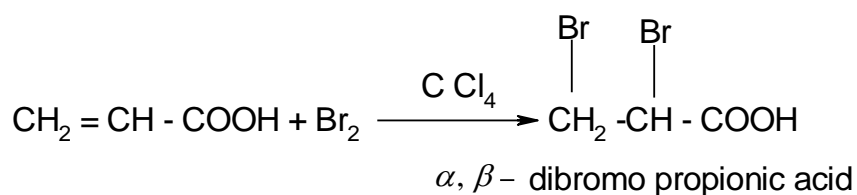
3. With halogen acids it gives β - halopropionic acid.

$$CH_2 = CH - COOH + HBr \longrightarrow Br - CH_2 - CH_2 - COOH$$
$$\beta - \text{brormo propionic acid}$$
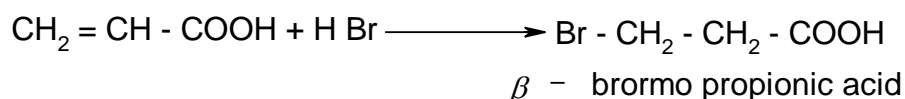
   This addition takes place in to Markovnikov Rule.

4. On hydration in presence of HgSO₄ and H₂SO₄, acrylic acid forms β - halopropionic acid and not the markovnikov product.

$$CH_2 = CH - COOH + H - OH \longrightarrow HO - CH_2 - CH_2 - COOH$$
$$\beta - \text{hydrory propionic acid}$$
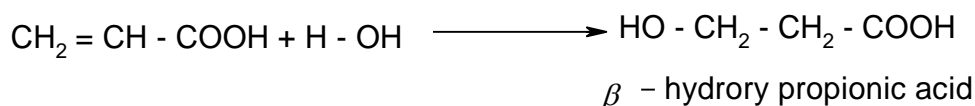
5. On hydroxylation with dilute permanganate solution, it gives glyceric acid which on vigorous oxidation decomposes to oxalic acid.

6. On standing, it slowly polymeriees to a glassy solid.

$$CH_2 = CH\ COOH + H_2O + [O] \xrightarrow{\text{dil. KMn O}_4} \overset{\overset{\displaystyle OH \quad OH}{|\quad\quad|}}{CH_2 - CH - COOH} \xrightarrow{[O]} \overset{\overset{\displaystyle COOH}{|}}{COOH}$$
$$\text{glycertc acid} \qquad\qquad \text{onalic acid}$$
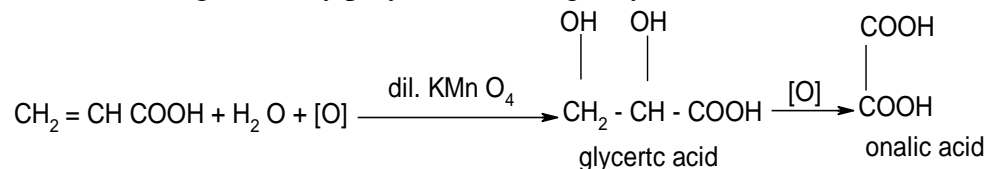
B. Reaction of the Carboxyl group:

1. It forms salts with metal carbonates and alkalis.

$$2\ CH_2 = CH\ COOH + Na_2CO_3 \longrightarrow 2\ CH_2 = CH\ CO\overset{-}{O}\overset{+}{Na} + CO_2 + H_2O$$
$$\text{sod acrylate}$$

$$CH_2 = CH\ COOH + KOH \longrightarrow CH_2 = CH\ CO\overset{-}{O}\overset{+}{K} + H_2O$$
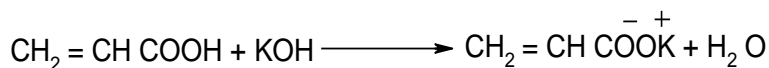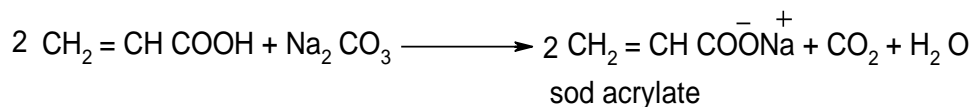
2. On esterification with absolute ethanol in presence of acid, it forms ethyl acrylate.

$$CH_2 = CH - COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_2 = CH - COOC_2H_5 + H_2O$$

ethyl acrylate
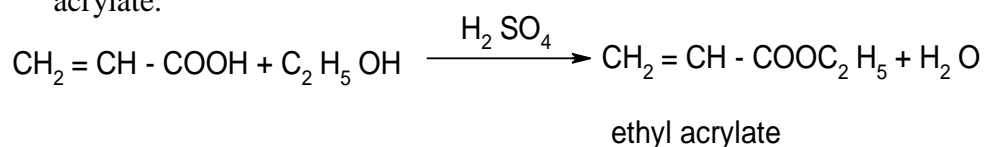
3. With phosphorus halides, it forms acryl chloride which on treatement with ammonia gives acrylamide.

$$CH_2 = CH - COOH \xrightarrow{PCl_5} CH_2 = CH - COCl \xrightarrow{2NH_3} CH_2 = CH - CONH_2 + NH_4Cl$$

acryl chloride
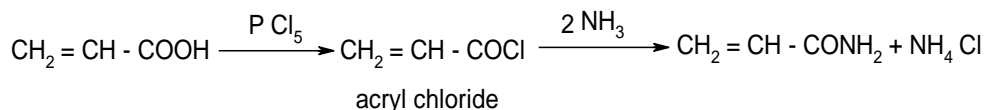
Uses:

1. Because of its irritating odour, apparent even in very low concentration, it is added to closed system of gases and volaitle liquids for easy detection of leaks.

2. It is used primarily to make esters which are important sources of plastic and other commercially valuable polymers.

3. Acrylonitrile, $CH = CH – CN$, a derivative of acrylic acid, it is used as a monomer in the manufacture of Acrilan, Orlon, and other acrylic fibres.

$$CH_2 = CH - C \equiv N \xrightarrow{Polymericeation}$$

acrylonitrite

a portion of the orlon polyoner
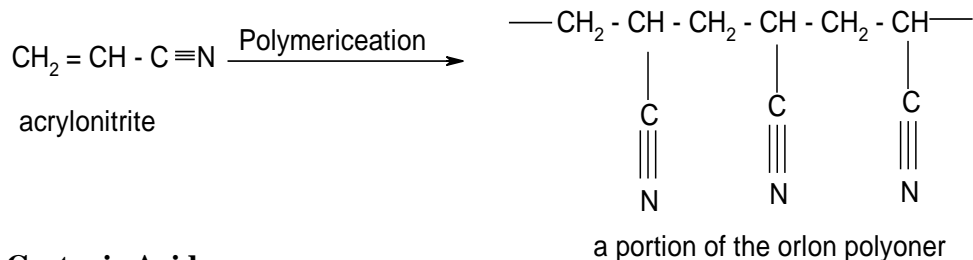
Crotonic Acid:

But – 2 – enoic Acid

$CH_3CH = CH – COOH$

It is the transform of the structure $CH_3CH = CH – COOH$, while the CiS form exists as isocrotonic acid.
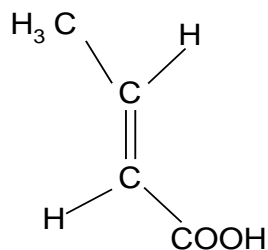
Crotonic acid,

trans - but –2 enoic acid
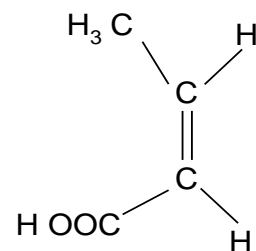
isocrotonic acid,

cis - but –2 enoic acid

Isocrotonic acid when heated at 100°, changes to the more stable crotonic acid.

Crotonic acid occurs in croton oil in the form of its glyceryl esters.

Preparation:

1. By the oxidation of crotonaldehyde with ammonical silver nitrate.

2. By heating acetaldehyde and diethyl malonate in the presence of diethylamine or pirperidine followed by hydrolysis and decarboxylation.

$$CH_3 - CH = CHO + [O] \longrightarrow CH_3 - CH = CH - COOH$$

Crotonaldehyde   crotonic acid

acetade hyde
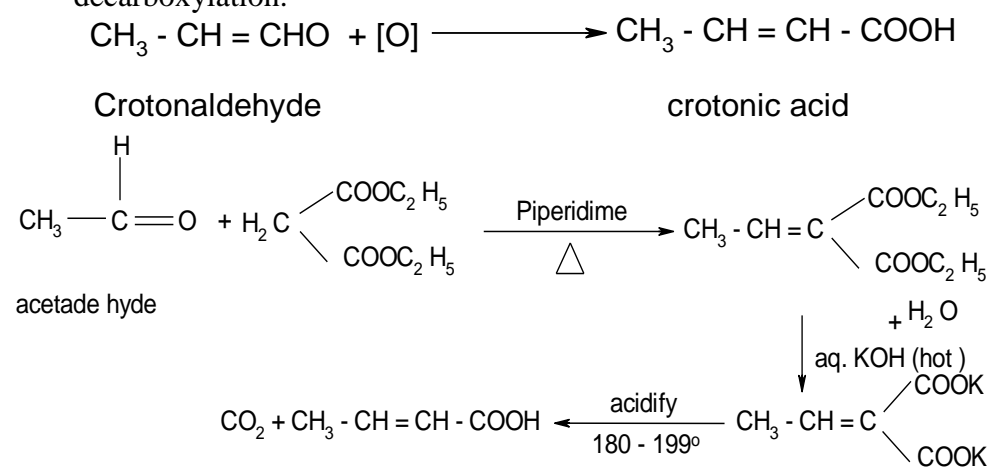
Properties:

Crotonic acid is a colourless solid, melting point 72°, like acrylic acid, it gives reactions both of an alkene and a carboxylic acid. On bromination with N – bromosuccinimide (NBS), it forms γ - bromocrotonic acid.

crotonic acid

δ - bromo crotonic acid
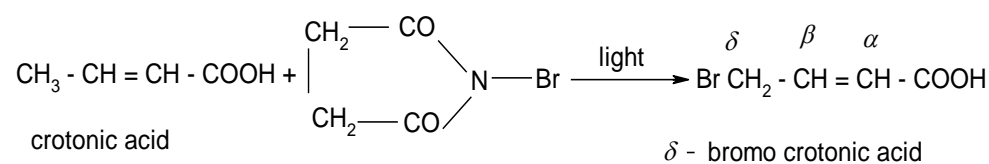
Cinnamic Acid:
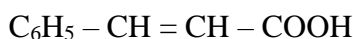
$$C_6H_5 – CH = CH – COOH$$

(Trans - β - phenylacrylic acid)

Owing to the presence of a double bond in the molecule, β - phenylacrylic acid, $C_6H_5 – CH = CH – COOH$ crists in two geometrical forms.

trans cinnamic acid   cis allocinnamic acid
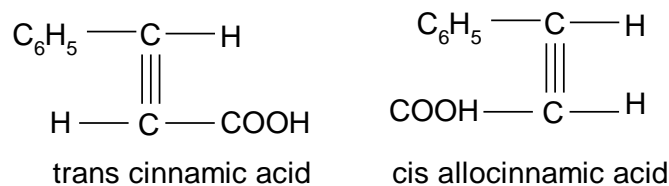
Preparation:

1. It may be prepared by heating benzaldehyde with acetic anhydrate and sodium acetate.

$$C_6H_5 - CH = O + CH_3 - CO - O - CO - CH_3 \xrightarrow[100^\circ]{CH_3 COONa} C_6H_5 - CH = CH - COOH + CH_3 COOH$$

benzaldehyde Acetic anhydride   cinnamic acid
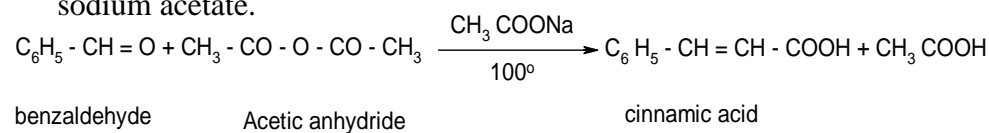
2. It is also produced by the condensation of benzaldehyde with ethyl acetate in the presence of sodium ethoxide.

$$C_6H_5 - CH = O + CH_3 - COOC_2H_5 \xrightarrow{C_2H_5ONa} C_6H_5 - CH = CH - COOC_2H_5$$

ethyl cinnamate

$$\downarrow H^+ \mid H_2O$$

$$C_6H_5 - CH = CH - COOH$$
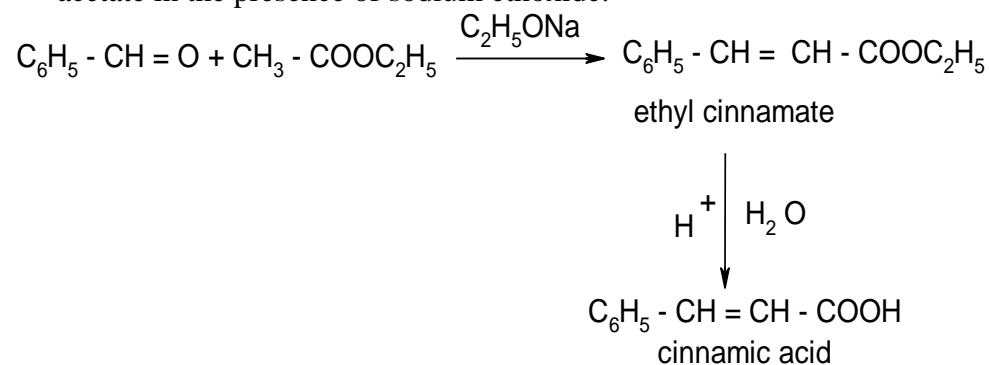
cinnamic acid

3. It is made commercially by the oxidation of benyalacetone with alkaline sodium hypochlorite.

$$C_6H_5 - CH = CH - CO - CH_3 \xrightarrow{Na\ OCl} C_6H_5 - CH = CH - COOH$$

Benzalacetone   cinnamic acid
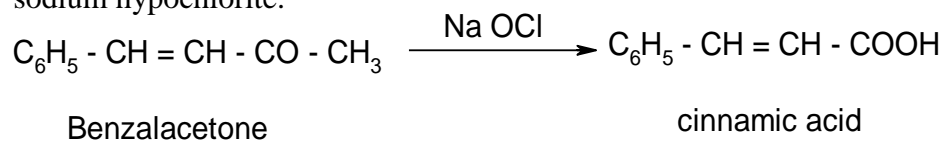
Properties:

  Cinnamic acid is a white solid melting point 133°,having a persistant sharp colour. It is very sparnigly soluble in water. It gives the reactions of an $\alpha, \beta -$ unsaturated acid and the phenyl group.

1. When reduced with sodium amalgam and water, it gives β - phenylpropionic acid.

$$C_6C_5 - CH = CH - CHOOH + 2\ [\ H\ ] \xrightarrow{Na - Hg\ /H_2\ O} C_6H_5 - CH_2 - CH_2 - COOH$$

                  $\beta -$ Phenyl propionic

cinnamic acid
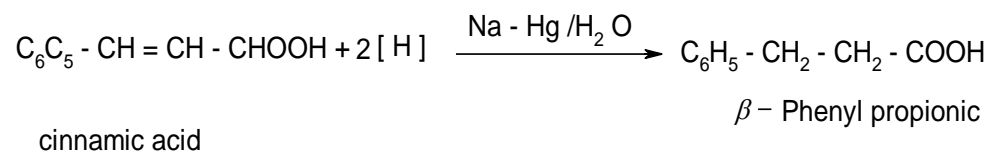
  With lithium aluminium hydride both the double bond and the carbonyl group are reduced, yielding 3 - phenyl propanol.

$$C_6C_5 - CH = CH - CHOOH + 6\ [\ H\ ] \xrightarrow{Li\ Al\ H_4} C_6H_5 - CH_2 - CH_2 - CH_2\ OH$$

                  $3 -$ Phenylpropionic alcohol
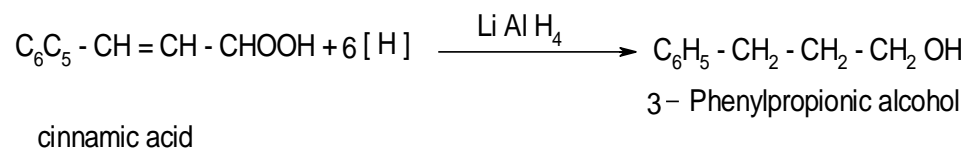
cinnamic acid

2. On oxidation with cold potassium permanganate, the double bond and the carbonyl group are leaves to form benzaldehyde, while vigorous oxidation yields benzoic acid.

$$C_6C_5 - CH = CH - CHOOH \xrightarrow{[O]} C_6H_5 - CH = O \xrightarrow{[O]} C_6H_5 - COOH$$

      cinnamic acid   benzaldehyde   vigorous
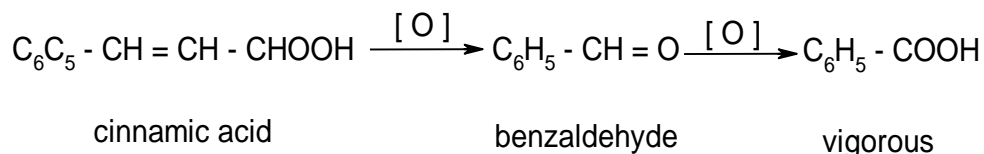
3. At the COOH group, cinnamic acid reacts with alkalis to form salts, and with alcohols to form esters. On heating with sodalime, it decarboxylates to styrene.

$$C_6C_5 - CH = CH - CHOOH \xrightarrow[\triangle]{\text{Sodalime}} C_6C_5 - CH = CH_2 + CO_2$$

        cinnamic acid   styrene
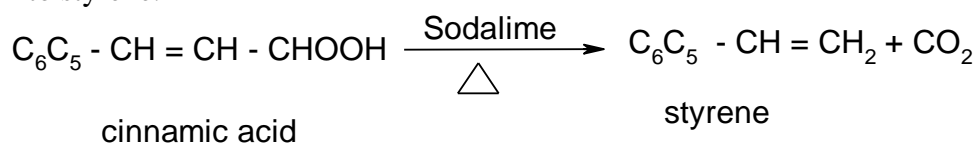
4. Nitration with concentrated nitric acid yields a mixture of O and P – nitrocinnamic acids.

CH = CH - COOH

ConC. HNO$_3$

O - nitrocinnamic acid

+

P - nitrocinnamic acid
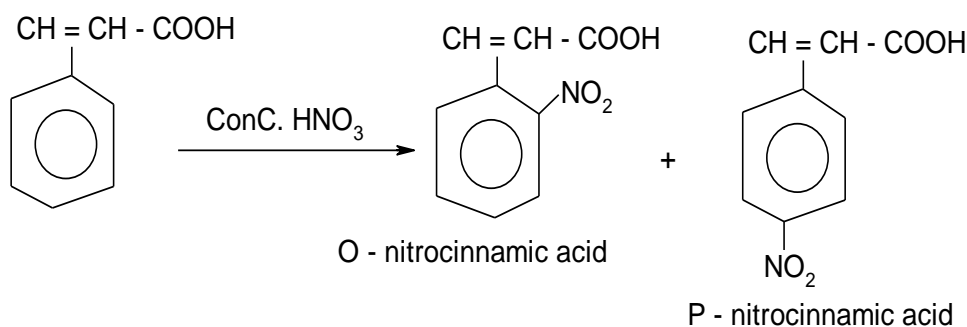
5. When exposed to sunlight, cinnamic acid dimerises to two isomeric cyclobutane derivatives – trurinic acid and trurillic acid.

$$C_6C_5 - CH = CH - CHOOH \xrightarrow{h\delta} C_6H_5 - CH_2 - CH_2 - COOH$$

                                      diradical

$2 C_6C_5 - CH = CH - CHOOH \longrightarrow$

trurinic acid

+

trurilic acid
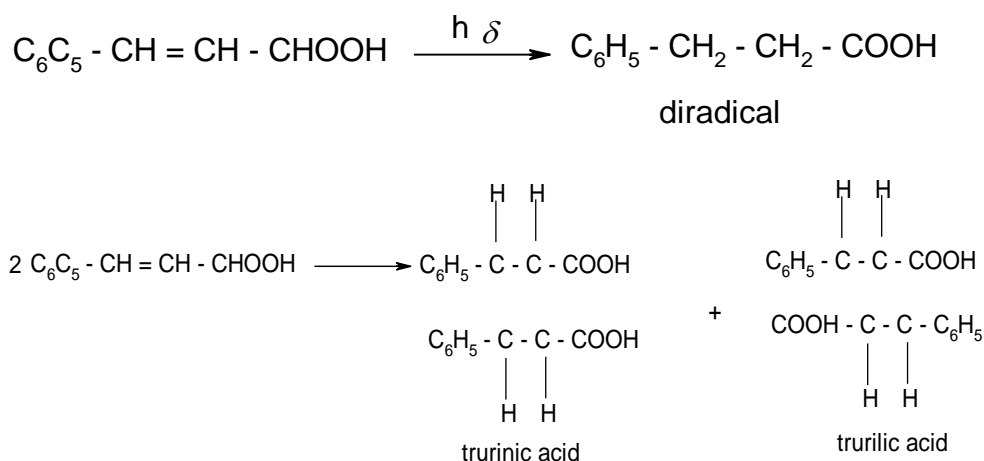
3.2.2 Hydroxycarboxylic Acids:

Organic compounds which contain an alcoholic OH group and a COOH group within a single molecule are called hydroxycarboxylic acids or simply hydroxyl acids. They could be regarded derived from carboxylic acids by replacement of one or more hydrogen in the hydrocarbon part of the molecule by corresponding number of OH groups.

Names of some hydroxy acids

Formula	Common Name	IUPAC NAME
$HO - CH_2 - COOH$	hydroxy acetic acid glycollic acid	hydroxyethanoic acid
$CH_2 - CHOH - COOH$	α - hydroxy propionic acid lactic acid	2 – hydroxy propionic acid
$CH(OH) - COOH$ | $CH(OH) - COOH$	α - α^1- dihydroxy succinic acid tartaric acid	2,3 – dihydroxy hastamedioic acid
$CH(OH) - COOH$ | $CH_2 - COOH$	α - dihydroxy succinic acid Malic acid	2 – hydroxy butanic acid
$CH_2 - COOH$ | $C(OH) - COOH$ | $CH_2 - COOH$	citric acid	2 – hydroxy propance 1,2,3 – tricarboxylic acid

It may also be noted that monohydroxy acids are classified as α - hydroxy acids, β - hydroxy acids, γ - hydroxy acids, δ - hydroxy acids, depending on the OH is bonded to the $\alpha, \beta, \gamma \, or \, \delta$ carbon of the chain with respect to the COOH group.

Preparation of Glycollic Acid:

Hydroxyacetic acid (2 – Hydroxyethanoic AcidHO – CH_2COOH

It is the simplest hydroxy acid known and occurs in urripe grapes, sugar cane and beet.

Preparation:

1. Glycollic acid is prepared by the hydrolysis of chloroacetic acid with boiling dilute alkali, followed by acidification with dilute hydrochloric acid.

$$Cl - CH_2\,COOH + 2\,NaOH \longrightarrow HO - CH_2\,COONa + NaCl + H_2O$$
$$\text{sod glycollate}$$

$$HO - CH_2\,COONa + HCl \longrightarrow HO - CH_2\,COOH + NaCl$$
$$\text{glycollic acid}$$
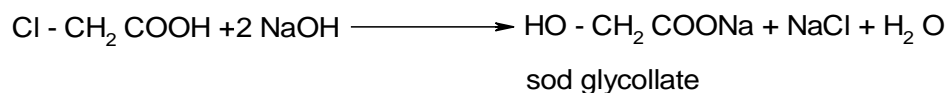
2. Technically it is obtained by the electrolytic reduction of oxalic acid.

$$HO - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - OH + 4\,[\,H\,] \longrightarrow HO - CH_2\,COOH$$
$$\text{oxalic acid} \qquad\qquad\qquad \text{glycollic acid}$$
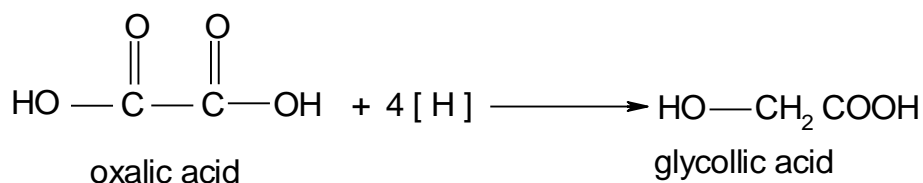
3. According to a recent method, glycollic acid manufactured by heating a mixture of formaldehyde, carbon monoxide and water at $160^o - 170^o$ under pressure in presence of sulphuric acid as catalyst.

$$H - \overset{\overset{\displaystyle H}{|}}{C} = O + CO + H_2O \xrightarrow[\triangle]{H^+} HO - CH_2\,COOH$$
$$\text{formaldehyde} \qquad\qquad\qquad \text{glycollic acid}$$
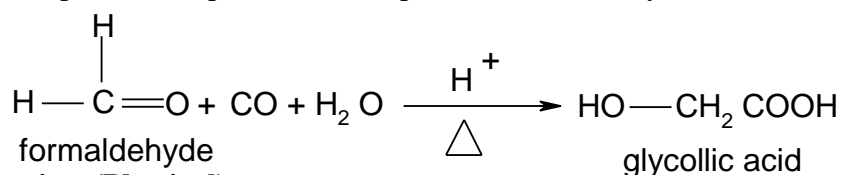
Properties: (Physical)

Glycollic acid is a white crystalline solid, mp 80°. It is readily soluble in water, ethanol and ether. It is a stronger acid than acetic acid though weaker than chloroacetic acid.

Chemical Properties:

It gives the reactions of both a primary alcohol and a monocarboxylic acid.

1. As a primary alcohol, glycollic acid gives the following reactions.

$$HOOC\,CH_2\,OH$$
glycollic acid

$+ O \xrightarrow[(\text{Orid})]{HNO_3} HOOC - CHO \xrightarrow[HNO_3]{[\,O\,]} HOOC - COOH$
Oxalic acid

$+ HBr \xrightarrow{\triangle} HOOC - CH_2\,Br + H_2O$
α – bromoaccetic acid

$+ 2\,HI \xrightarrow[(\text{red P})]{\triangle} HOOC - CH_3 + I_2 + H_2O$
acetic acid

$+ CH3\,COCl \longrightarrow HOOC - CH_2\,O - COCH_3 + HCl$
acetylglycollic acid
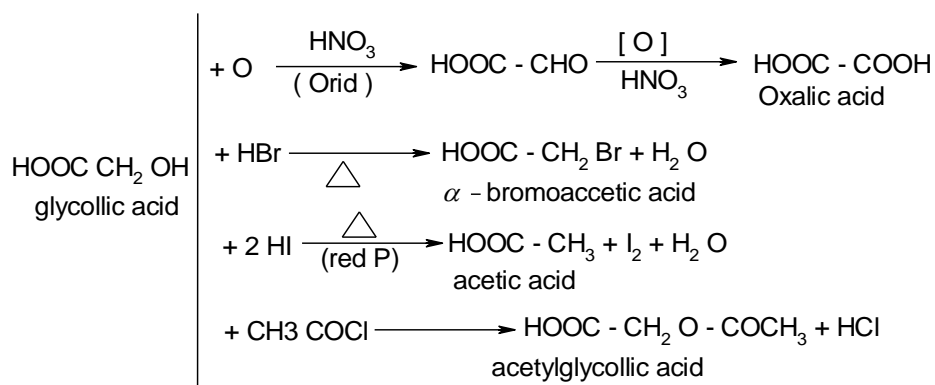
2. As carboxylic acid, it forms salts with alkalis and decomposes dicarbonates as also carbonates. In presence of concentrated H_2SO_4 glycollic acid reacts with alcohols to form esters.

$$HO\ CH_2\ COOH + Na\ OH \longrightarrow HO - CH_2\ COONa + H_2\ O$$
$$\text{Sod - glycollate}$$

$$HO\ CH_2\ COOH + CH_3\ OH \overset{H_2\ SO_4}{\rightleftharpoons} HO - CH_2\ COOCH_3 + H_2\ O$$
$$\text{Methanol} \qquad\qquad \text{Methyl glycollate}$$
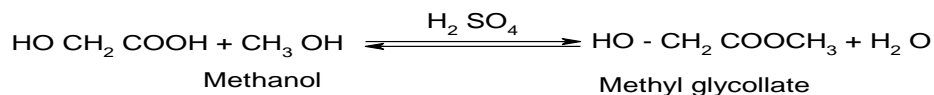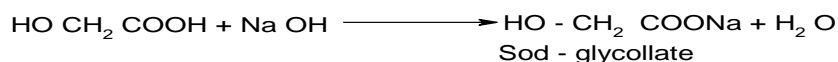
3. With PCl_5 and Na, the reaction takes place at both the hydroxy groups and carbonyl group independently to form di – derivatives.

$$HO - CH_2 - COOH + 2\ PCl_5 \longrightarrow Cl - CH_2 - COCl + _2POCl_3 + _2HCl$$

glycollic acid $\qquad\qquad\qquad$ Chloroacetyl chlorides

$$HO - CH_2 - COOH + _2Na \longrightarrow Na\ OCH_2 - COONa + H_2$$
$$\text{disodium glycollate}$$
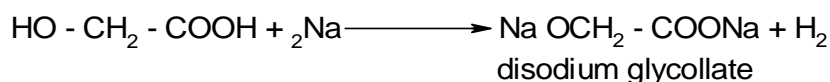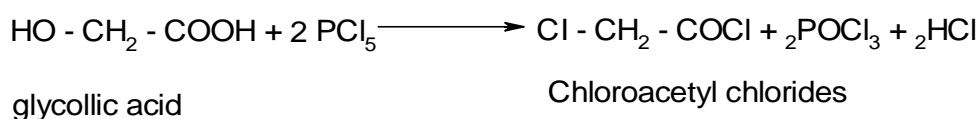
4. On heating, two molecules of glycollic acid eliminate two molecules of water to form a lactide called glycollide.

glycollide (alactide)
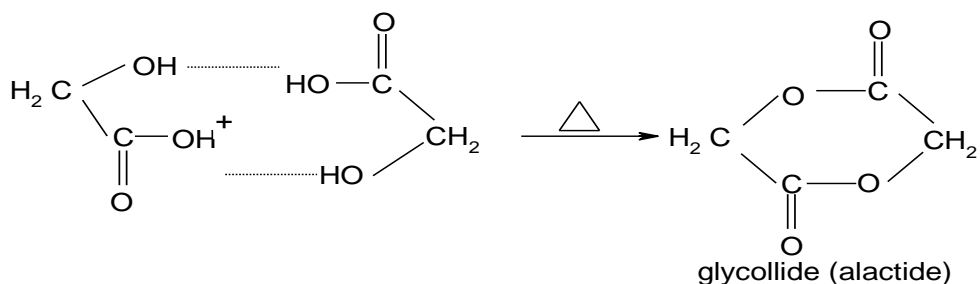
5. When warmed with concentrated sulphuric acid, it forms formaldehyde and carbon monoxide.

$$HO - CH_2 - COOH \longrightarrow H - CH = O + CO + H_2\ O$$
$$\text{glycollic acid} \qquad\qquad \text{formaldehyde}$$
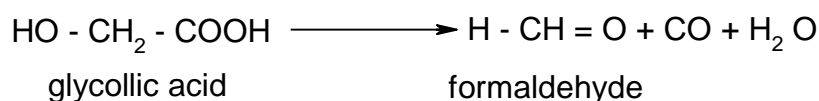
Uses:

Glycollic acid is used chiefly in cloth printing, and as a synthetic reagent.

Action of heat on $\alpha, \beta, \gamma\ or\ \delta$ hydroxy acids:

1. α - hydroxy acids on heating give cyclic esters known as Lactides. This name was originally assigned to the cyclic diester obtained from lactic acid.

Here the ester formation takes place between two molecules of the hydroxy acid so as to get a stable six – membered ring in the product.

$$\alpha - \text{hydroxy acid (2 molecules)} \xrightarrow[-2\ H_2O]{\triangle} \text{a lactide}$$
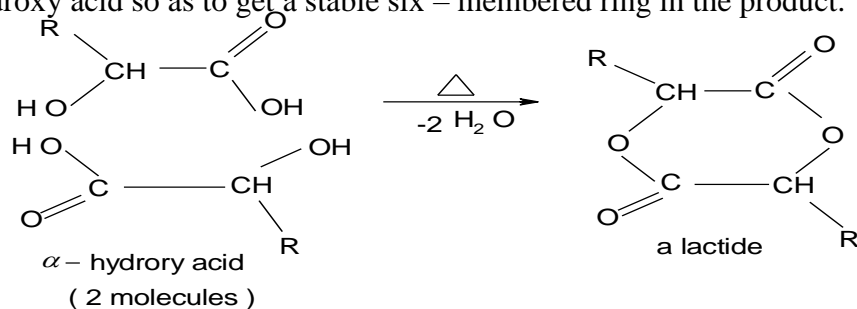
This lactic acid undergoes intermolecular eaterification to form a lactide as follows.

$$\text{lactic acid (2 molecules)} \xrightarrow[-2\ H_2O]{\triangle} \text{Lactide}$$
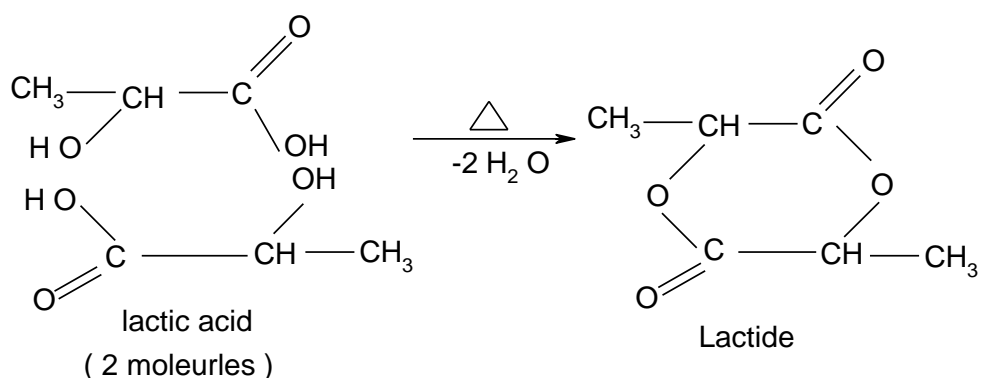
Similarly, glycollic acid yields the lactide commonly known as glycollide.

2. β - hydroxy acids are not converted to cyclic esters on heating. On the other hand, when heated alone or treated with a strong mineral acid, β - hydroxy acids undergo elimination of a molecule of water to yield unsaturated acids. The α , β - unsaturated acids, rather than the β , δ - unsaturated acids, is formed preferentially because the α , β - unsaturated acids are more stable due to the conjugation between the carbon – carbon and the carbon – oxygen double bonds.

$$\overset{\delta}{C}H_2 - \overset{\beta}{C}H - \overset{\alpha}{C}H - COOH \underset{-H_2O}{\overset{\triangle\ \text{or}\ H^+}{\longrightarrow}} \overset{\delta}{C}H_3 - \overset{\beta}{C}H = \overset{\alpha}{C}H - \overset{O}{\overset{\|}{C}} - OH$$

with OH and H substituents. Crotonic acid
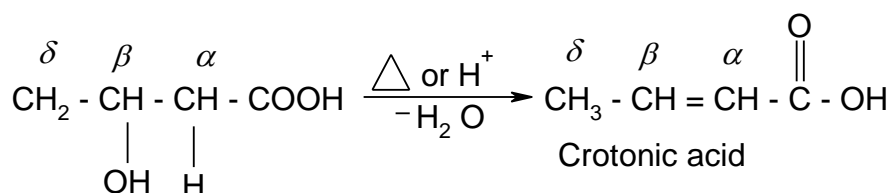
This reaction is similar to dehydration of an alcohol to an alkene.

3. γ - hydroxy acids when heated undergo an intra molecular esterification to form a five membered cyclic esters or internal ester known as a lactone.

$$\overset{\delta}{CH_2} - \overset{\beta}{CH_2} - \overset{\alpha}{CH_2} - COOH \xrightarrow[\triangle]{-H_2O} \quad CH_2 - C \overset{O}{<}_{O}$$

δ − hydroxy bntyric acid δ – butyrolactone
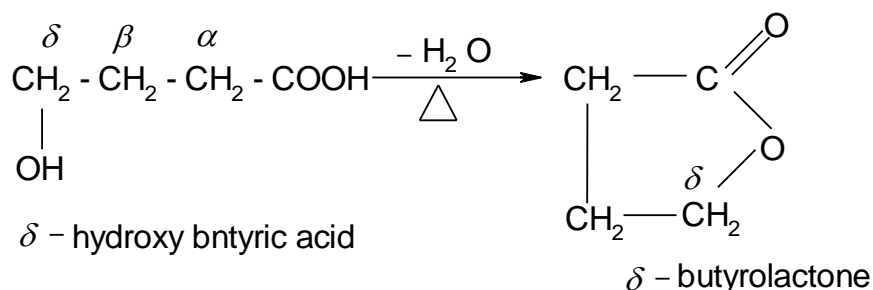
The lactone produced from a γ - hydroxy acid is known as γ - lactone.

4. δ - hydroxy acids also undergo an intra molecular esterification spontaneously to form a six - membered cyclic esters or internal ester known as a δ - lactone.

Dicarboxylic Acids:

The dicarboxylic acids contain two carbonyl groups (COOH) in their molecules. Of these most important are those which are carry the carbonyl groups at the two ends of the saturated carbon chain.

$(CH_2)_n(COOH)_2$ (or) $HOOC – (CH_2)_n - COOH$

$$CH_2 - CH_2 - CH_2 - CH_2 - COOH \xrightarrow{-H_2O} H_2C \cdots$$

δ − hydrony valeric acid δ – valerolactone

Oxalic Acid:
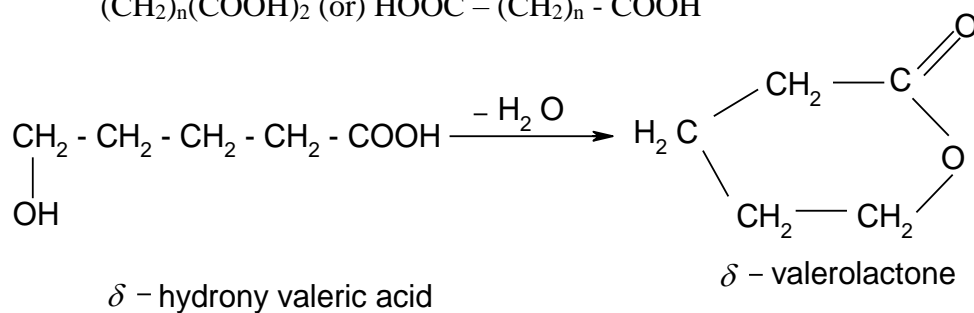
$(COOH)_2$ – ethane – 1, 2 dioic acid.

Preparation:

Oxalic acid may be obtained by the oxidation of glycol and also by the hydrolysis of cyanogen.

$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + 4\,[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2\,H_2O$$

ethylene glycol   Onalic acid

$$\begin{array}{c} C\equiv N \\ | \\ C\equiv N \end{array} + 4\,H_2O + 2\,HCl \xrightarrow{\text{boil}} \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2\,NH_4Cl$$
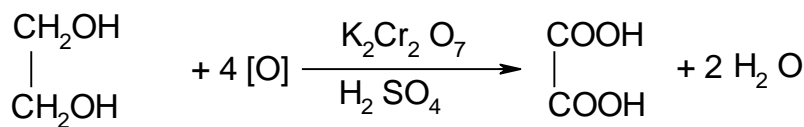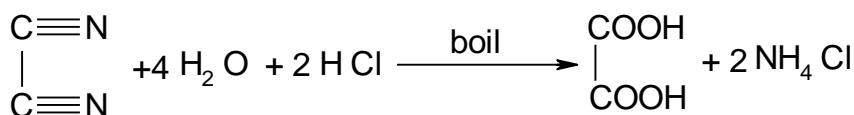
cyanogon

Laboratory Preparation:

In the laboratory, oxalic acid is prepared by the oxidation of can sugar i.e., surose with concentrated nitric acid in presence of vanadium pentoxide as the catalyst.

$$C_{12}H_{22}O_{11} + {}_{18}[O] \xrightarrow[V_2O_5]{HNO_3} 6 \begin{array}{c} COOH \\ | \\ COOH \end{array} + 5\,H_2O$$
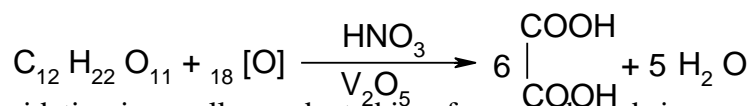
The oxidation is usually conducted in a fume cupboard since copours oxides of nitrogen are produced during the reaction.

Manufacture:

1. From sodium formate, oxalic acid is prepared industrially by heating sodium formate rapidly at 375o when sodium oxalate is produced. This is then converted to calcium oxalate by treatment with lime which when reached with dilute sulphuric acid forms oxalic acid.

$$\begin{array}{c} H-COONa \\ H-COONa \end{array} \xrightarrow{375^o} \begin{array}{c} COONa \\ | \\ COONa \end{array} + H_2$$

Sod oralate

$$\begin{array}{c} COONa \\ | \\ COONa \end{array} + Ca(OH)_2 \longrightarrow \begin{array}{c} COO \\ | \quad\quad\ Ca \\ COO \end{array} + 2\,NaOH$$

Calcium oxalate

$$\begin{array}{c} COO \\ | \quad\quad\ Ca \\ COO \end{array} + H_2SO_4 \longrightarrow \begin{array}{c} COOH \\ | \\ COOH \end{array} + CaSO_4$$
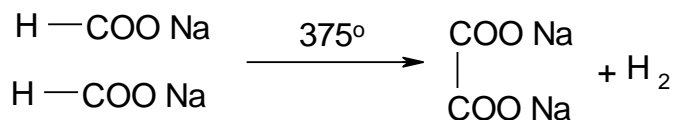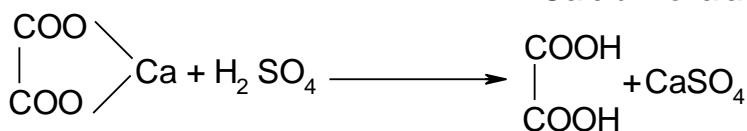
Oxalic acid

2. By direct combination of CO_2 and metallic sodium at 360°.

$$2\,CO_2 + 2\,Na \xrightarrow{\ 360°\ } \begin{array}{c} COO\,Na \\ | \\ COO\,Na \end{array}$$

Sod oxalate
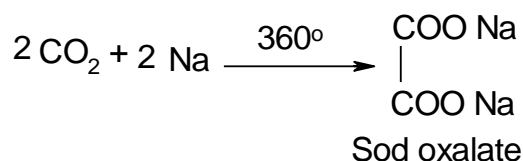
Sodium oxalate is worked for oxlic acid as in method (I)

3. Oxalic acid is also obtained commercially by the oxidation of carbohydrates such as glucose, sucrose, cellulose with nitric acid in the presence of a catalyst.

$$C_6H_{12}O_6 + {}_6HNO_3 \longrightarrow 3\begin{array}{c} COOH \\ | \\ COOH \end{array} +6\,NO + 6\,H_2O$$

dextrose
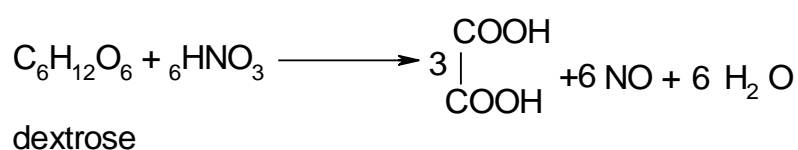
4. Formerly, oxalic acid was obtained on a large scale by heating saw dust at 240 – 250o with a concentrated solution of sodium hydroxide. The sodium oxalate thus produces was converted to oxalic acid as described in method (I). This method is now obsolute.

Malonic Acid:

$CH_2(COOH)_2$ – Propane – 1, 3 dioic acid.

Malonic acid was so named because it was first obtained by the oxidation of malic acid.

Preparation:

It is ordinarily prepared from sodium chloroacetate by the following sequence of reactions.

$$Cl - CH_2\,COOH + Na + H\bar{C}O_2 \longrightarrow Cl - CH_2\,COONa + H_2O + CO_2$$

Chloroacetic acid

$$Cl - CH_2\,COO\overset{+}{N}a + \overset{+}{K}\bar{C}N \longrightarrow N \equiv C - CH_2 - \bar{C}OO\overset{+}{N}a + \overset{+}{K}\bar{Cl}$$

Sod cyanoacetate

$$N \equiv C - CH_2 - COONa + 2\,H\,Cl + 2\,H_2O \longrightarrow HOOC - CH_2 - COOH + \overset{+}{N}H_4\,\bar{Cl} + \overset{+}{Na}\,\bar{Cl}$$

malonic acid
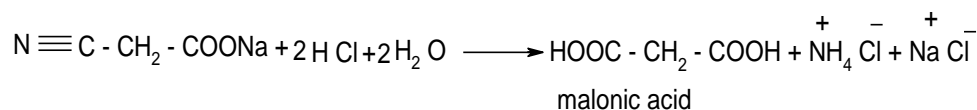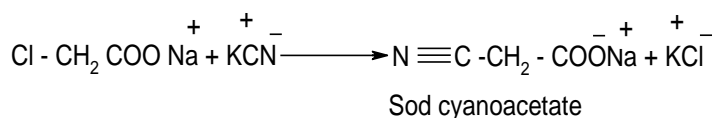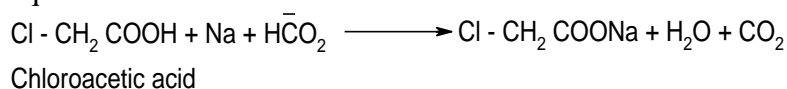
Succinic Acid:

Succinic acid was first obtained as a result of distillation of the fossil resin nmber and hence its name. It occurs widely in nature in numerous

plants and unripe fruits. It is also produced in small amount during the alcoholic fermentation of sugar.

Preparation:

1. Succinic acid is prepared from ethylene bromide by treating with potassium cyanide and subsequent hydrolysis of cyanide.

$$\underset{\substack{\text{ethylene}\\\text{bromine}}}{\underset{\displaystyle CH_2\,Br}{\overset{\displaystyle CH_2\,Br}{|}}} \xrightarrow{\;-2\;KCN\;} \underset{\substack{\text{ethylene}\\\text{cyanide}}}{\underset{\displaystyle CH_2\,CN}{\overset{\displaystyle CH_2\,CN}{|}}} \xrightarrow[\text{Hydrolyris}]{\;H_2O\,/\,HCl\;} \underset{\text{Succinic acid}}{\underset{\displaystyle CH_2\,COOH}{\overset{\displaystyle CH_2\,COOH}{|}}}$$
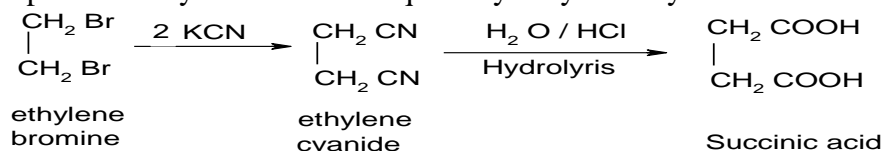
2. By heating malic or tartaric acid in a sealed tube with hydroiodic acid and red phosphorus.

$$\underset{\text{Malic acid}}{\underset{\displaystyle CH_2\,COOH}{\overset{\displaystyle CH\,(OH)\,COOH}{|}}} +\,2\,H\,I \xrightarrow[\triangle]{\text{red P}} \underset{\text{Succinic acid}}{\underset{\displaystyle CH_2\,COOH}{\overset{\displaystyle CH_2\,COOH}{|}}} +\,I_2 + H_2O$$

$$\underset{\displaystyle CH_2\,(OH)\,COOH}{\overset{\displaystyle CH\,(OH)\,COOH}{|}} +\,4\,H\,I \xrightarrow[\triangle]{\text{red P}} \underset{\displaystyle CH_2\,COOH}{\overset{\displaystyle CH_2\,COOH}{|}}$$
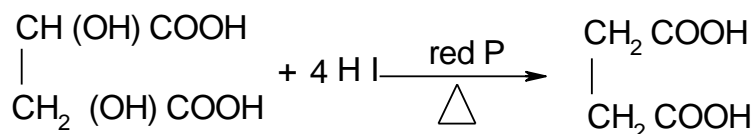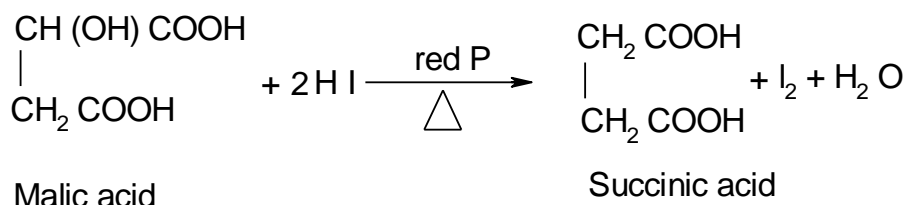
3. It is prepared commercially by the catalytic reduction of malic acid.

$$\underset{\text{Malic acid}}{\underset{\displaystyle CH\,COOH}{\overset{\displaystyle CH\,COOH}{\|}}} +\,H_2 \xrightarrow[\triangle]{\text{Ni}} \underset{\text{Succinic acid}}{\underset{\displaystyle CH_2\,COOH}{\overset{\displaystyle CH_2\,COOH}{|}}}$$
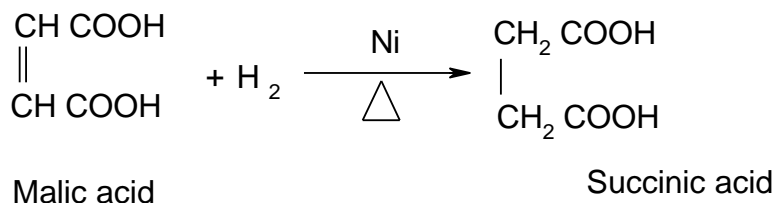
Glutaric Acid:

Pentane – 1,5 dioic acid, $HOOC – (CH_2)_3 – COOH$

Glutaric acid was prepared from Glutanic acid as follows and hence its name.

$$HOOC - CH_2 - CH_2 - \overset{\overset{\displaystyle NH_2}{|}}{CH} - COOH \xrightarrow{HNO_2} HOOC - CH_2 - CH_2 - \overset{\overset{\displaystyle OH}{|}}{CH} - COOH$$
$$\alpha – \text{hydroxyglutaric acid}$$

$$\xrightarrow{H\,I} HOOC\;CH_2\;CH_2\;CH_2\;COOH$$
$$\text{glutaric acid}$$
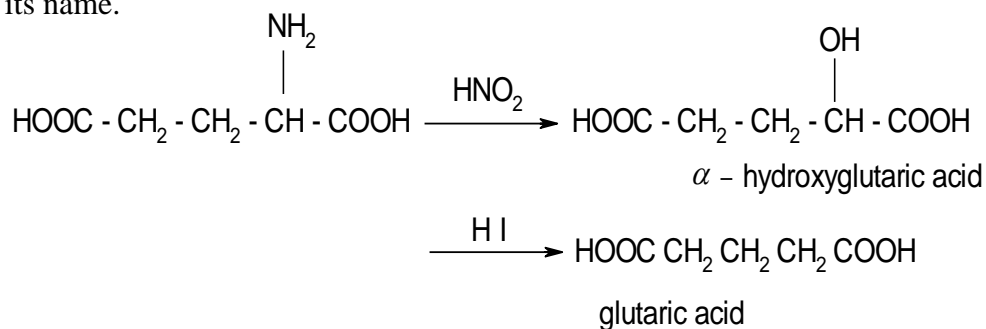
It is not a commercial product and it made in the laboratory by the following synthetic methods.

1. By hydrolysis of trimethylene cyanide.

$$H_2C \begin{cases} CH_2\,CN \\ \\ CH_2\,CN \end{cases} + 4\,H_2O + 2\,HCl \xrightarrow{\text{boil}} H_2C \begin{cases} CH_2\,COOH \\ \\ CH_2\,COOH \end{cases} + 2\,NH_4^+\,\overset{-}{Cl}$$

triemethylene cyamide   glutaric acid
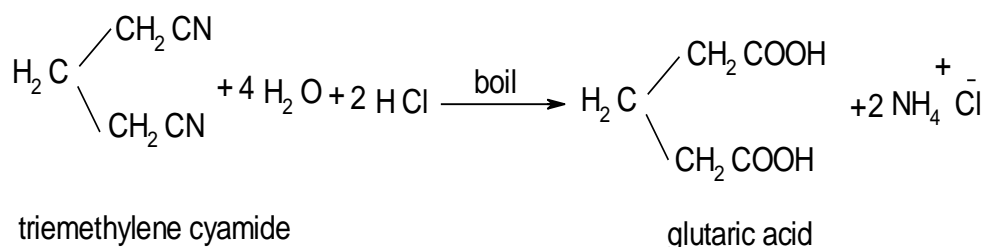
2. By oxidation of cyclopentanone with nitric acid.

$$\begin{matrix} CH_2 - CH_2 \\ | \\ CH_2 - CH_2 \end{matrix} C = O + 3\,[O] \xrightarrow{HNO_3} H_2C \begin{cases} CH_2 - COOH \\ \\ CH_2 - COOH \end{cases}$$

cyclopen tanone   glutaric acid
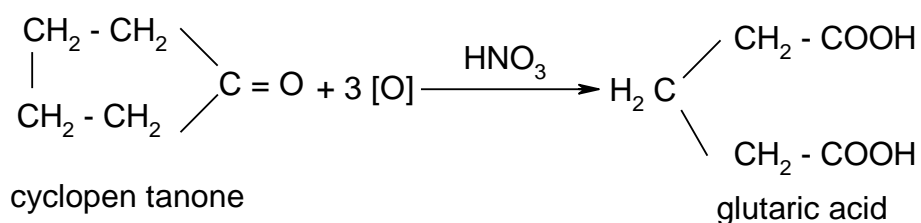
3. By the action of methylene iodide on monosodimalonic ester..

Adipic Acid:

Henane 1,6 – dioic acid, $HOOC – CH_2CH_2CH_2 – COOH$

Preparation:

1. It can be prepared by the reaction of monosodiomalonic ester with ethylene bromide.

2. It is obtained commercially by the oxidation of cyclohexanol prepared form phenol, or cyclohexanone with nitric acid in the presence of SeO_2 catalyst.

phenol   cyclohexanol   cyclohexanone   Adipic Acid
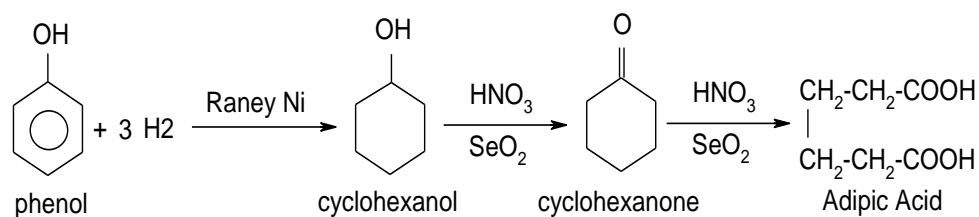
3. It is also prepared on a large scale by the reaction of tetra hydrofuran with carbon monoxide and water.

$$\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix} O + 2\,CO + H_2O \longrightarrow \begin{matrix} CH_2-CH_2-COOH \\ | \\ CH_2-CH_2-COOH \end{matrix}$$
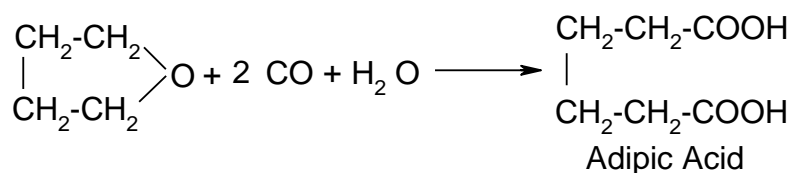
Adipic Acid

4. Now a days adipic acid is prepared by the catalytic oxidation of cyclohexane in two steps. In the first step cyclohexane is converted to cyclohexaone by air oxidation in the presence of cobalt catalyst at $100^{\circ}C$ under a pressure of 150 psi. In the second step the cyclohexanone is oxidised to adipic acid with the help of nitric acid.

Benzene → cyclohexanol → cyclohexanone → Adipic Acid
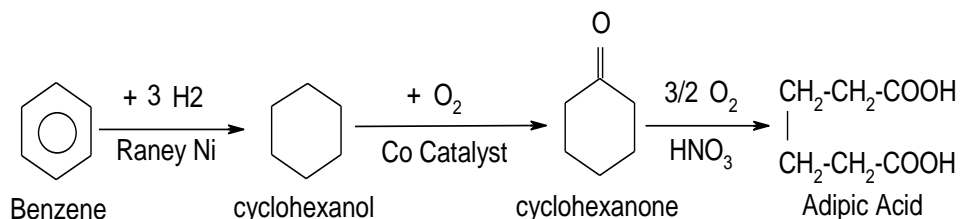
Action of heat on Dicarboxylic Acid:

1. When heated alone, oxalic acid decomposes above its melting point giving formic acid and carbon dioxide.

$$HOOC\text{-}COOH \xrightarrow{\text{190-200}^{\circ}} HCOOH + CO_2$$

formic acid
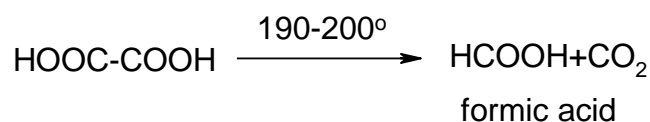
2. When Malonic acid heated to 140 – 150oC or when refluxed in sulphuric acid solution it loses a molecule of CO_2 to produce acetic acid.

$$HOOC\text{-}CH_2\text{-}COOH \xrightarrow{\text{140-150}^{\circ}} CH_3COOH + CO_2$$

malonic acid → acetic acid
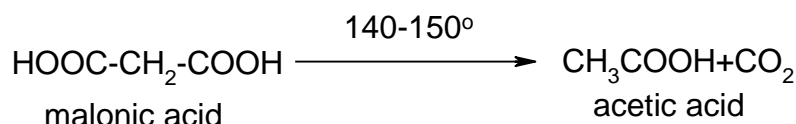
The decarboxylation probably occurs by the following mechanism.

Malonic Acid → Intermediate → Acetic Acid
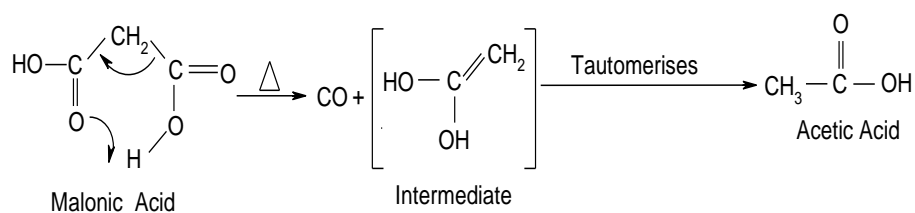
3. When Succinic acid heated above its melting point, succinic acid sublimes largely and the rest being converted into the anhydride.

Succinic anhydride

117
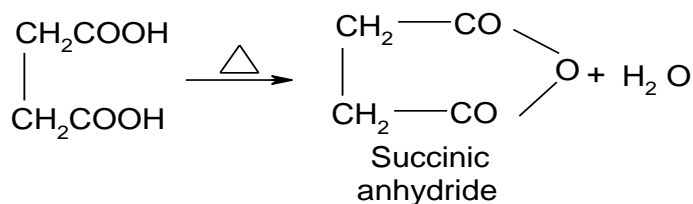
4. Glutaric acid also loses a molecule of water when heated alone, or with anhydride or thionyl chloride.

$$H_2C \underset{CH_2\text{-CO-OH}}{\overset{CH_2\text{-CO-OH}}{<}} \xrightarrow{\triangle} H_2C \underset{CH_2\text{-CO}}{\overset{CH_2\text{-CO}}{<}} O + H_2O$$

glutaric acid   glutaric anhydride
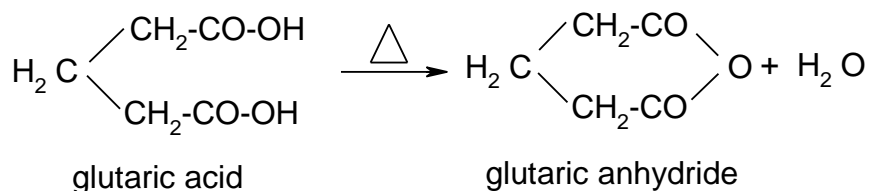
5. Adipic acid when heated in presence of Ba(OH)2, it is converted into cyclopentanone.

$$\begin{array}{c} CH_2\text{-}CH_2\text{-COOH} \\ | \\ CH_2\text{-}CH_2\text{-COOH} \end{array} \xrightarrow[280\text{-}300°]{Ba(OH)_2} \begin{array}{c} CH_2\text{-}CH_2 \\ | \\ CH_2\text{-}CH_2 \end{array}{>}C{=}O + CO_2 + H_2O$$

adipic acid   cyclopentanone
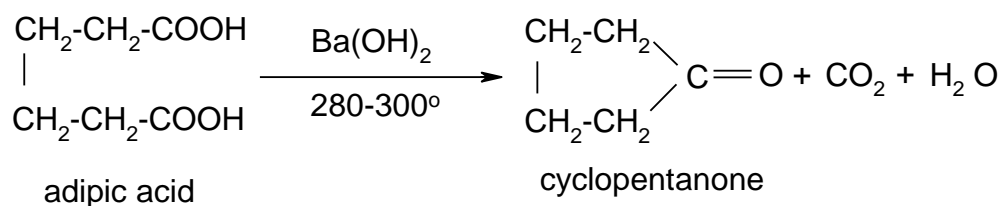
Upon heating with acetic anhydride, it gives linear polymeric anhydride.

$(x+_1)$ HOOC(CH$_2$)$_4$COOH+x(CH$_3$CO)$_2$O $\xrightarrow{\triangle}$

adipic acid   acetic anhydride

$$HOOC(CH_2)_4\overset{O}{\overset{\|}{C}}\text{-O}\left[\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-O-}\right]\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4COOH + 2\ X\ CH_2COOH$$

poly(adipic)anhydride
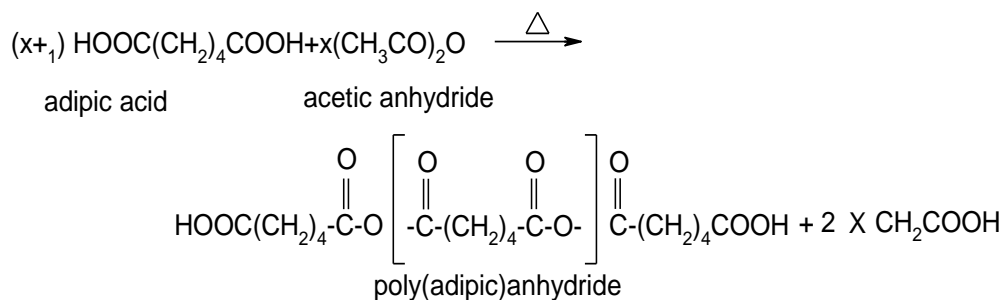
3.3 Reaction Mechanism VII

3.3.1 Mechanism of Esterification Including Trans Esterification:

Esterification:

The process of formation of ester by reacting alcohol with an acid is called esterification.

Mechanism:

Esterification is a reversible reaction.
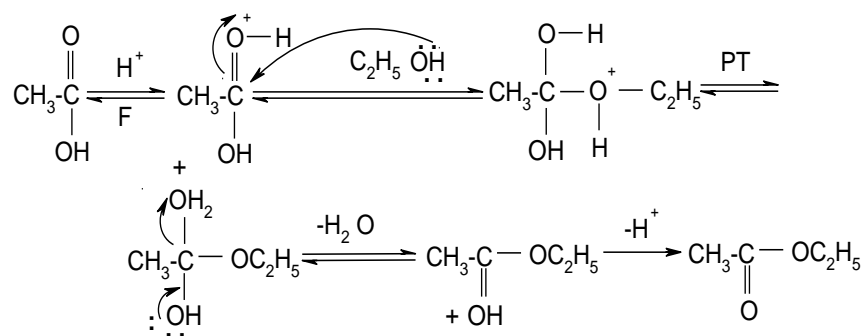
F = Fast, S = Slow, PT = Proton Transfer.

$$C_2H_5OH + ClCOCH_3 \longrightarrow CH_3COOC_2H_5 + HCl$$
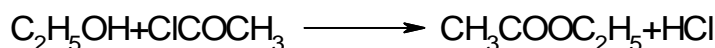
Alcohol react with acyl chloride to form ester.

This is called Acylation.

$$C_2H_5OH + ClCOC_6H_5 \longrightarrow C_6H_5COOC_2H_5 + HCl$$

Benzyl Chloride   ethyl benzonate
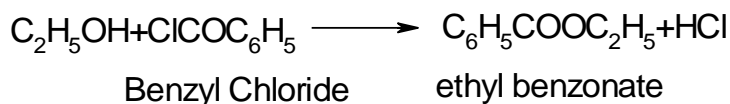
This is called Benzoylation.

Trans Esterification:

When an ester gets refluxed with an alcohol (other than the one used in its preparation) preferably in the presence of a small quantity of acid or sodium alkoxide as catalyst, the original alcohol residue in the ester gets replaced by the new alcohol. This ester interchanges, which is actually alcoholysis (splitting by alcohol) of an ester is called Trans Esterification.

$$CH_3COOC_4H_9 + C_2H_5OH \xrightarrow{C_2H_5ONa} CH_3COOC_2H_5 + C_4H_9OH$$

n butyl acetone   ethyl acetate
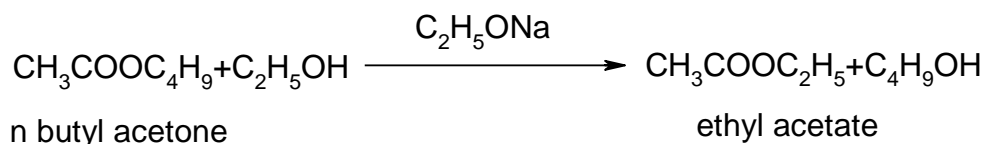
It is generally used for preparing the ester of a higher alcohol (C_4H_9OH) from that of a lower (C_2H_5OH) one. This reaction is called Trans Esterification.

Esterification:

The process of formation of ester by reacting alcohol with an acid is called esterification.

This reaction acid or base are used for the catalysted. AC refers to the acyl – oxygen clevage and AL refers to the alkyl – oxygen clevage and number 1 and 2 refers to unimolecular and bimolecular reaction.

1. Acid catalysed unimolecular acyl – oxygen fission (A_{AC}^1).
2. Acid catalysed bimolecular acyl – oxygen fission (A_{AC}^2).
3. Acid catalysed unimolecular alkyl – oxygen fission (A_{AL}^1).
4. Acid catalysed bimolecular alkyl – oxygen fission (A_{AL}^2).
5. Acid catalysed unimolecular acyl – oxygen fission (B_{AC}^1).
6. Acid catalysed bimolecular acyl – oxygen fission (B_{AC}^2).
7. Acid catalysed unimolecular alkyl – oxygen fission (B_{AL}^1).
8. Acid catalysed bimolecular alkyl – oxygen fission (B_{AL}^2).

Mechanism:

1. **Acid Hydrolysis:**

It is reversible reaction. The reaction involved three step.

i. Hydrogen attack carbonyl oxygen to obtain 1 and 11 structure.
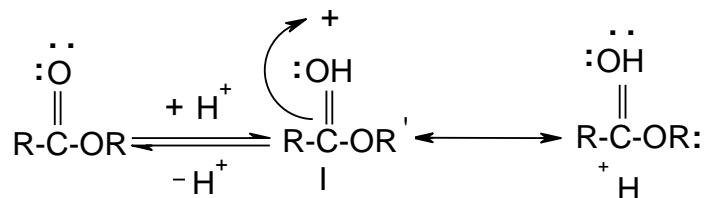
ii. Water molecule involved reaction.
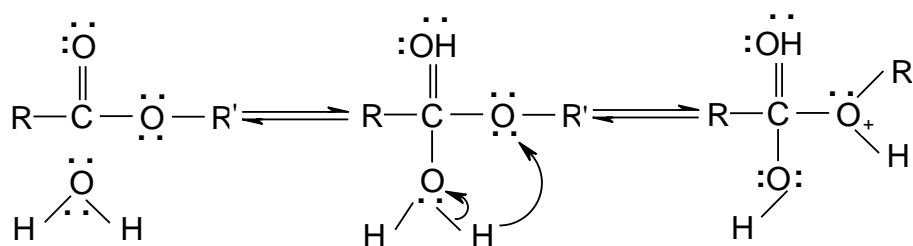
iii. Acid obtained removed from R^3OH.
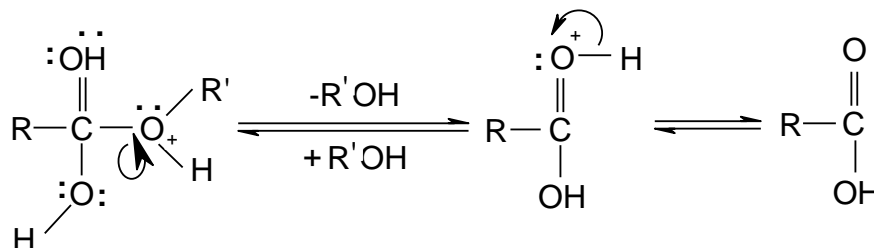
2. Base Hydrolysis:

Mechanism involved in three steps.

i. Hydroxyl ion attack carbonyl oxygen to obtain 1 structure.

ii. 1 gives structure 11 and 111.
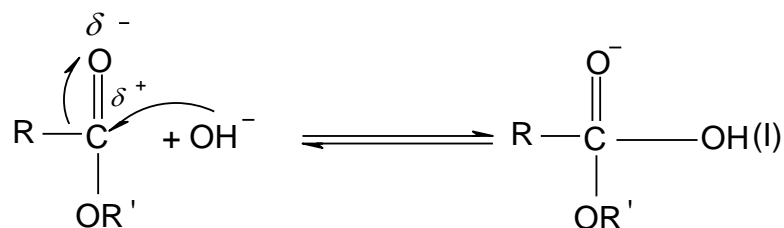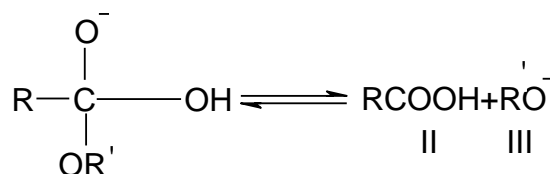
iii. Proton transfer.

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - O - H + RO^- \longrightarrow RCOO^- + R\,OH$$
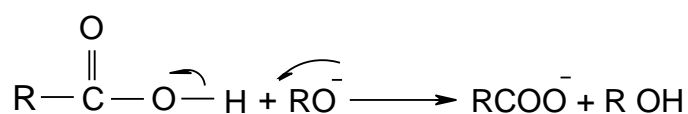
Of these the three esterification mechanisms observed are $A_{AC}{}^1$, $A_{AC}{}^2$, $A_{AL}{}^1$.

3.3.2 Hydrolysis of Esters – Mechanism:

Hydrolysis of acid chloride.

$$CH_3COCl \xrightarrow{\;H_2O\;} CH_3COOH + HCl$$
$$\text{acetyl chloride} \qquad\qquad \text{acetic acid}$$

$$C_6H_5COCl \xrightarrow[\text{dil.NaOH}]{H_2O \text{ (or)}} C_6H_5COOH$$
$$\text{benzyl chloride} \qquad\qquad \text{benzoic acid}$$
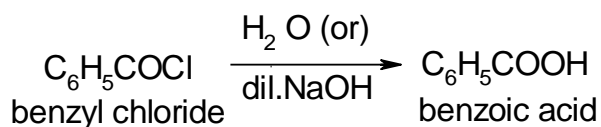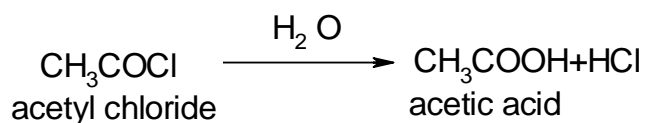
Acetic anhydride slowly hydrolysis of water. But fastly hydrolysis by base.

$$(CH_3\,CO)_2O + H_2O \longrightarrow 2\;CH_3COOH$$
$$\text{acetic anhydride} \qquad\qquad \text{acetic acid}$$

$$(C_6H_5\,CO)_2O + H_2O \longrightarrow 2\;C_6H_5COOH$$
$$\text{benzyl anhydride} \qquad\qquad \text{benzoic acid}$$
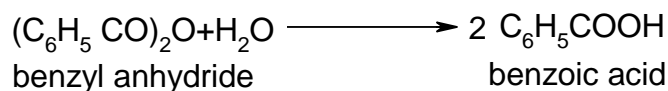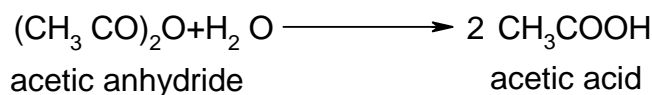
Acid amide slowly hydrolysis of water. But fastly hydrolysis by base.

$$CH_3CONH_2 \xrightarrow[\text{Base}]{H_2O} CH_3COOH + NH_3$$

$$C_6H_5CONH_2 \xrightarrow{\text{acid(or)base}} C_6H_5COOH$$
$$\text{Benzoamide} \qquad\qquad \text{Benzoic acid}$$
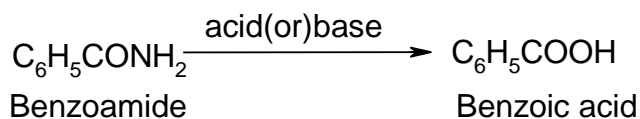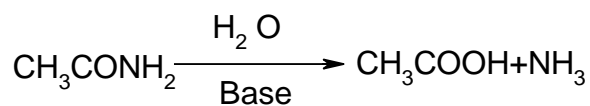
Esters are hydrolysis by acid and base. Ester gives alcohol and acid or its salt. Eg.,

$$CH_3COOC_2H_5 \xrightarrow[\quad H^+ \quad]{\quad H_2O \quad} CH_3COOH + C_2H_5OH$$

ethyl acetate   acetic acid, ethanol

$$CH_3COOC_2H_5 \xrightarrow{\quad [H_2O] \quad} CH_3COONa + C_2H_5OH$$
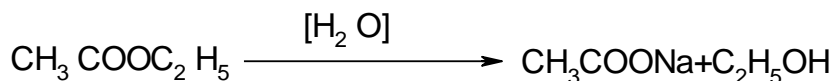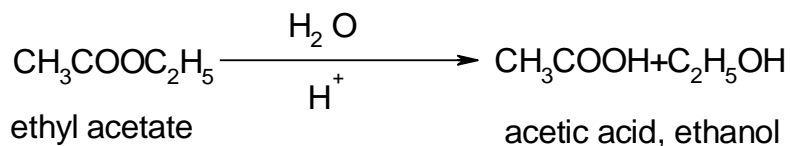
Sponification:

During alkaline hydrolysis of an ester, sodium or potassium salt of the acid is formed. As alkali salts of the higher fatty acids are soaps, alkaline hydrolysis of an ester is called sponification.

$$
\begin{array}{l}
CH_2OCOC_{17}H_{35} \\
| \\
CHOCOC_{17}H_{35} \\
| \\
CH_2OCOC_{17}H_{35}
\end{array}
+ 3\ NaOH \longrightarrow
\begin{array}{l}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+ 3\ C_{17}H_{35}COONa
$$

    fat (or) oil   Base   glycerol   soap
    triglyceride

3.3.4 Malonic Ester:

$$
H_2C \Bigg\langle\!\!\!\!\!\!\!\!\!\!\times
\begin{array}{l}
COOC_2H_5 \\
COOC_2H_5
\end{array}
$$
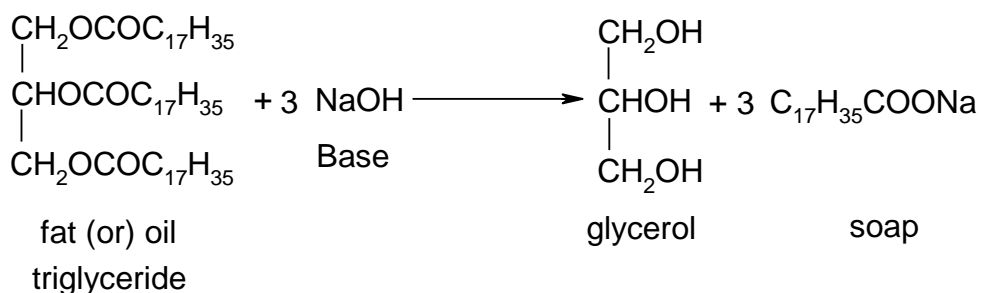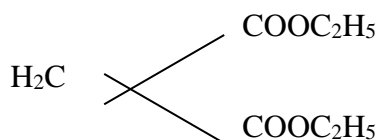
Preparation:

1. From Chloroacetic Acid:

$$ClCH_2COOH \xrightarrow{\quad K_2CO_3 \quad} ClCH_2COOK \xrightarrow{\quad KCN \quad} CNCH_2COOK$$

Chloroacetic   Potassium   Potassium
    Acid   Chloroacetate   Cyanoacetate

$$
\xrightarrow[\quad H_2SO_4 \quad]{\quad C_2H_5OH \quad}
H_2C \Big\langle
\begin{array}{l}
COOC_2H_5 \\
COOC_2H_5
\end{array}
$$
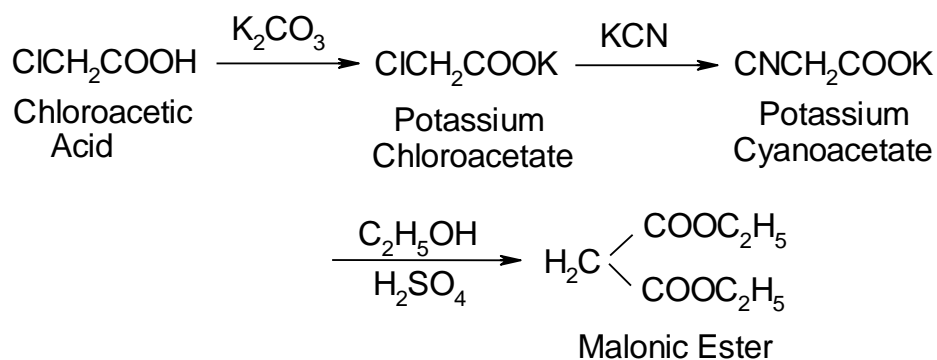
                             Malonic Ester

2. From Methylene Chloride:

Methylene chloride is converted into Methylene cyanide. Methylene cyanide is hydrolysed and then esterified.

$$Cl\text{-}CH_2\text{-}Cl \xrightarrow{NaCN} NC\text{-}CH_2\text{-}CN \xrightarrow[C_2H_5OH]{HCl} H_5C_2OOC\text{-}CH_2COOC_2H_5$$

Diethyl Malonate
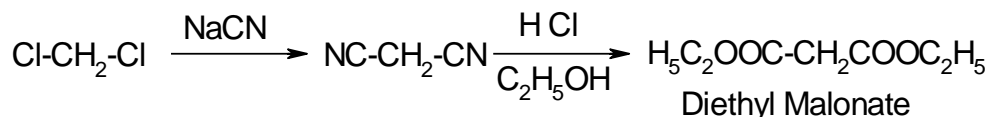
Synthetic Uses:

Active Methylene Group:

Malonic ester contains an active methylene group, i.e., one methylene group is bonded to two CO groups.

$$H_5C_2O - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5$$
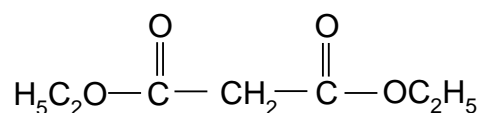
Since the methylene group is between two negative groups which are electron attracting groups, the hydrogen atoms in CH_2 are reactive one of there hydrogen atoms is readily replaced by sodium when treated with alcoholic C_2H_5O Na. At the second step, the other hydrogen is also replaced. Malonic ester is much stronger acid than ordinary esters or other compounds containing a single COOH group.

Starting from malonic ester the following organic compounds can be synthesised.

1. Substituted Malonic Acids:

$$H_2C \begin{matrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{matrix} + NaOC_2H_5 \longrightarrow NaHC \begin{matrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{matrix}$$

Malonic Ester   Sodium Ethoxide

$$\xrightarrow{CH_3I} (CH_3)HC \begin{matrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{matrix} \xrightarrow[-2\ C_2H_5OH]{H_2O\ Acid} (CH_3)HC \begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix}$$

Methylmalonic Ester   Methylmalonic Acid
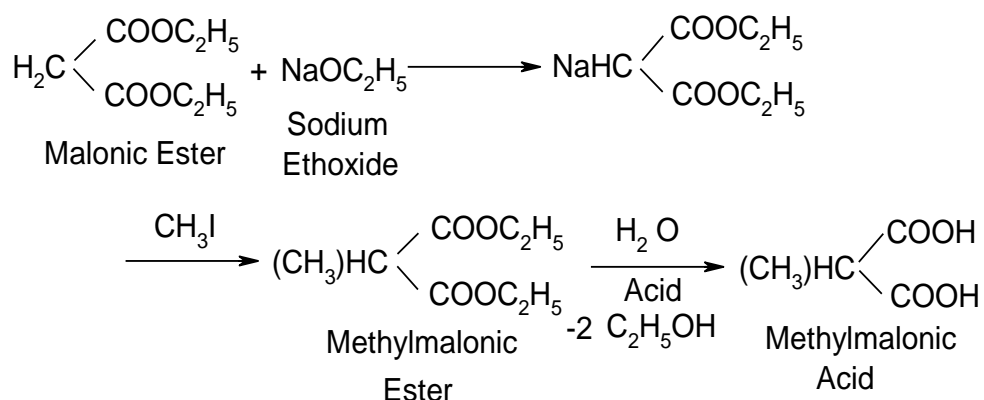
2. Monocarboxylic Acid:

When methyl malonic acid obtained form the above reaction is heated propionic acid is obtained.

i. Malonic acid is heating at 420K to give acetic acid.

$$CH_2(COOH)_2 \xrightarrow{\triangle} CH_3COOH$$

Malonic Acid   Acetic Acid

$$(CH_3)CH \begin{cases} COOH \\ COOH \end{cases} \xrightarrow{CO_2} CH_3CH_2COOH$$

Propionic Acid

ii.

$$CH_3CH_2COOH \xrightarrow[LiALH_4]{[H]} CH_3CH_2CH_2OH$$

n propyl alcohol

iii.

$$NaHC \begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases} \xrightarrow{C_2H_5I} C_2H_5HC \begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases}$$

$$\xrightarrow[acid]{H_2O} C_2H_5HC \begin{cases} COOH \\ COOH \end{cases} \xrightarrow{\triangle} C_2H_5CH_2COOH$$
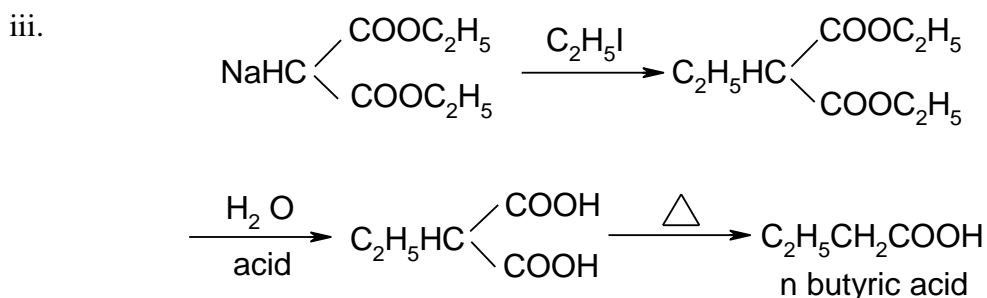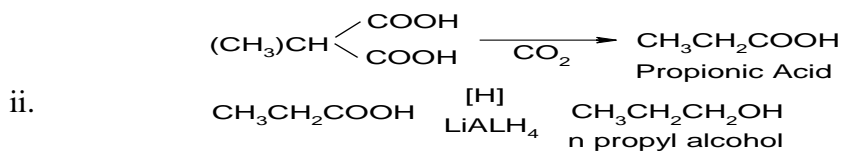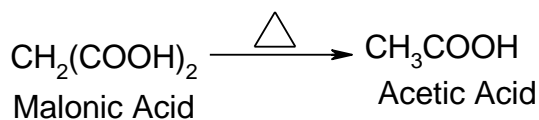
n butyric acid

Note: For preparing Valeric acid (n – Pentanoic acid) use C_3H_7I and Caproic acid (n – hexanoic acid) use C_4H_9I in the first step as shows above.

Similarly dimethyl malonic acid on heating gives iso – butyric acid.

$$(CH_3)_2 C \begin{cases} COOH \\ COOH \end{cases} \xrightarrow[-CO_2]{\triangle} (CH_3)_2 CH\ COOH$$

iso - butyric acid
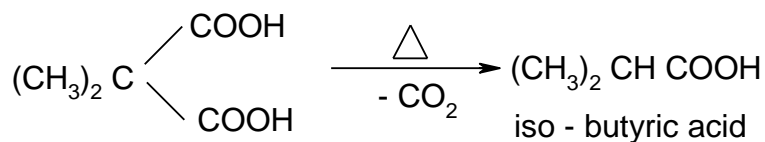
3. Dicarboxylic Acids:

Malonic Ester is treated with ethyl chloroacetate to get succinic acid.

For the preparations of other dicarboxylic acids, viz., succinic acid, Glutaric acid and Adipic acid.

$$H_5C_2OOCCH_2Cl+NaHC \begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases} \xrightarrow{-NaCl} H_5C_2OOCCH_2HC \begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases}$$

ethyl chloroacetate   Sodiomalonic erter

$$\xrightarrow[HCl/H_2O]{KOH/H_2O} \begin{matrix} CH\text{-}(COOH)_2 \\ | \\ CH_2\text{-}COOH \end{matrix} \xrightarrow[-CO_2]{\triangle} \begin{matrix} CH_2\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{matrix}$$

Succinic acid
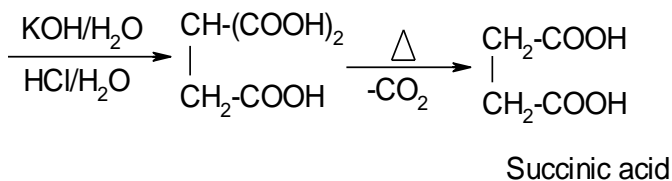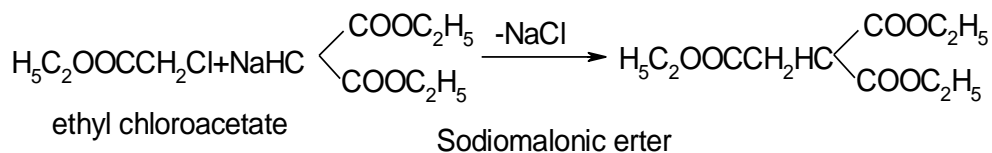
4. Unsaturated Acids:

Malonic ester is treated with an aldehyde and the product obtained is hydrolysed to get the unsaturated acid. For example, malonic ester is treated with acetaldehyde to get crotonic acid.

$$CH_3CHO + H_2C \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \longrightarrow CH_3CH=C \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \xrightarrow[\text{Acid}]{H_2O}$$

$$CH_3CH=C \begin{array}{c} COOH \\ COOH \end{array} \xrightarrow[-CO_2]{\triangle} CH_3C=CHCOOH$$

Crotonic Acid

$$C_6H_5CHO + H_2C \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \longrightarrow C_6H_5CH=C \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array}$$

$$\xrightarrow[\text{Acid}]{H_2O} C_6H_5CH=C \begin{array}{c} COOH \\ COOH \end{array} \xrightarrow[-CO_2]{\triangle} C_6H_5CH=CHCOOH$$

Cinnamic Acid
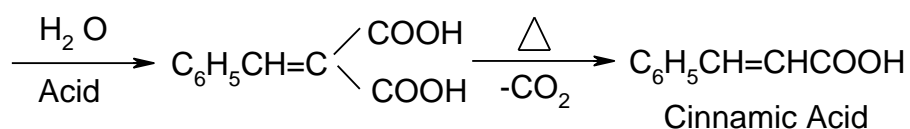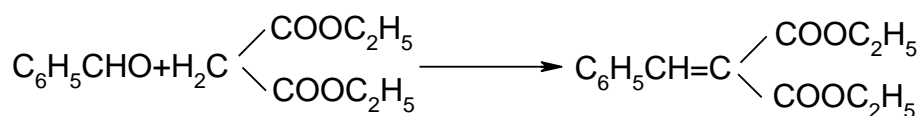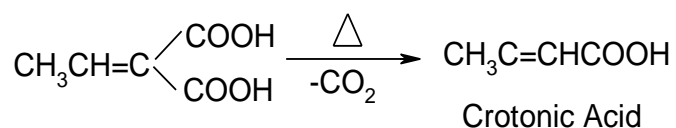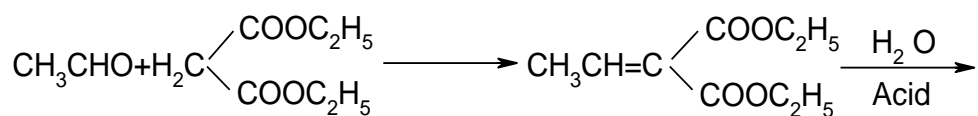
5. Ketonic Acids:

Laevulinic acid may be synthesised as follows.

$$H_5C_2OOCCH_2\text{-}CH_2COCl + NaHC \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \xrightarrow{-NaCl}$$

$$H_5C_2OOCCH_2\text{-}CH_2COHC \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \xrightarrow[HCl/H_2O]{KOH/H_2O}$$

$$HOOCCH_2CH_2COHC \begin{array}{c} COOH \\ COOH \end{array} \xrightarrow[-CO_2]{\triangle} HOOCCH_2CH_2COCH_3$$

Laevulinic Acid

6. Ketones:

$$RHC \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \xrightarrow[CH_3COCl]{Na} CH_3CORC \begin{array}{c} COOC_2H_5 \\ COOC_2H_5 \end{array} \xrightarrow[\text{reflux} -2\,CO_2]{CH_3COOH} CH_3COCH_2R$$

Alkylmalonic Ester
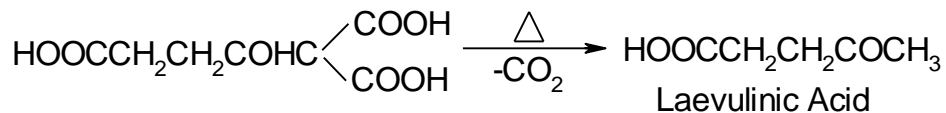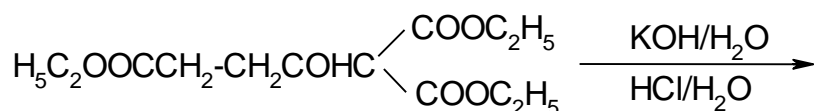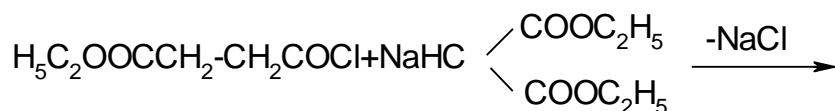
Ketone
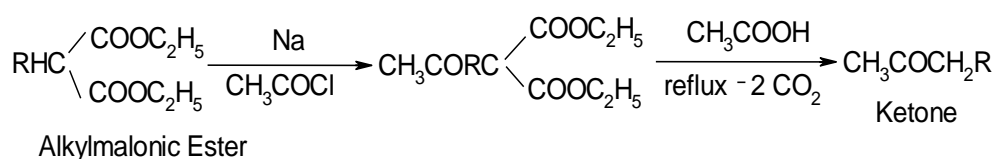
7. Amino Acids:

Glycine may be prepared as follows.

$HON = O + H_2C$ <COOC_2H_5 / COOC_2H_5 ... $\xrightarrow{- H_2O}$ ... $HON = C$ <COOC_2H_5 / COOC_2H_5

Nitrous acid   Malenic erter

$\xrightarrow[- HCl]{Zn / CH_3COOH}$ H_2NHC <COOC_2H_5 / COOC_2H_5 $\xrightarrow[- HCl]{CH_3COCl}$ $CH_3COHNHC$ <COOC_2H_5 / COOC_2H_5

$\xrightarrow[HCl]{KOH / H_2O}$ H_2NHC <COOH / COOH $\xrightarrow[- CO_2]{\triangle}$ H_2NCH_2COOH

Glycine
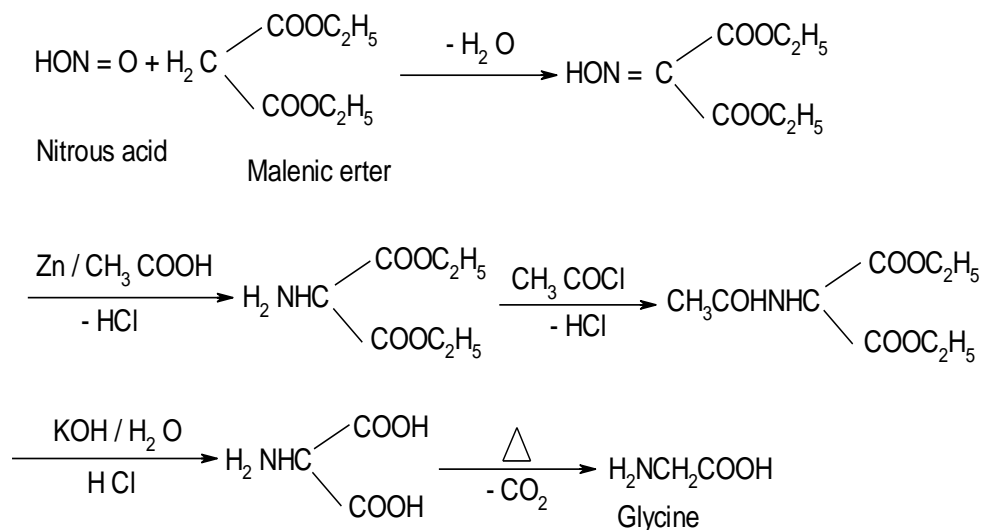
8. Hetrocyclic Compounds:

Diethyl malonate condenses with urea to form malonyl urea barbituric acid.

H_2C <COOC_2H_5 / COOC_2H_5 $+$ HNH | CO | HNH (urea) $\xrightarrow[C_2H_5OH]{C_2H_5ONa}$ CO - NH | | CH_2 CO $+ 2 C_2H_5OH$ | | CO - NH

Malenic erter   urea   Barbituric acid

9. Ring Compounds:

$CH_2 - CH_2Br$ | $CH_2 - CH_2Br$ $+ Na_2C$ <COOC_2H_5 / COOC_2H_5 $\longrightarrow$ $CH_2 - CH_2$ | $CH_2 - CH_2$ C <COOC_2H_5 / COOC_2H_5

Tetramethylene bromide   Disodiomalonic erter

$\xrightarrow{H_2O}$ $CH_2 - CH_2$ | $CH_2 - CH_2$ C <COOH / COOH $\xrightarrow[- CO_2]{\triangle}$ $CH_2 - CH_2$ | $CH_2 - CH_2$ $CHCOOH$

Cyclopentane
Monocarborcylic acid
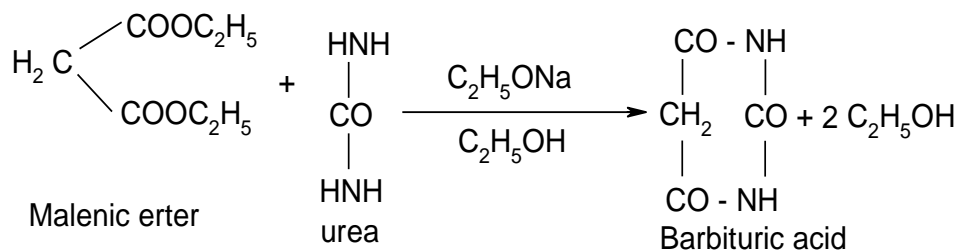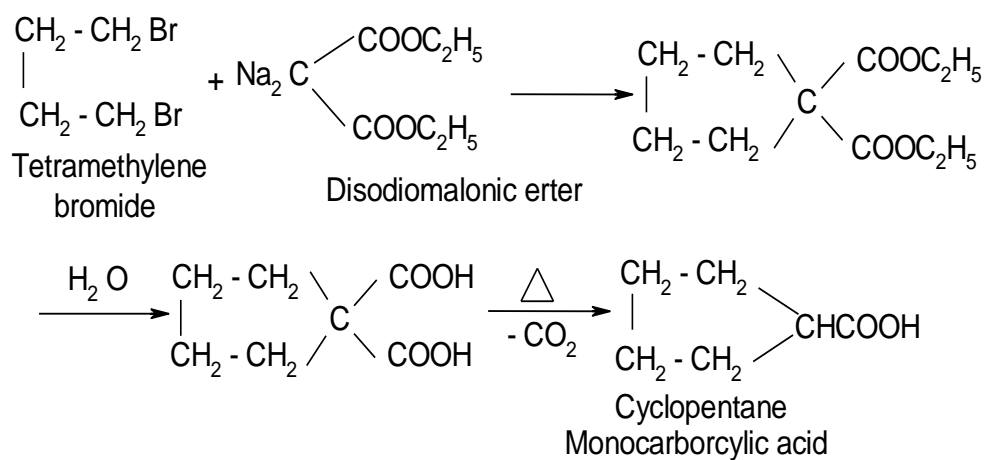
Acetoacetic Ester:

(Ethyl Acetoacetate) $CH_2COCH_2COOC_2H_5$

Preparation:

Acetoacetic ester is prepared by the condensation of two molecules of ethyl acetate in presence of sodium ethoxide as cataslyst. This is a claisen condensation reaction. Claisen condensation reaction is a in which two molecules of an ester having α - hydrogen atoms condense togather to give a ketoester.

$$CH_3COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

ethylacetate   acetoacetic erter

Mechanism:

$C_2H_5O + H - CH_2 COO Et \rightleftharpoons C_2H_5O + H - CH_2 COO Et$

$CH_3 - C + CH_2COOEt \rightleftharpoons CH_3 - C - CH_2COOEt$
(with O, OEt)

$CH_3 - C - CHCOOEt + EtO \rightleftharpoons EtOH + CH_3 C = CHCOOEt$

$\xrightarrow{CH_3COOH} CH_3 C = CHCOOEt \rightleftharpoons CH_3 CH_2 COOEt$
(OH)   (O)
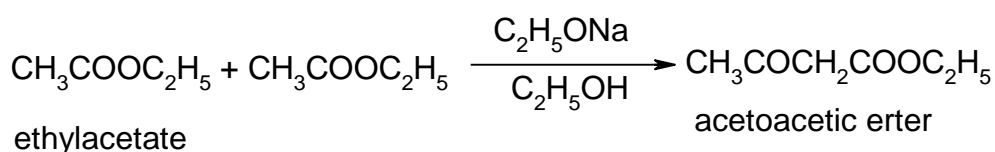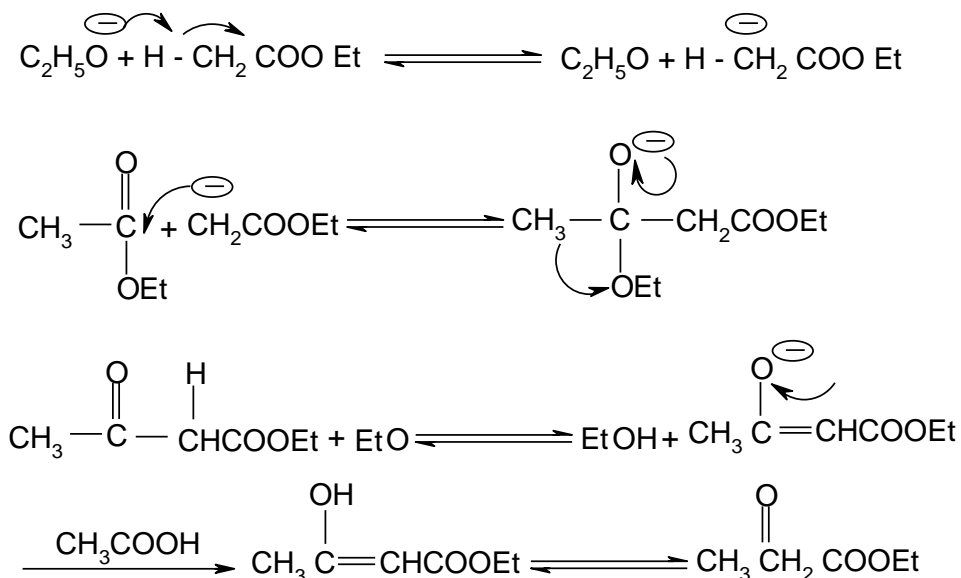
Explanation:

Step 1: OEt abstracts the hydrogen of ethylacetate giving a carbonion.

Step 2: The anion got in step 1 combines with a second molecule of the ester and forms another ion.

Step 3: The ion obtained in step 2 eliminates EtOH and forms the enolate of aceto acetic ester.

Step 4: The enolate abstracts a proton from acetic acid and gives the enol which undergoes tautomeric shift of a proton to give the keto form of the aceto acetic ester.

Synthetic Uses:

Starting from aceto acetic ester the following organic compounds can be synthesised.

1. Alkyl Substituted Esters:

Sodium acetoacetic ester reacts with alkyl halide to give alkyl substituted esters.

$$CH_3COCHCOOC_2H_5 + RI \xrightarrow{- Na\ I} CH_3COCHCOOC_2H_5$$

Na (below first) ; R (below second)

Sodium acetoacetic ester   Mono alkyl acetoacetic ester

$$\xrightarrow{NaOC_2H_5} CH_3COCCOOC_2H_5 \xrightarrow[- Na\ I]{RI} CH_3CO-C-COOC_2H_5$$

Na, R (on central carbon); R above and below C

Dialkyl acetoacetic acid
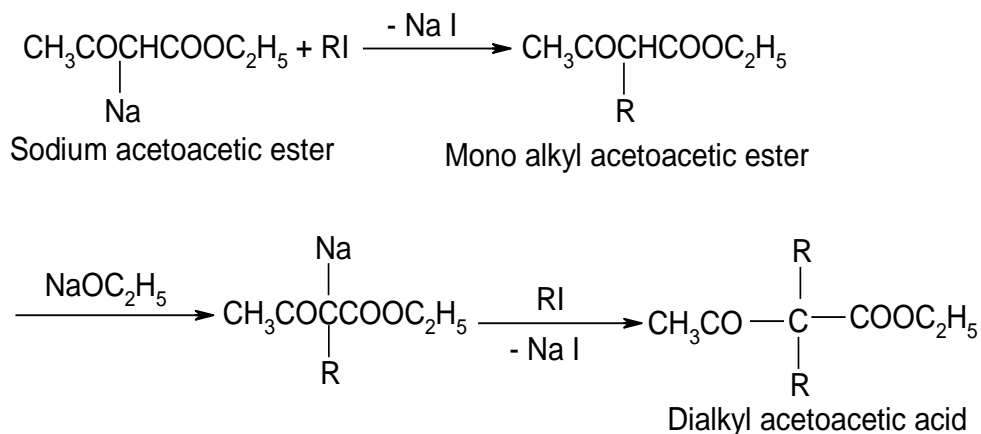
Acetyl Substituted Esters:

Sodio aceto acetic ester reacts with acetyl chloride to give acetyl substituted esters.

$$CH_3COCHCOOC_2H_5 + CH_3COCl \xrightarrow{- Na\ I} CH_3COCHCOOC_2H_5$$

Na (below)   COCH₃ (below)

Sodium acetoacetic ester

$$\xrightarrow[H^+]{H_2O} CH_3COCH_2COCH_3 + C_2H_5OH + CO_2$$

acetyl acetone
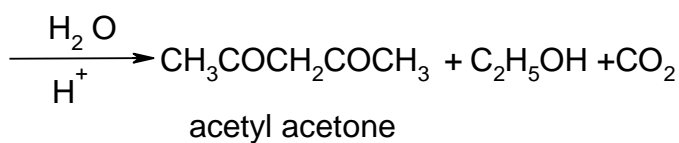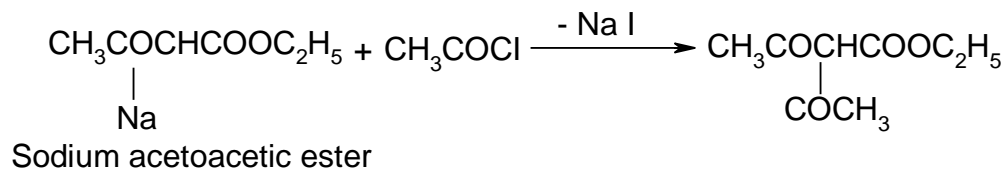
3. Ketone:

When acetoacetic ester is heated with dilute HCl it undergoes hydrolysis to give a ketone. This type of hydrolysis which yields a ketone is called ketonic hydrolysis.

$$CH_3 - CO - CH_2 - CO - O - C_2H_5 \xrightarrow{H_2O} CH_3 - CO - CH_3 + C_2H_5OH + CO_2$$

acetoacetic ester   Acetone
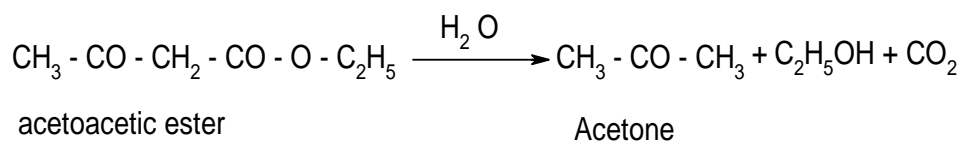
(Acetone may be reduced catalytically to get isopropyl alcohol).

Similarly mono and dialkyl substituted acetoacetic esters on "Ketonic Hydrolysis" give ketones of the type CH_3COCH_2R and CH_3COCHR_2.

i.
$$CH_3COCH-CH_3 | CO | O -O | H -C_2H_5 \longrightarrow C_2H_5OH + CO_2 + CH_3COCH_2CH_3$$

aceto acetic ester

Ethyl methyl ketone (Butanone)

ii
$$CH_3COCH-C_2H_5 | H | CO | O -O | H -C_2H_5 \longrightarrow CH_3COC_3H_7 + C_2H_5 + CO_2$$

aceto acetic ester

Methyl propyl ketone

iii.
$$CH_3COCH \genfrac{}{}{0}{}{CH_3}{CH_3} | CO | O -O | H -C_2H_5 \longrightarrow CH_3COCH \genfrac{}{}{0}{}{CH_3}{CH_3} + C_2H_5OH + CO_2$$

aceto acetic ester

methyl isopropyl Ketone

iv.
$$CH_3COC-CH_3 | H | CO | O -O | H -C_2H_5 \longrightarrow CH_3 - CO - CH - CH_2 - CH_3 | CH_3 + C_2H_5OH + CO_2$$

aceto acetic ester

3 - methyl pentan -2- one

4. Fatty Acids:

When acetoacetic ester is heated with concentrated KOH and then acidified with HCl, an acid is formed. Since an acid is formed during hydrolysis, it is called "Acid Hydrolysis".

i $CH_3 - CO \mid CH_2 - CO \mid OC_2H_5$ $\xrightarrow{2\ H_2O}$ $2\ CH_3COOH + C_2H_5OH$

       $HO|H$ $HO|H$ acetoc acid
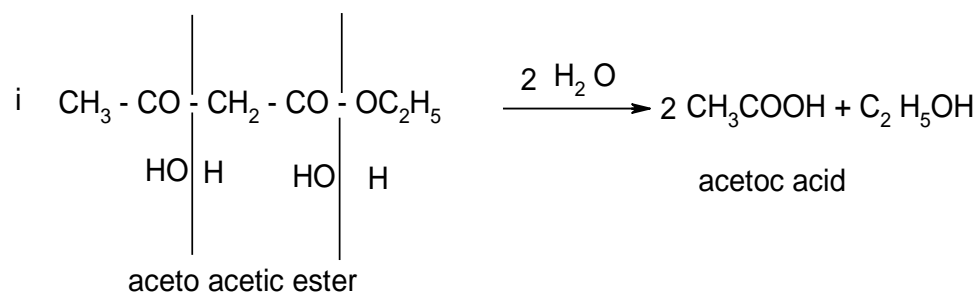
aceto acetic ester

When alkyl derivatives of a aceto acetic ester are subjected to acid hydrolysis, acids of the type RCH_2COOH and $CHCOOH$ are obtained.

ii $CH_3 - CO - CHCO - OC_2H_5$ $\longrightarrow$ $CH_3COOH + C_2H_5CH_2COOH + C_2H_5OH$

              $|$
              C_2H_5

                                                              acetic acid   n-butyric acid

       $OH|H$ $HO|H$

ethyl aceto acetic ester

iii $CH_3 - CO - \overset{\overset{\displaystyle CH_3}{|}}{C} - CO - O- C_2H_5$ $\longrightarrow$ $CH_3COOH + C_2H_5OH + \overset{H_3C}{\underset{H_3C}{>}}CHCOOH$

                    $|$
                    C_2H_5

                                                                            Isobutyric acid

       $OH|H$ $HO|H$

dimethyl aceto acetic ester

$CH_3 - CO - CH_2 - COOC_2H_5$ $\xrightarrow[\text{NaOEt} / (CH_3)_2\ CHI]{\text{NaOEt} / CH_3\ I}$

$CH_3 - CO - \overset{\overset{\displaystyle CH_3}{|}}{C} - CO - O- C_2H_5$ $\longrightarrow$ $CH_3 - CH - CH - COOH + CH_3COOH + C_2H_5OH$

                    $|$ $|$ $|$
                    $CH(CH_3)_2$ CH_3 CH_3

       $OH|H$

2, 3, dimethyl butyric acid
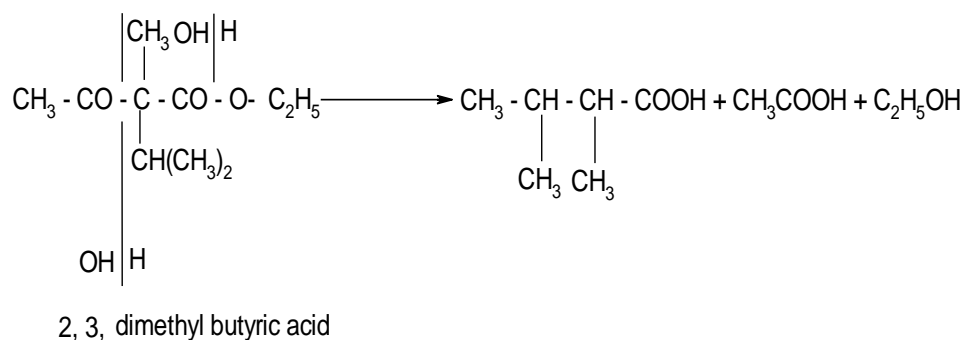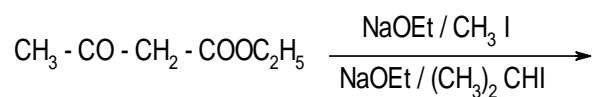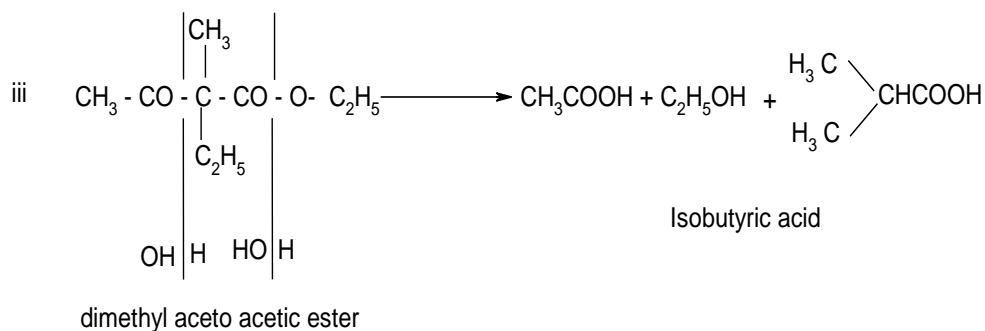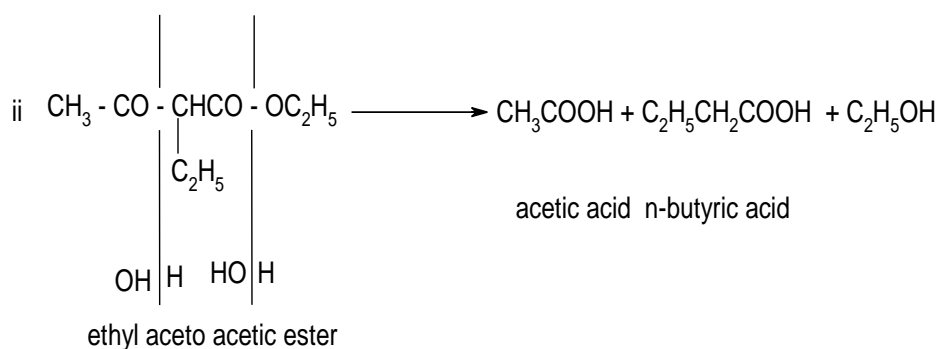
5. Dicarboxylic Acids:

Refer the preparation of dicarboxylic acids.

$$CH_3 - CO - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Na}{|}}{C}} - COOC_2H_5 \quad + \quad Cl - \overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - COOC_2H \longrightarrow$$

Sodia methyl acetoacetic ester α – chlora propionic ester

$$CH_3 - CO - \overset{CH_3}{\underset{|}{\overset{|}{C}}} - CO - OC_2H_5 \xrightarrow[H2O]{[H]^+}$$

$$CH_3 - \overset{}{\underset{|}{CH}} - COOH \quad + CH_3COOH + {}_2C_2H_5OH$$
$$CH_3 - CH - COOH$$

Dimethyl succinic acid

i $CH_3 - CO - CHCO - OC_2H_5 \longrightarrow CH_3COOH + CH_3 CO_2 COOH_5 + C_2H_5OH$

CH₃

OH H   HO H

acetic acid propanoind acid

methyl aceto acetic ester
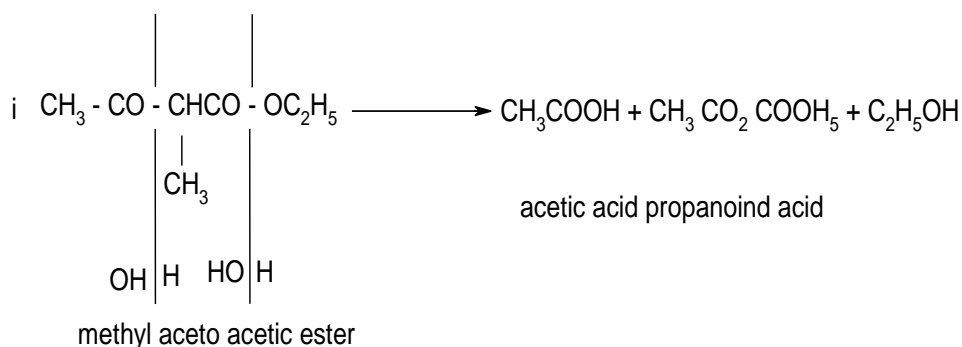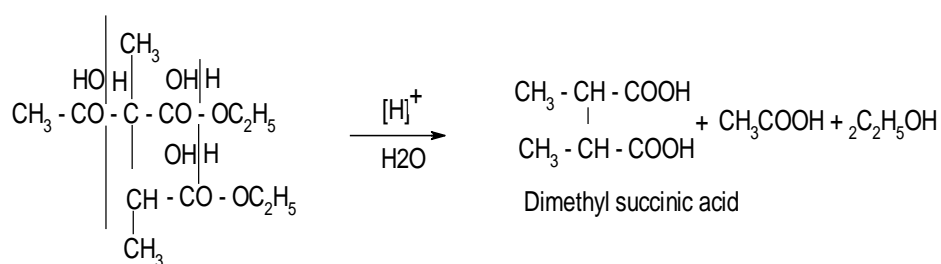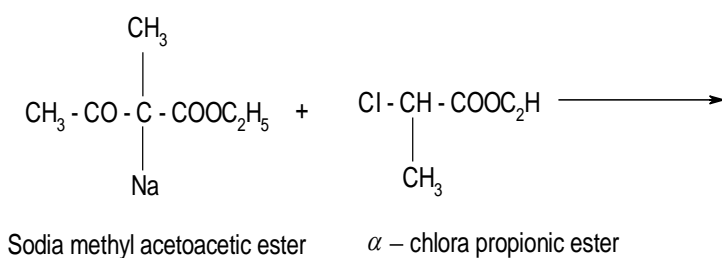
6. Ketonic Acids:

Laevulic acid is also called Lavulinec acid.

$$CH_3CO\overset{}{\underset{\underset{\displaystyle Na}{|}}{C}}HCOOC_2H_5 \quad + \quad ClCH_2COOC_2H_5 \longrightarrow$$

Sodio acetoacetic ester   Ethyl chloroacetate

$$CH_3COCHC_2H_5 - CO - OC_2H_5 \xrightarrow[\text{Hydrolysis}]{\text{Ketonic}} CH_3COCH_2CH_2COOH + C_2H_5 + CO_2$$

OH H

CH₃ - CO - OC₂H₅

Laevulic acid

131
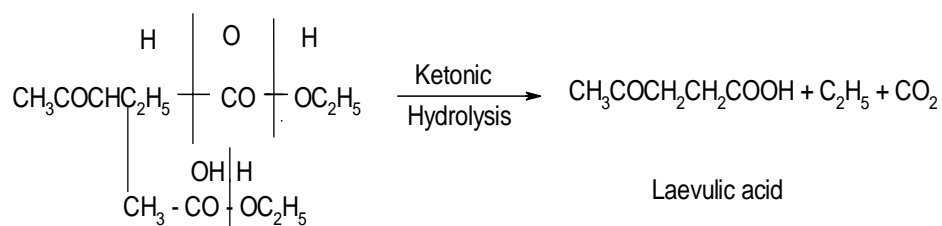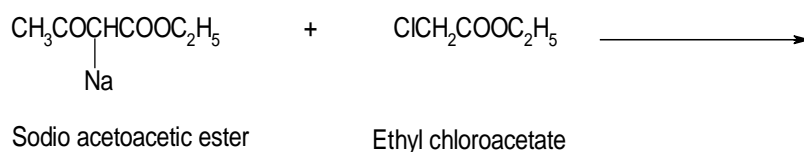
7. α, β Unsaturated Acids:

Acetoacetic ester undergoes knoevenagel reaction to give $\alpha, \beta-$ unsaturated acids. Knoevenagel reaction is one in which an aldehyde reacts with a compound containing reactive methylene group in the presence of an organic base like Pyridine. Both malonic ester and acetonic ester contain reactive methylene group. So they give this reaction.

$$CH_3CHO + H_2\overset{\overset{\displaystyle OC-CH_3}{|}}{=}C-COOC_2H_5 \xrightarrow{\text{Pyirdine}} CH_3-CH=\overset{\overset{\displaystyle OCCH_3}{|}}{C}-COO\,C_2H_5$$

$$\xrightarrow{\text{Acid hydrolysis}} CH_3-CH=CH\,COOH \quad + \quad CH_3CHOOH + C_2H_5OH$$

Crotonic acid
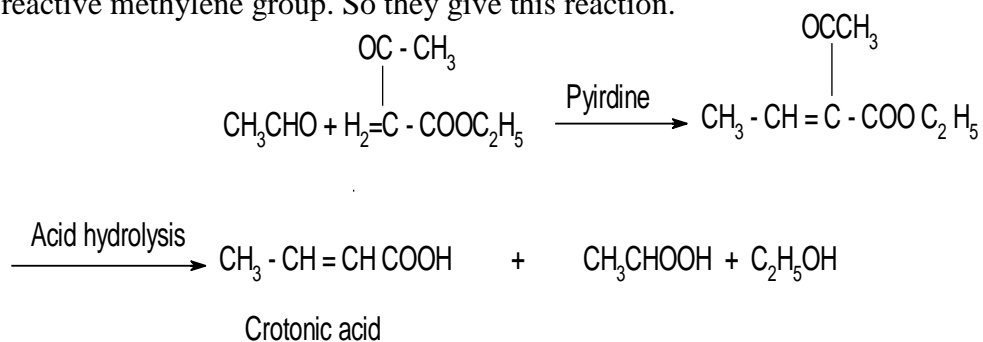
8. Diketones:

Acetoacetic ester is treated with acetyl chloride in presence of magnesium and the product is subjected to ketonic hydrolysis to get acetonyl acetone, diketone.

$$CH_3COCH_2COOC_2H_5 \ + \ CH_3COCl \xrightarrow{Mg} CH_3-CO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3CO}{|}}{CH}}\overset{\overset{\displaystyle O}{|}}{\underset{\displaystyle |}{CO}}\overset{\overset{\displaystyle H}{|}}{OC_2H_5}$$

$$\xrightarrow[\text{hydrolyris}]{\text{Ketonic}} CH_3COCH_2COCH_3 \ + \ CO_2 \ + \ C_2H_5OH$$

Acetonyl

9. Hetrocyclic Compounds:

$$\overset{\displaystyle NHH}{\underset{\displaystyle NHH}{\overset{|}{\underset{|}{CO}}}} \quad \overset{\displaystyle H_5C_2O-C=O}{\underset{\displaystyle OH-C-CH_3}{\overset{|}{\underset{\|}{CH}}}} \quad \overset{\displaystyle HN \!-\! CO}{\underset{\displaystyle HN \!-\! C \!-\! CH_3}{\overset{|\quad|}{\underset{|\quad\|}{CO\quad CH}}}} + \ H_2O + C_2H_5OH$$

Urea   Enolic form   4 - Methyl uracil
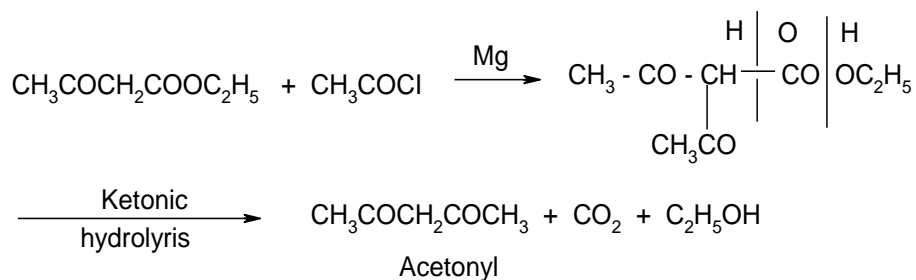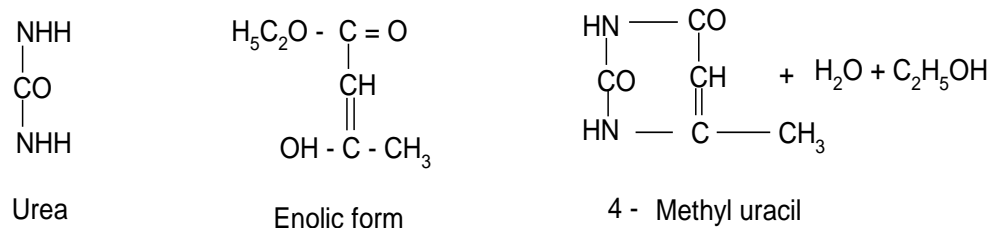
10. Hydrocarbons:

On electrolytic reduction acetoacetic ester gives hydrocarbon.

$$CH_3COCH_2COOH_2COOC_2H_5 \xrightarrow{\hspace{2cm}} CH_3CH_2CH_2CH_3$$

n-Butane
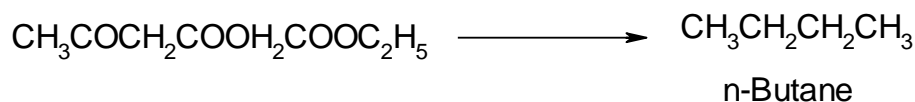
Characteristic of reactive methylene group:

When a methylone group –CH$_2$ is linked by two electron with drawing groups, the hydrogen atoms bonded to carbon become acidic and reactive. The compounds containing such methylene groups are referred to as "Acive methylene Compounds." Some importants compounds of this type are.

$$CH_3 - C - CH_2 - C - OC_2H_5 \qquad H_5C_2O - C - CH_2 - C - OC_2H_5$$

Active methylene groups
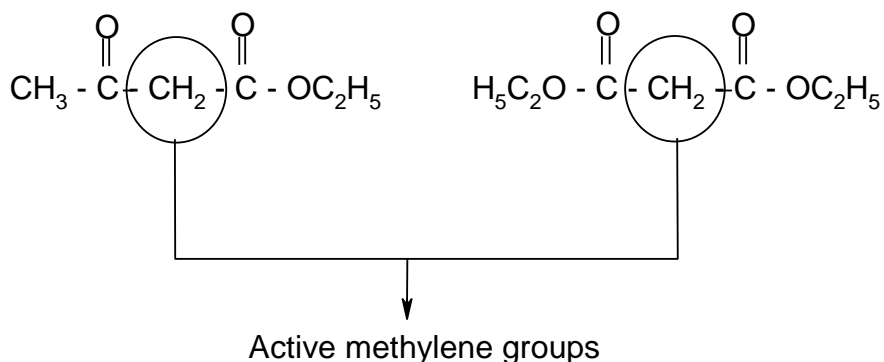
The enchanced activity of the active methylene groups is attributed to the influence of the adjacent electron with drawing groups and the formation of resonance stabilized carbonion. The carbon-hydrogen bonds of the methylone group are thus weaken so as to make its H atoms acidic and reactive. In the presence of a base such as ethoxide ion, carbonion is formed as follows.

The carbonion so generated acts as a strong nucleophilc agent and participates in quite a number of S$_N$^{2} reaction.

TAUTOMERISM

This is the type of information in which the isomers are inter-convertible under normal conditions. (tauto-same:meres-part),A tautomerism substance is a mixture of two mutually interconvertible isomers called tatomers. It one form is to be changed another a definite amount energy must be supplied to take away from the substance.It this amount of energy is very small than the transformation will be quite easy. The result in an eqlibrium mixture of the tautomers. Since the tautomerism change is rapid and reversible, the separation of the mixture into tautomerism is difficult. Tautomeric change is possible only in the liquid state on solution or in the gaseous state.

$$Z - C - C - OC_2H_5 + OC_2H_5 \longrightarrow Z - C - C - OC_2H_5 + C_2H_5OH$$

H   Ethoxide ion   Carbanion
Active Methylene Compound   Ethyl alcohol
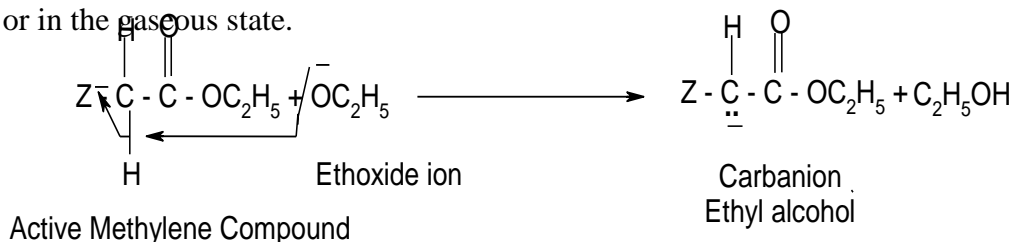
Type of Tautomerism:

Various compounds that exhibit tautomerism can be classified follows.

1. Open – system of tautomerism or Ionotropy.
2. Ring – chain tautomerism.
3. Valence tautomerism.

Open system of Tautomerism or Ionotropy:

In this type of tautomerism, both tautomers are open chain substances. This can be further sub – divided into two groups.

a. Cationotropy

b. Anionotropy

a. Cationotropy:

Tautomerism is referred to as cationotropy when atoms or groups of atoms shifts as cations. A large majority of carer of cationotropy however is prototropy wherein protons are involved.

i. For example prototropy in case of keto – enol tautomerism.

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2COOC_2H_5 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CHCOOC_2H_5$$

Keto form   Enol form
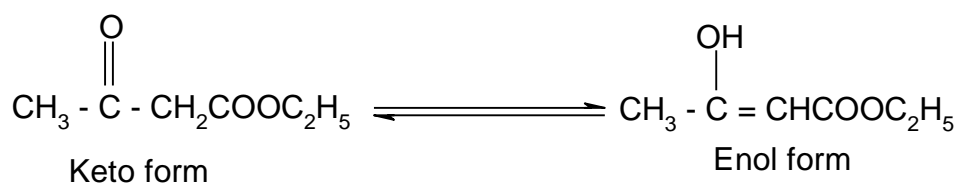
ii. Another type of protogropy involves the amide – imido tautomerism of the amides of Carbonylic acids.

Amide form   Jmido form
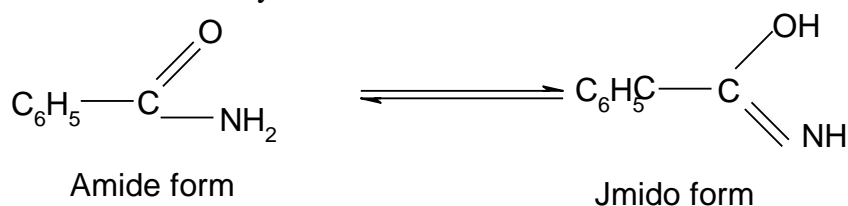
iii. Primary and Secoundary nitroparaffins are also found to exist mainly as nitro compounds in equlibrium with small proporations of aciisomerism. This is called nitro – aci nitro tautomerism.

Nitro form   Aci - nitro form

b. Aninotropy:
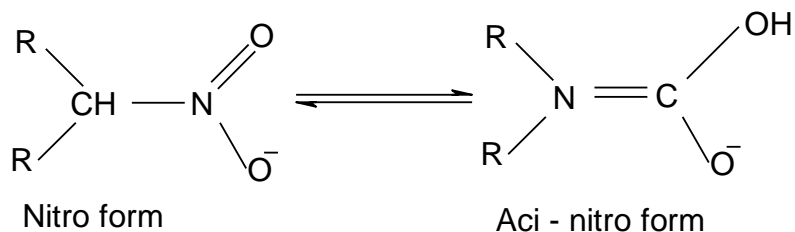
Tautomerism is referred to as anisotropy when atoms or groups of anisotropy in following.

$$CH_3 - CH = CH - CH_2 Cl \rightleftharpoons CH_3 - CHCl - CH = CH_2$$

Crotyl Chloride   Methylvinyl Carbinyl Chloride
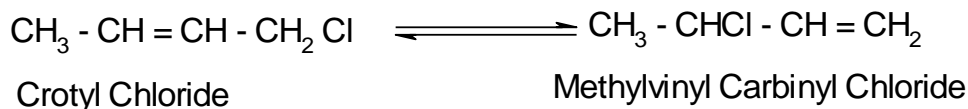
2.Ring – chain Tautomerism:

In this of tautomerism, one form is cyclic and other is acyclic (open – chain). The two forms of this type differ in the positions of either a proton or anionic atom   or group. This type of tautomerism is found in carbohydrates.

3.Valence tautomerism:

Keto – End Tautomerism:

When a methylene group is attached to two carbonyl groups, the hydrogen atom migrates to one or other carbonyl group. Thus enol form arises. This type of tautomerism is called the Keto – Enol tautomerism. In this tautomerism a hydrogen atom migrates from a carbon atom to oxygen atom. The Keto – Enol tautomerism in acetoacetic ester is shown below.

$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH - \overset{\overset{\displaystyle O}{\|}}{C} - OC_2H_5$$

Keto - form   Enol - form
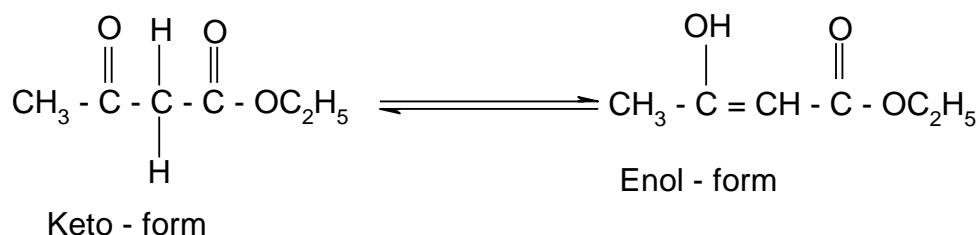
Keto end tautomerism of acetoacetic ester:

Acetoacetic ester behaviou as though it is an enol and also a Ketone in its reactions. We say this is due to tautomerism. Thus if a compounds behaves as a Ketone and as an enol we can conclude that there is tautomerism. Since there is an equilibrium during testing the compound would behave as though it consists of enol or Keto form only.

Acid and base catalysed mechanism:

The Keto – enol tautomerism of acetoacetic ester is catalysed both by acids and base.

1. Acid catalysed Mechanism:

$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - \overset{\overset{O}{\|}}{C} - OC_2H_5 + H^+ \longrightarrow$$

Keto - form

$$H - \overset{+}{O} \searrow H \quad \overset{\overset{O}{\|}}{C}$$
$$CH_3 - \overset{\overset{}{C}}{C} - \overset{|}{C} - \overset{}{C} - OC_2H_5$$
$$\overset{|}{H}$$

$$\longrightarrow \quad H - O \quad H \quad \overset{O}{\|}$$
$$CH_3 - \overset{|}{C} - \overset{|}{C} - C - OC_2H_5$$

Keto - form

2.Base catalysed Mechanism:

$$CH_3 - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{C} - \overset{\overset{O}{\|}}{C} - OC_2H_5 + OH^- \xrightarrow[- H_2O]{- H^+} CH_3 - \overset{\overset{O}{\|}}{C} - \overset{\overline{C}}{\underset{\overset{|}{H}}{C}} \quad C - OC_2H_5$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - \overset{\overset{|}{\overline{C}}}{\underset{\overset{|}{H}}{C}} - \overset{\overset{O}{\|}}{C} - OC_2H_5 \longrightarrow CH_3 - \overset{\overset{-O}{|}}{C} = \overset{}{\underset{\overset{|}{H}}{C}} - \overset{\overset{O}{\|}}{C} - OC_2H_5$$

Keto - form

$$CH_3 - \overset{\overset{-O}{|}}{C} = \overset{}{\underset{\overset{|}{H}}{C}} - \overset{\overset{O}{\|}}{C} - OC_2H_5 + OH^+ \longrightarrow CH_3 - \overset{\overset{H}{|}}{C} = \overset{}{\underset{\overset{|}{H}}{C}} - \overset{\overset{O}{\|}}{C} - OC_2H_5$$

Enol - form
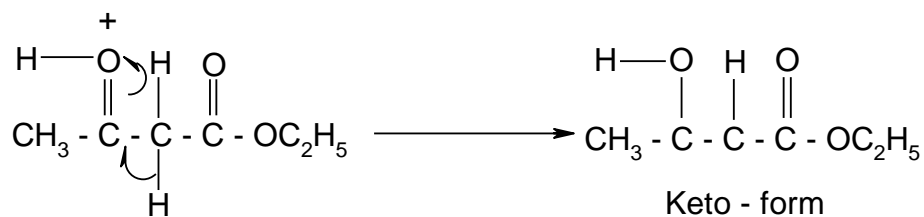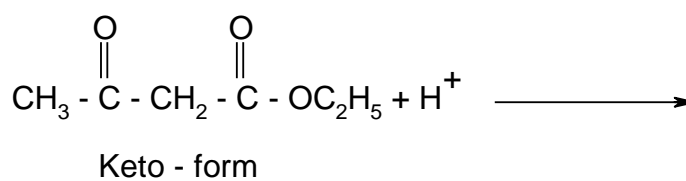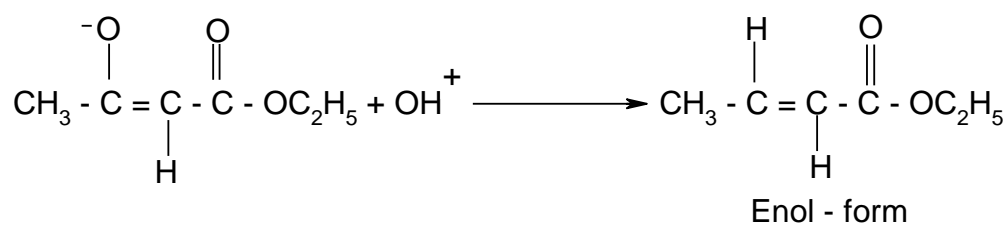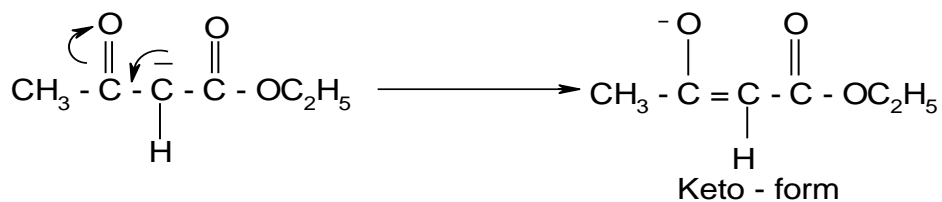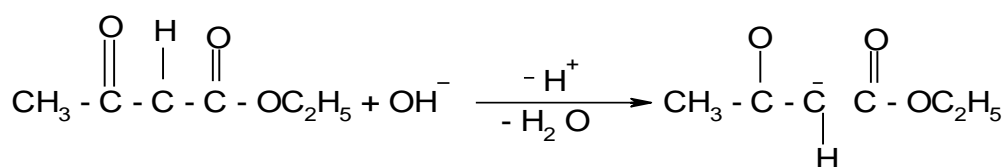
Reactins in favour of Keto from:

1. Addition reactions:

It gives addition compounds with HCN and $NaHSO_3$

$$CH_3 - \overset{\overset{\text{O}}{\|}}{C} - CH_2\ COOC_2H_5 + HCN \longrightarrow CH_3 - \underset{\underset{\text{CN}}{|}}{\overset{\overset{\text{OH}}{|}}{C}} - CH_2COOC_2H_5$$

Aceto acetic ester   Cyanohydrin

$$CH_3 - \overset{\overset{\text{O}}{\|}}{C} - CH_2\ COOC_2H_5 + NaHSO_3 \longrightarrow CH_3 - \underset{\underset{\text{SO}_3\text{ Na}}{|}}{\overset{\overset{\text{OH}}{|}}{C}} - CH_2COOC_2H_5$$

Aceto acetic ester   Bisulphite Compound
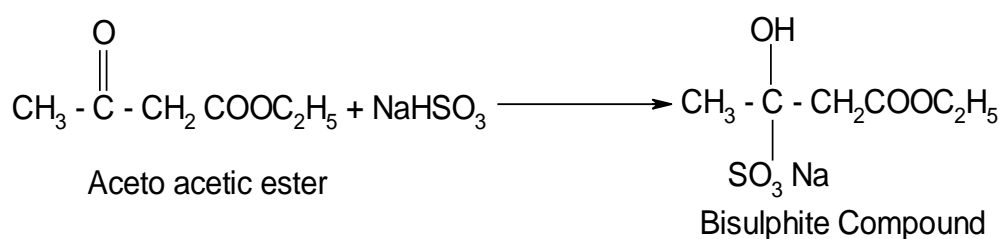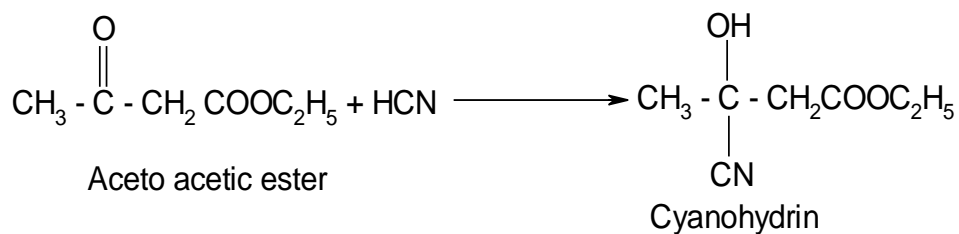
2. Condensation reaction:

It gives condensation product with hydroxylamine and phenylhydrazine.

i

Oxime

Methyliso - oxazolone

ii.

Acetoacetic ester

3. Methyl phenyl pyrazolone
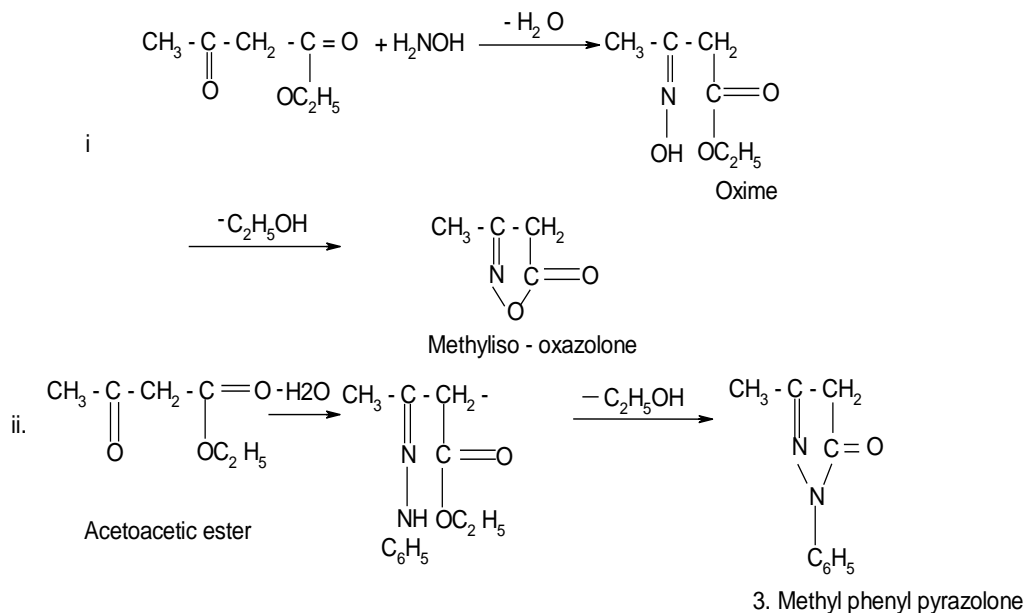
3. Reduction:

Acetoacetic ester on reduction with sodium amalgam gives ethyl β - hydroxybutyrate.

$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - CH_2 - COOC_2H_5 + 2H \xrightarrow[\text{H}_2\text{O}]{\text{Na / Hg}} CH_3CHOCH_3COOC_2H_5$$

Acetoacetic ester   Ethyl - β - hydroxy butyrate
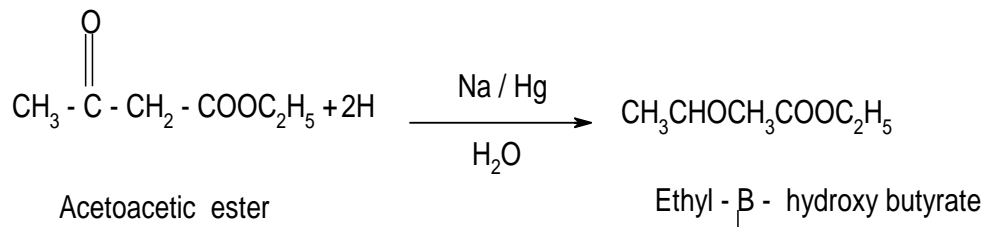
Reduction with LiAL H_4 gives 1, 3 – butanediol

$$CH_3 - \overset{\overset{\textstyle O}{\|}}{C} - CH_2 - COOC_2H_5 + 6H \xrightarrow{\text{LiAlH}_4} CH_3CHOHCH_2CH_2OH$$

Acetoacetic ester   1,3 - butanediol
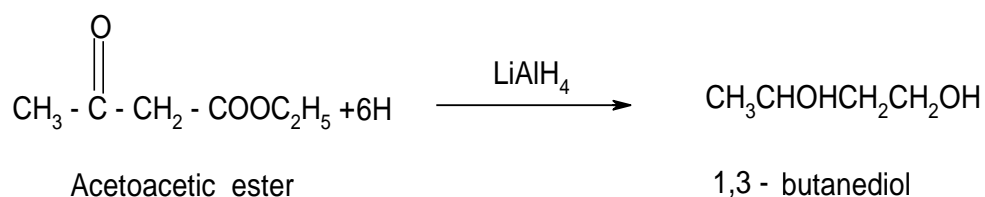
4. Ketonic hydrolysis:

As we have seen earlier Ketonic hydrolysis yields ketones.

Reaction in favour of end form

1. Formation of sodium salt:

The hydrogen of the hydroxy group of the ethanol form of acetoacetic ester is weakly acidis. Hence it reacts with alkalies to gives salts.

$$CH_3 - \overset{\overset{\textstyle OH}{|}}{C} = CH - COOC_2H_5 \xrightarrow[-\text{H}_2\text{O}]{\text{NaOH}} CH_3 - \overset{\overset{\textstyle ONa}{|}}{C} = CHCOOC_2H_5$$
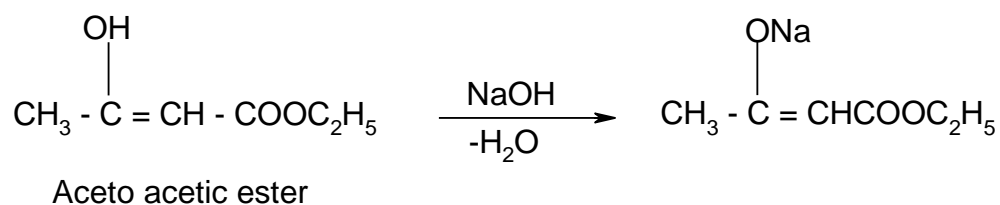
Aceto acetic ester

2. With ammonia:

Acetoacetic ester reacts with ammonia to from β - aminoethylcrotonate.

$$CH_3 - \overset{\overset{\textstyle OH}{|}}{C} = CH - COOC_2H_5 \xrightarrow[-\text{H}_2\text{O}]{\text{NH}_3} CH_3 - \overset{\overset{\textstyle NH_2}{|}}{C} = CHCOOC_2H_5$$

Aceto acetic ester β - Aminoethyl crotonate
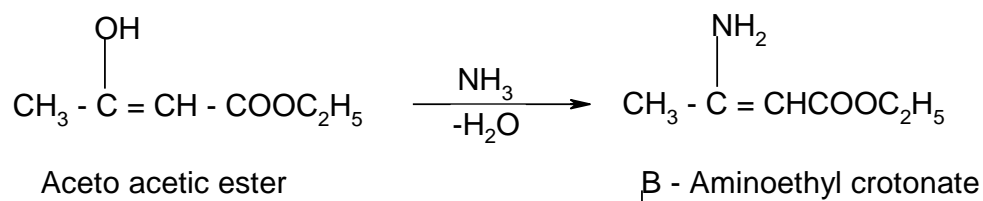
3. With gromine:

It decolourises bromine water. Bromine adds to the double bond of the end form.

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH - COOC_2H_5 + Br_2 \longrightarrow CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} - \overset{}{\underset{\underset{\displaystyle Br}{|}}{CH}} - COOC_2H_5$$

$$\overset{+\ H\ Br}{\longrightarrow} CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - \overset{}{\underset{\underset{\displaystyle Br}{|}}{CH}} - COOC_2H_5$$
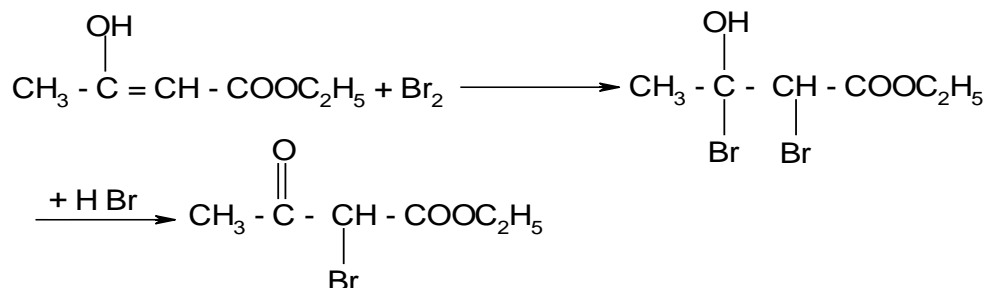
4. With ferric chloride:

Acetoacetic ester gives violet colour with ferric chlorides. This colour reaction is a characteristics reaction of phenol and enolic compounds.

$$\text{The group } - \overset{\overset{\displaystyle OH}{|}}{C} = C -$$
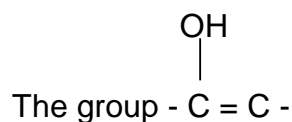
5. With Benzene diazonium chloride:

It couples with benzene diazonium chloride as phenol.

Reaction (4) (5) indicate that aceto aceticester resembles phenol. In phenol also there is end structure.

OH
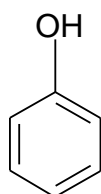
6. With grignard reagent:

The enol form of acetoacetic ester reacts with Grignard reagent.

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CHCOOC_2H_5 + CH_3 MgI \longrightarrow CH_3 - \overset{\overset{\displaystyle O\,MgI}{|}}{C} - CH - COOC_2H_5 + CH_4$$
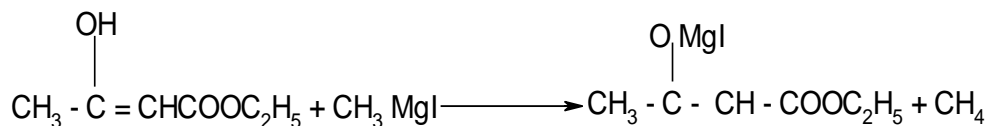
The above evidence in favour of Keto form and end form show the acetoacetic ester is in two tautomeric forms.

Separation of Keto and enol forms [Knorr]

Separation of Keto form:

A solution of acetoacetic ester in petrolium ether is cooled to 78°C. A colourless Crystalline solid separates. It does not give violet colour with ferric chloride and it does not decolour bromine solution. Therefore it is the Keto form.

Separated of end form:

A suspension of the sodium salt of acetoacetic ester in petroleum ether is taken HCl gas is passed through it. Sodium chloride present the mixture is separated by filtration. The filtrate contains the enolic form. It gives intense violet colour with ferric chloride and decolourise bromine solution.

The Keto form the end form if allowed to stand for some time gives the tautomerism mixture only.

Estimation of Keto and enol forms:

Now, it is well established that acetoacteic ester exists in Keto and enol form and equilibrium exists between these two forms under ordinary conditions. The exact composition of each form can be determined by physical as also by chemically methods However, one should select such a method that should not disturb the equilibrium of the mixture during estimation. Because of this reason, physical methods are preferred.

Physical methods:

1. By measurements of refractive index :

In this method first of all, the refractive index of the ordinary ester in determined. Then, its value is compared with the values of the different mixtures of the Keto and enol forms of Known composition. Knorr used this method and found that the equlibrium mixture of acetoacetic ester contains 7.7% of the end form and 92.3% of the Keto form.

2. By measurement of electrical conducitivity:

In this method when we use one form which is an electrolyte and measure its electrical condictivity which may be employed to determine its percentage in the mixture.

3. By N.M.R and infrared spectroscopy:

There techniques have been used successfully for determining the equlibrium composition of tautomers.

4. By optical rotation measurements:

This method has been used successfully to determine the quantity of the two tatomeric forms in any equlibrium mixture.

Chemical methods:

The various methods are as follows.

1. Kurt meyer method:

This method is based upon the observation that the end form of acetacetic ester, but not its Keto form, reacts rapidly with bromine, forming bromo Ketones.

The process consists in treating weighted example of ester with the excess of standard ethonolic solution of bromine. The excess of bromine, that may distrub the equilibrium, is removed by the addition of β - naphthol. After acidifying this reaction mixture with hydrochloric acid, potassium iodide, added to it when the α - bromo –Ketone is reduced by the hydrogen iodide, liberating iodine. This is then titrated with sodium thiosulphate. Each molecule of iodine so produced corresponds to molecule of end form in the original sample.

The main drawback of this method is that final reductin is very slow.

2. Flow method:

In this method, the solution of the Keto – enol mixture and an acidified bromide – bromate solution are simultaneously mixed and diluted in a mixing chamber and the mixture is made to flow fast a platinum electrode. Then, the relative quantilies of the two solution are adjusted. So that the potential measured at the platinum electrode shows a sharp rise that correspond to the end point in the titration of the end form by the bromine. Point in the titration of the enol form by the bromine. This method gives results of end contents as low as 10^{-5} percent.

3. Ozonide method:

When a tautomeric mixture is treated with Ozone, the enol form forms Ozonide. This is decomposed with water and the products are characterized and estimated.

3.3.5 Diazonium Compounds:

Diazotisation:

When an aliphatic Primary amine is treated with nitous acid, nitrogen is evolved. But when a Primary aromatics amine is treated with nitrous acid in a well cooled solution, the product obtained is known as diazonium salt.

$$CH_3 - \underset{\underset{\displaystyle }{|}}{\overset{\displaystyle O-H}{C}} = \underset{\curvearrowleft}{CHCOOC_2H_5} + Br - Br \longrightarrow CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - Br \ COOC_2H_5 + HBr$$

$$CH_3 - \overset{\displaystyle O}{\overset{||}{C}} = CHBr \ COOC_2H_5 + KI \longrightarrow CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - CHICOOC_2H_5 + KBr$$

$$KI + HCl \longrightarrow KCl + HI$$

$$CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - CHICOOC_2H_5 + HI \longrightarrow CH_3 - \overset{\displaystyle O}{\overset{||}{C}} - CH_2COOC_2H_5 + I_2$$

$$\text{aniline} \quad -NH_2 \xrightarrow[- H_2O]{HNO_2 / HCl} \quad -N = N - Cl$$

aniline

benzene amonium chloride
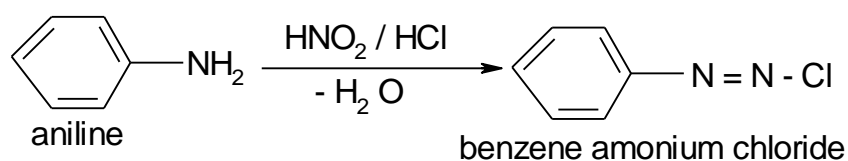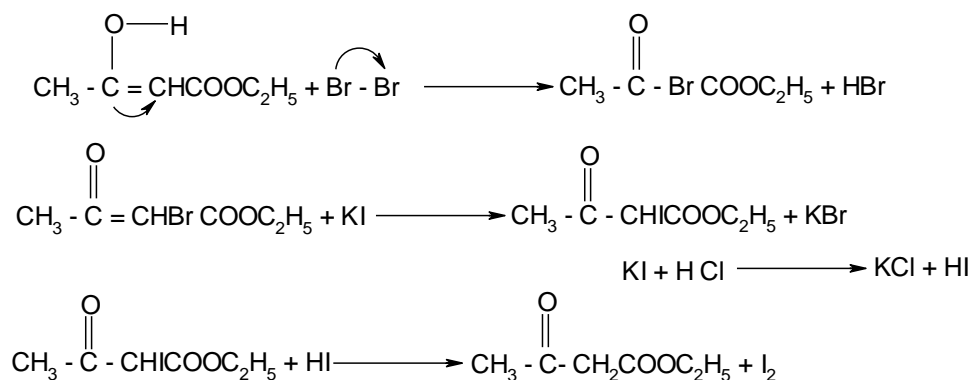
The reaction of an armotic primary amine with nitrous acid (Sodiumnitrate + Hydrochloric acid) and hydrochloric acid to give a diazonium compound is know as diazotisation reaction. This reaction was discovered by Griess.

Mechanism:

Nitrous acid furnishes nitrosonium ion in presence of acid. Nitrosonium ion combine with aniline to form nitrosoaniline. Nitrosoaniline undergoes rearrangements followed by dehydration to form diazonium ion.

$$HO - NO + H^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} H_2O - NO \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} H_2O + NO^+$$

$$-H_2O + NO^+ \xrightarrow{\text{Slow}} -NH_2 + NO \xrightarrow[-H^+]{\text{fast}} -NHNO$$

$$-NHNO \xrightarrow[\text{rearranges}]{\text{fast}} -\overset{..}{N} = \overset{..}{N} - OH \xrightarrow[\text{fast}]{-H^+}$$

$$-\overset{..}{N} = N - \overset{+}{OH_2} \xrightarrow{\text{fast}} -N = \overset{+}{N} + H_2O$$

142
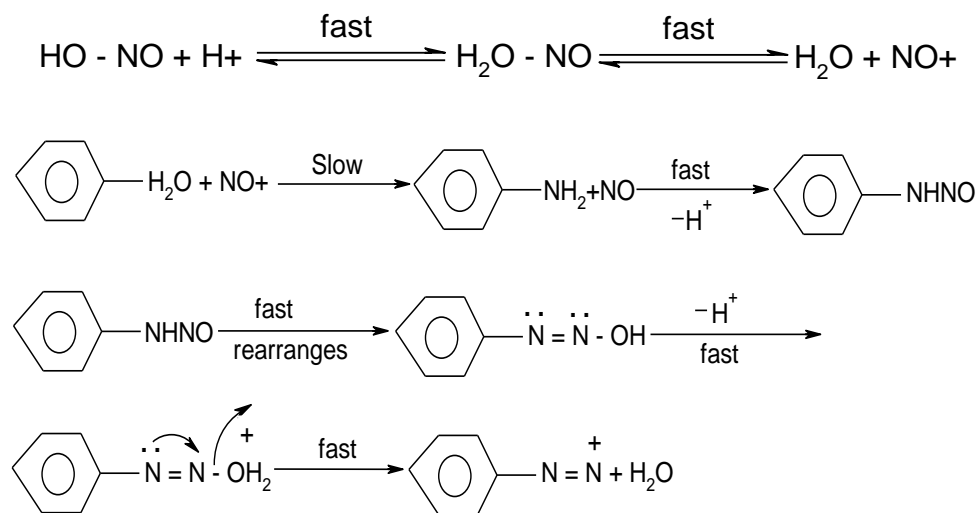
Diazonium ion is a weak electrophile:

Diazonium salts have the structure.
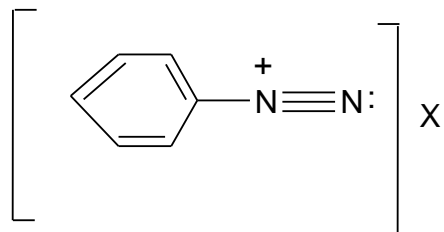
They are electrolytes in solution. The stability of diazonium salts is due to the following resonance structure.
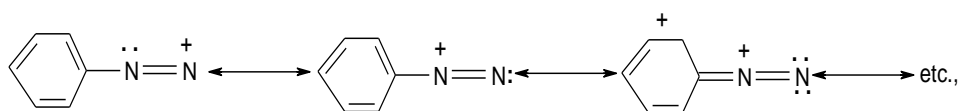
Diazonium salts are highly reactive and they form the starting material for the preparation of a number of dyes.

Diazonium salt involves in coupling reactions. With amines and phenols coupling takes place only in acivated nuclears and hence its considered as a weak electrophilic.

Diazomethane

Preparation:

1. From methylamine:

(Von pechamann) Methylamine is treated with ethyl chloroformate to get N – methylurethane. This on treatment with nitrous acid in ether gives N – methyl N-Nitrosourethan this on warming with methanolic KOH gives diazomethane.

$$CH_3NH_2 + ClCOOC_2H_5 \longrightarrow CH_3NHCOOC_2H_5 \xrightarrow{HNO_2}$$

Methylamine   ethyl Chloro formate   N - methylurethan

$$\underset{\underset{NO}{|}}{CH_3NCOOC_2H_5} \xrightarrow{KOH} CH_2N_2 + CO_2 + C_2H_5OH$$
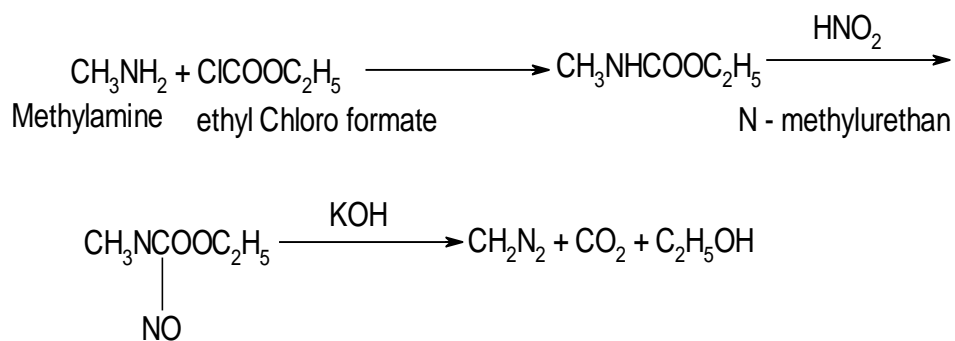
2. From methyl urea:

This is an improvement to the above method.

$$CH_3NHCONH_2 \xrightarrow{HNO_2} \underset{\underset{NO}{|}}{CH_3NCONH_2} \xrightarrow{KOH} CH_2N_2 + KNCO + 2\,H_2O$$
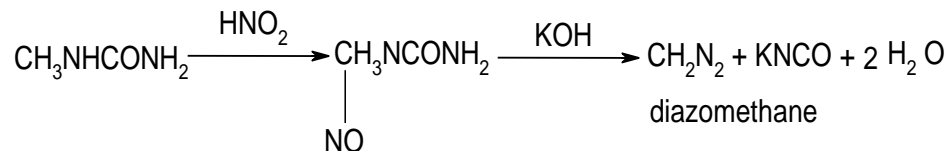
diazomethane

3. Method of Backeretal:

This nitroro – derivative of p- toluene N- methylsulphonamide is ≡disfilled with ethanolic KOH we get diazomethane.
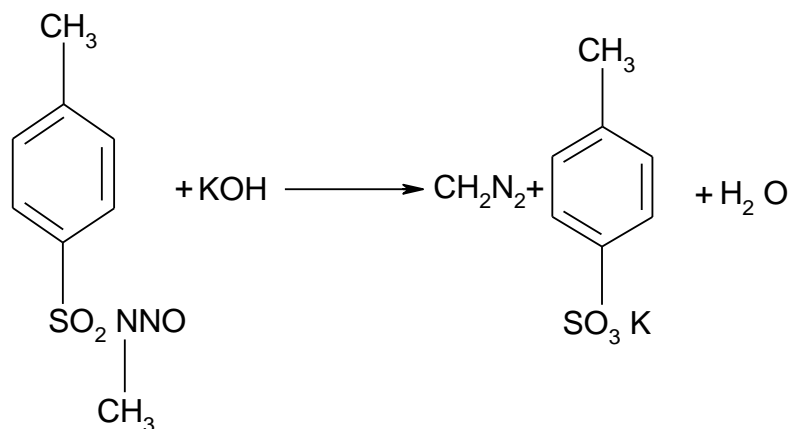
P Toluene - N - methyl sulphoneamide

Structure:

1. Curtius represented diazomethane by a cyclic structure. The cyclic structrure is highly unstable. However the cyclic structure.
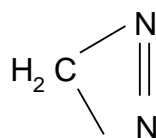
is confirmed by curtius from the preparation of diazomethane from formaldehyde.
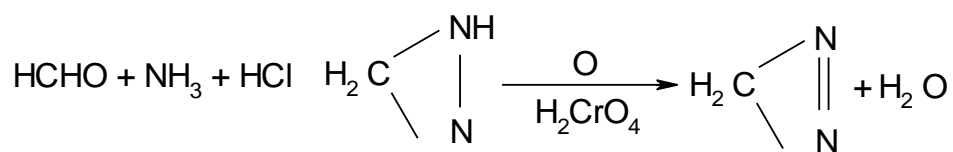
2.   Angeli suggested a lined structure for diazermethane as $CH_2=N\cong N$. This contains a pentavalent nitrogen. Electron diffraction measurements support the linear structure. The bond measurements and other factors show that diazomethane is a resonance hybrid of the following structures.

$$CH_2 = \overset{+}{N} = \overset{..}{\underset{..}{N}}{}^{-} \longleftrightarrow \overset{..}{CH_2} - \overset{-}{N_3} \equiv \overset{+}{N} \longleftrightarrow -\overset{..}{CH_2} - \overset{..}{\underset{..}{N_4}} = \overset{..}{N}{}^{+}$$
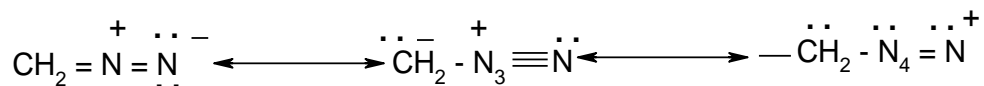
Synthetic uses:

1. Formation of Methyl ester:

Diazomethane reacts with acids to give methyl esters.

$$CH_2N_2 + RCOOH \longrightarrow RCOOCH_3 + N_2$$

$$CH_2N_2 + CH_2COOH \longrightarrow CH_3COOCH_3 + N_2$$
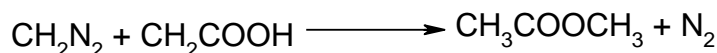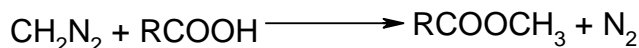
2. Formation of ethers:

Diazomethane methylates alcohols and phenols.

E.g.

a. $CH_2N_2 + C_2H_5OH \xrightarrow{Al\,(OR)_3} CH_3OC_2H_5 + N_2$

$C_6H_5OH + CH_2N_2 \longrightarrow C_6H_5OCH_3 + N_2$

Methylphenyl ester

b.
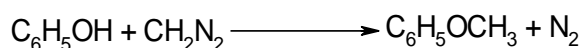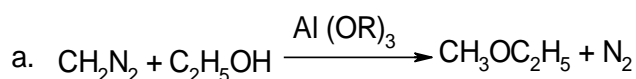
P - hydroxy benzyl alochol   P - Methoxy, benzyl methyl ester
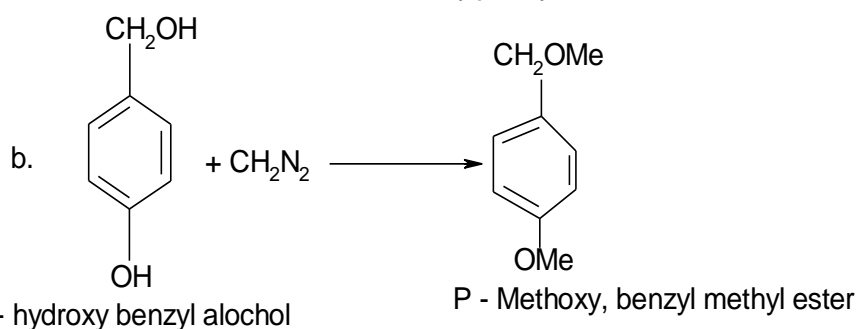
3. Conversion of an aldehyde to Ketone:

Aldehydes react with diazomethane to give methyl Ketones.

4. Conversion of Ketone to higher homologue:

A Ketone reacts with diazomethane give the next higher homologue.

$$RCHO + CH_2N_2 \longrightarrow RCOCH_3 + N_2$$

$$RCHO + CH_2N_2 \longrightarrow RCH_2COR + N_2$$
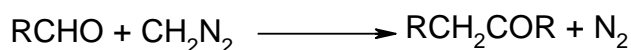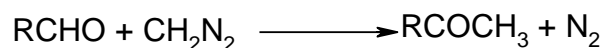
5. Formation of Methyl Chloride:

Diazomethane reacts with HCl to give methyl chloride.

$$CH_2N_2 + HCl \longrightarrow CH_3Cl + N_2$$
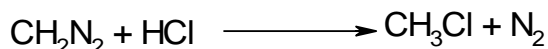
6. Formation of Methyl cyanide:

Diazomethane reacts with HCN to give methyl cyanide which on hydrolysis give acetic acid.

$$CH_3N_2 + HCN \xrightarrow{-N_2} CH_3CN \xrightarrow{HOH} CH_3COOH$$
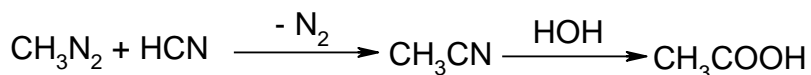
7. Ardt-eistert reaction:

This is also called Ardt eistert Synthesis. In this an acyl halide is converted to a corboxylic acid with one additional carbon.

$$RCOCl + CH_2N_2 \longrightarrow RCO\,CHN_2 + HCl$$

$$RCOCHN_2 + H_2O \longrightarrow RCH_2COOH + N_2$$
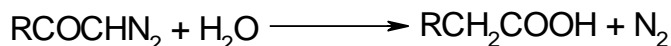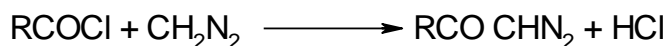
This reaction affords a method of ascending a series.

8. Formation of heterocyclic compounds:

Diazomethane adds on to alkynes and alkanes to form hetercyclic compound ethylene gives pyrazoline and acetylene give pyrazole.

Ethylene
Pyrazoline

Ethylene
Pyrazole
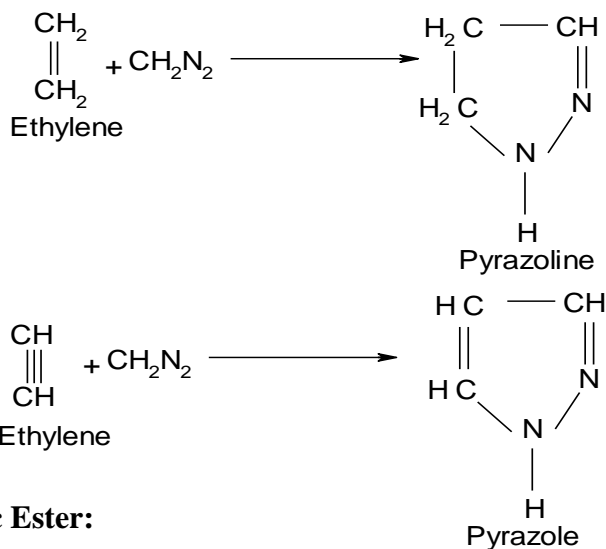
Diazoacetic Ester:

Preparation:

It is prepared by treating on ice cold solution of hydrochloride of ethylaminoacetate with ice cold sodium nitrite solution

$$ClHH_2NH_2C - COOC_2H_5 + NaNO_2 \longrightarrow N_2CHCOOC_2H_5 + NaCl + 2\,H_2O$$
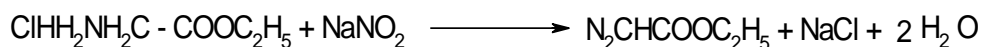
Diazoacetic ester is also called ethyldiazoacetate.

Structure:

Diazoacetic ester is a stable compound. The stability is attributed to the extended resonance. It is more stable than diazomethane. Diazomethane ester has higher resonance energy than diazomethane. The following resonance structure are given to diazoacetic ester.

Synthetic uses:

1.   Preparation of halogenated acids:

Diazoacetic ester reacts with conc.hydrochloric acid to give ethyl chloroacetate wthich on hydrolysis gives chlororacetic acid.

$$\overset{-}{\underset{\cdot\cdot}{N}} = \overset{+}{N} = CH - \overset{O}{\overset{\|}{C}} - OC_2H_5 \longleftrightarrow :N \equiv \overset{+}{N} = CH - \overset{O}{\overset{\|}{C}} - OC_2H_5 \longleftrightarrow :N = \overset{+}{N} = CH - C - OC_2H_5$$

$$N_2CHCOOC_2H_5 + HCL \xrightarrow{N_2} CH_2CLCOOC_2H_5 \xrightarrow{H_2O} CH_2CLCOOH + C_2H_5OH$$

Diazoacetic ester   Chloroacetic acid
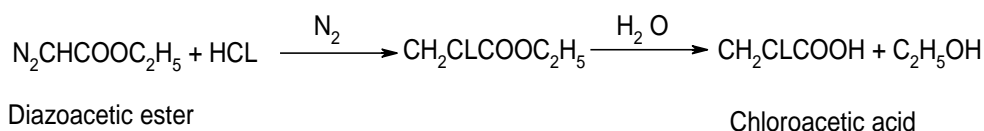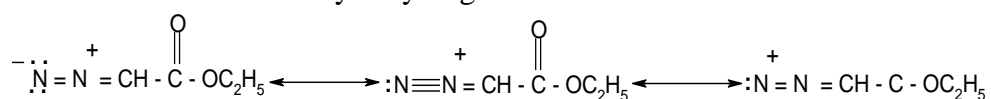
[Conc. HBr and HI react in a similar fashion]

2. preparation of glycollic acids:

Diazoacetic ester is boiled with dilute HCL and ethyl glycollate is obtained. It is hydrolysed to get glycollic acid.

$$N_2CHCOOC_2H_5 + H_2O \xrightarrow{dil / HCL} CH_2OHCOOC_2H_5 \longrightarrow CH_2OHCOOH + C_2H_5OH$$

Diazoacetic ester   glyeolic acid
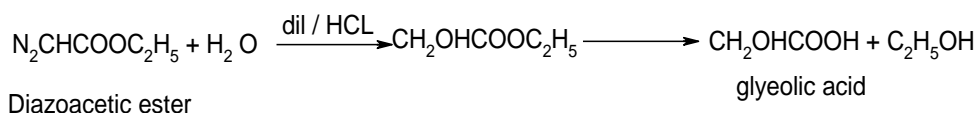
3. Preparation of heterocylic compounds:

Ethylene and acetylene react with diazoacetic ester to give heterocyclic compounds.

Pyrazoline -3- carboxylic ester

$$CH \parallel\parallel CH \quad \text{(Acetylene)} + N_2CHCOOC_2H_5 \longrightarrow$$

Pyrazole -3- carboxylic ester
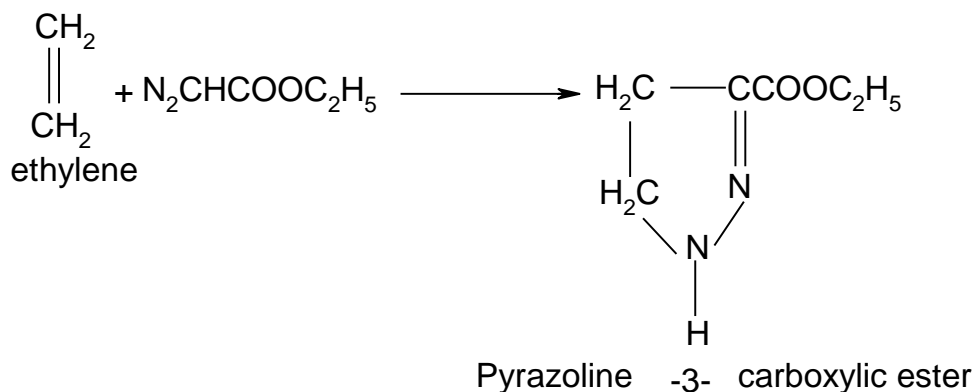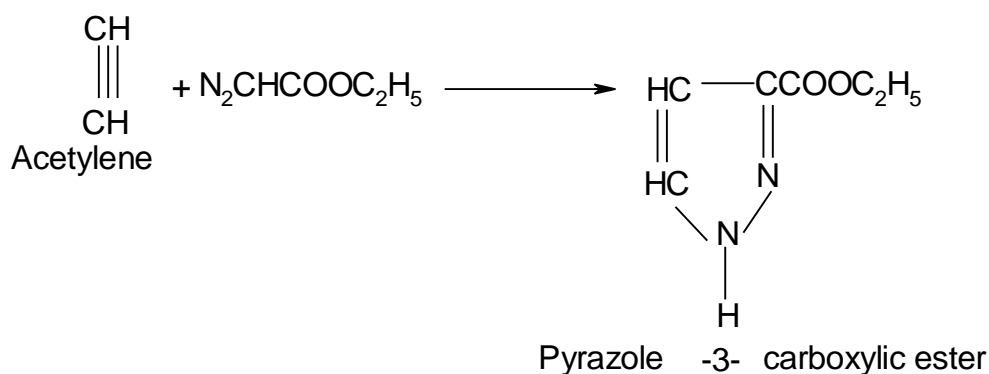
4. Preparation of glycine ester:

Reduction of diazoacetic ester with zinc and acetic acid gives glycine ester.

$$N_2CHCOOC_2H_5 \xrightarrow{\text{4 H}} H_2NCH_2COOC_2H_5 + N_2$$
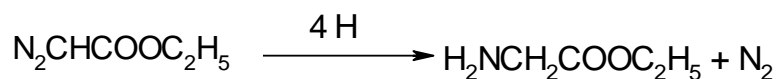
5. With compounds containing active hydrogen atom:

Diazoacetic ester reacts with compounds containning on active hydrogen atom with acetic acid it gives acetylglycollic ester. With ethanol it gives ethyl ether or glycollic ester.

$$CH_3COOH + N_2 CHCOOC_2H_5 \longrightarrow CH_3COOCH_2COOC_2H_5 + N_2$$

$$C_2H_5OH + N_2CHCOOC_2H_5 \longrightarrow \underset{\underset{OC_2H_5}{|}}{CH_2COOC_2H_5} + N_2$$
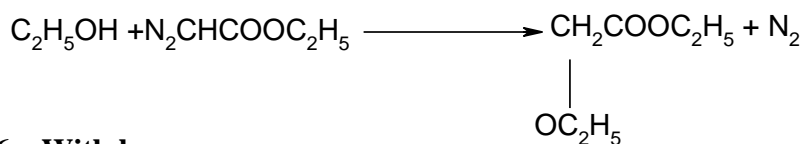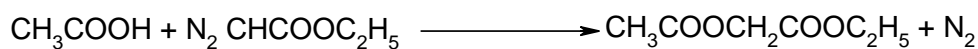
6. With benzene:

Diazoacetic ester decomposes to carbethoxy methylene. In the presence of benzene it gives cycloheptatriene carboxylic ester.

$$N_2CHCOOC_2H_5 \xrightarrow{h\delta} N_2 + H - C - COOC_2H_5 \xrightarrow{C_6H_6}$$

Cycloheptatriene carboxylic ester

NOTES

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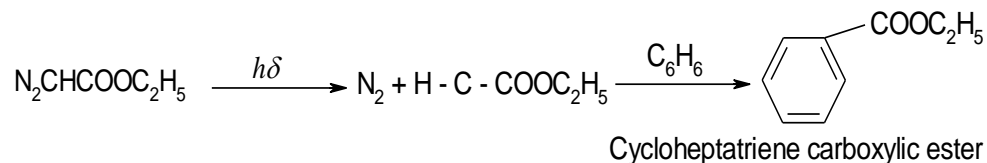
UNIT - IV

SOLID STATE

Solids are classified as crystalline and amorphous.

Crystalline Solids

crystalliane solids are solids which possess characteristic geometrical shapes and melting points. They are anisotropic. They have a long range order,i.e., the atoms or molecules constituting the crystals are in a perfect order over extended regions within each individual crystal. Throughout bulk of the crystalline solid, each particle has an identical environment . Examples of crystalliane solids are NaCI, KCI, diamond, graphite, metals etc.

Amorphous solids

Amorphous solids are solids which do not possess characteristic geometrical shapes and melting point. They gradually soften on heating. they are isotropic. They have only short range order. Examples of amorphous solids are glass, rubber, plastic etc.

Isotropic and Anisotropic solids :

Isotropic substances :

Some substances have equal values of properties in all directions. Some of the properties are ; refractive index, thermal expansion, electrical and thermal conductivity, solubility, tensile strength. These substances are called isotropic substances. Amorphous substances behave in this manner. so they are called isotropic. liquids and gases also behave in a similar manner, and hence they are also called isotropic.

Anisotropic crystals :

Some substances have different values for these properties in two or more direction. They are called anisotropic substances Most crystalline substance are anisotropic. For example, the velocity of light passing through crystal varies with the direction in which it is measured. Thus a ray of light entering such a crystal may split up in two components. Each components may follow a different path and travel with different velocity. This phenomenon is known as double refraction. The anisotropy in itself is a strong evidence for the existence of ordered molecular arrangement in crystal.
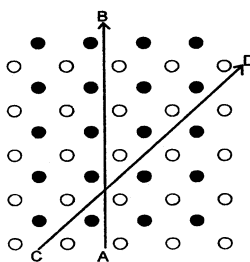
In figure a simple two dimensional arrangements of different atoms are shown. If the properties are measured along the line CD, they will be different from those measured along the line AB, The reason is that, along CD each row is made up of alternate types of atoms and along AB each row is made up of one type of atoms only.

E.g.:

i.   The coefficient of thermal expansion of AgI is positive in one direction while it is negative in another diection.

ii. The indices of refraction for   sodium D line for $K_2Cr_2O_7$ crystals are different along different axis.

Nature of the solid state :

In solid state, the atoms, ions or molecules i.e., the particle constitution the state are confined to a given position surrounded by others. In this state the particles are closely packed and are, held strongly by forces of attraction between them. Because of this, the state is characterised by (i) definite shape (ii) rigidity (iii) non-compressibility (iv) definite volume (v) anisotropy.

Seven Crystal Systems :

Origin of crystal system and their classifications :

It can be shown from geometrical consideration that their can be thirty two different combinations of elements of symmetry of a crystal. These are called point groups. These thirty two point groups are grouped, according to certain minimum symmetries, into seven crystal system. This is the basis on which the crystals are classified. The seven crystal systems are, cubic tetragonal, orthorhombic, hexagonal, rhombohedral and triclinic. Description i.e., the characteristics of the seven crystal systems are given in the following table.

Crystal system	Axes and angles	Minimum symmetry	Examples
1. Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^o$	4 three fold axes (along the diagonals of the cube)	NaCl, KCl, Ag, diamond
2. Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^o$	1 four fold axes	White tin, MgF_2, $NiSO_4$
3. Ortho rhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^o$	3 two fold axes	$HgCl_2$, KNO_3 Rhombic S.

4. Mono clinic	$a=b\neq c$ $\alpha=\gamma=90^o$ $\beta=90^o$		1 two fold axis	KClO$_3$ mono clinic S
5. Hexagonal	$a=b\neq c$ $\alpha=\beta=90^o$ $\gamma=120^o$		1 Six fold axis	Mg, graphite, ZnO, HgS.
6. Rhomo hedral	$a\neq b\neq c$ $\alpha=\beta=90^o$ $\gamma=120^o$ (or) $\alpha=\beta=\gamma$		1 three fold axis	Al$_2$O$_3$, calcite
7. Triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma\neq90^o$		None	CuSO$_4$. 5H$_2$O

Here a, b and c are the axis. The angle between 'a' and 'b' is 'α'; that between 'b' and 'c' is 'β' and that between 'c' and –a' is 'γ'. These seven systems are shown in the following figure.
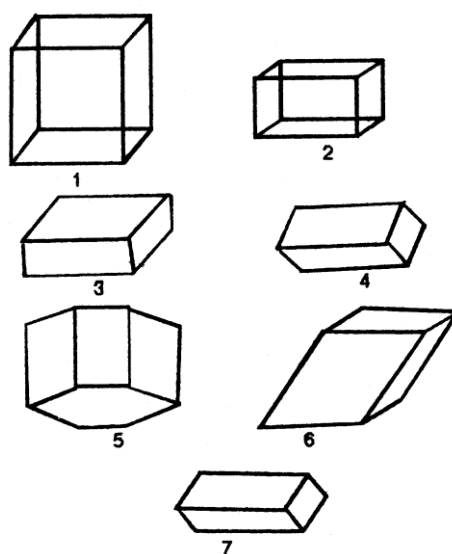
In the study of crystals two geometrical concepts are used, They are space lattice and unit cell.

Space lattice or Crystal lattice :

A space lattice is an array of points showing how molecules, atoms or ions arranged at different sites in three dimensional space.
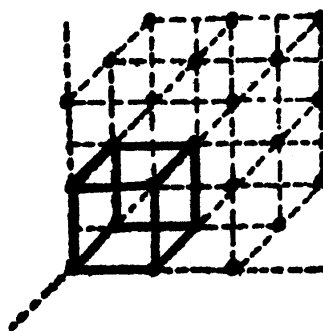
Such points indicate the positions of molecules, atoms or ions in a crystal relative to one another in space.

An example of the array of points in a three dimensional space lattice is shown in figure. Each point represents an identical atom, molecule or ion. The lines are imaginary.

The lattice points can be broken up into a number of unit cells.

Bravais Lattice :

Bravais showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged in a three dimensional space. Thus the total number of space lattices belonging to all the seven crystal systems put together is only 14 As shown in the table given below.

	Crystal system	Bravais Lattices	Total Lattices
1	Cubic	(i) Primitive (ii) face centered (iii) body centered.	3
2	Ortho rhombic	(i) Primitive (ii) face centered (iii) body centered (iv) end centered	4
3	Tetragonal	(i) Primitive (ii) body centered.	2
4	Mono clinic	(i) Primitive (ii) end centered	2
5	Triclinic	(i) Primitive	1
6	Hexagonal	(i) Primitive	1
7	Rhomohedral	(i) Primitive	1
	Total		

The crystals belonging to cubic system have three kinds of Bravais lattices depending upon the shapes of unit cells.

a) The simple or primitive cubic lattice (P) in which there are point only at the corners of each unit cell. In this arrangement the co-ordination number is 6. Total number of spheres (atoms) in an unit cell is 1.
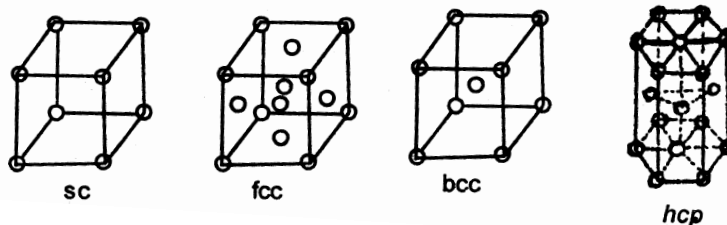
b. The face centered cubic lattice (F) In which there are points at the corners as well as at the centre of each of the six faces of the cube. Total number of spheres is 4. The co-ordination number is twelve.

c. The body centered cubic lattice (I) In which there are points at the corners as well as the center of each cube. The total number of spheres is 2. The co-ordination number is 8.

The crystal belonging to hexagonal system have only one kind of Bravais lattice – It is hexagonal close packed hcp system – The over all co-ordination number is twelve. The number of atoms present per unit cell in the hcp system is 2. The hcp arrangement has three unit cells in it. (Fig 8 b). The efficiency of packing decreases in the order of fcc = hcp > bcc > sc.

The other five systems are not discussed in this book.

Summary

Lattice	Co-ordination number	Number of atoms/unit cell	Examples
Cubic Simple/ primitive (sc)	6	1	Mn, Kcl
Body centered (bcc)	8	2	Ba, Cs, K, Li diamond, ZnS
Face centered (fcc)	12	4	Noble gases Ag, Al, Au, Cu, Ni, Pd, H_2, Nacl

Hexogonal close packed (hcp)	22	2	Noble gases Cd, Zn, Mg, ice

Unit Cell :

An unit cell is the smallest repeating space lattice which when repeating over and over results in a crystal of the given substance. The points joined by the thick lines in figure is one unit cell. Thus the space lattice contains a lot number of unit cells.

Lattice planes :

The points in a space lattice may be arranged in a large number of ways in a series of parallel and equidistant planes known as the lattice planes. In terms of three planes, it is convenient to describe a crystal lattice. Simplest types of crystals belong to the cubic system. The simple cubic crystal has the important planes (100) (110) and (111). The face centred, cubic crystal has the planes (200), (220) and (1 1 1). The body centred cubic crystal has planes (200), (110) and (222).

Born – Lande equation

The equation is used to calculate the latice energy of ioin compounds. The equation is

$$U_o = \frac{N_o A Z^2 e^2}{r_o}\left(\frac{1}{n} - 1\right)$$

U_o -   Unit of lattice energy per mole

N_o -   Avogadro number

A   -   Madelung constant

r_o -   Inter ionic distance

e   -   Electronic charge

n   -   Born exponent

z   -   Charge of ions $(Z_1 = Z_2 = Z)$

         Charges of the cation and anion

The equation may be further improved by considering the following correction factors.

i)   Vander Walls forces between the ions.

ii)   Zero point energy of the crystals. This type of energy is due to vibration of the ion in the crystal.

iii)   Resonance energy: This type of energy is due to covalent nature of the ionic bond.

Law of Rational Indices:

There are three fundamental laws is crystallography. The law of rational indices is one among them.

Law:

The intercepts of any face of a crystal along the crystallographic axis are either equal to the unit intercepts(a,b c) or some simple multipies of them".

(100)   (110)   (111)
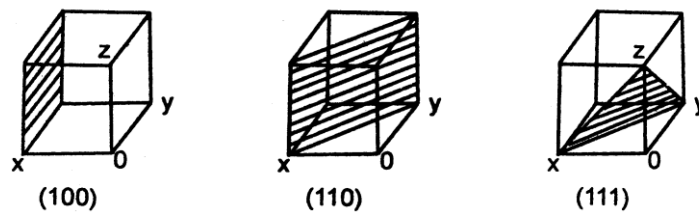
Explanation:

Let OX,OY AND OZ be the crystallorgraphic axis. Let ABC be a unit plane.
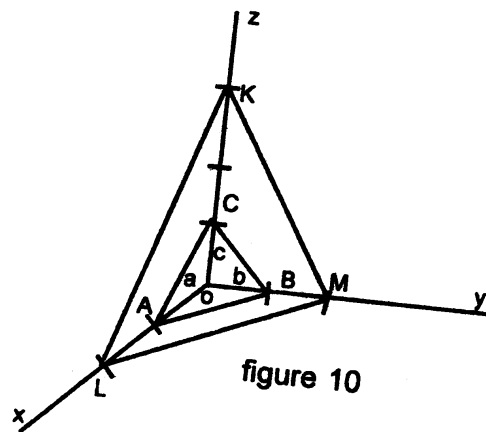
figure 10

The unit intercepts are a, b, and c. According to the law of rationality of indices or intercepts, the intercepts of any face such as KLM on the same three axis will be simple multiples of a, b and c. From the figure 10 the intercepts of the plane KLM on the three axis 2a: 2b: 3c.

The coefficient of a, b and c are known as 'Weiss indices' Weiss indices are not always whole numbers as in the given example. They

may have fractional values as infinity. Therefore instead of weiss indices, Miller indices have been introduced.

Miller Indices:

They are a set of integers'(h, k, l) Which is used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on the various axis.

To get the miller indices, the reciprocals of the Wesis indices are taken. They are converted into whole numbers by the least common denominator.

In figure for the plane KLM the Weiss indices of the planes are 2, 2 and 3. The reciprocals are ½, ½ and Multiplyiug them by least common denominator i.e., 6, we get 3 3, and 2. Thus the Miller indices for the plane KLM are 3 : 3 : 2. The plane is designated as (332) plane in figure 10, h=3, k=3 and i=2.

For the plane ABC in the figure 10, the Weiss indices are 1,1 and 1 and the Miller indices are also 1, 1 and 1. Therefore the plane ABC is called (111) plane.

Use:

Miller indices are used to calculate the distance between two parallel planes in a crystal, if the length of the side of the cube is known.

The distance between the parallel planes in a crystal are designated as d_{hkl}. For a cubic lattice.

$$d_{hkl} = \frac{a}{\sqrt{\left(h^2 + K^2 + l^2\right)}}$$

where a' is the length of the side of the cube and h, k and l are the Miller indices of the plane.

From d, the ratio $d_{100} : d_{110} : d_{111}$ are calculated. From these values we can determine the crystal system and the crystal class to which the crystal belongs. Some important crystal planes for a simple cubic crystal are shown in figure. 9

Symmetry Elements in Crystals

a) Centre of symmetry :

It is a point in a crystal through which if an imaginary straight line is drawn, it meets equivalent points at equal distances on either side. For any crystal only one centre of symmetry is possible.

b) Plane of symmetry :

It is an imaginary plane which divides the crystal into two halves so that one half is the mirror image of the other.

Centre of Symmetry   Plane of Symmetry   axis of symmetry
(4 - fold axis)
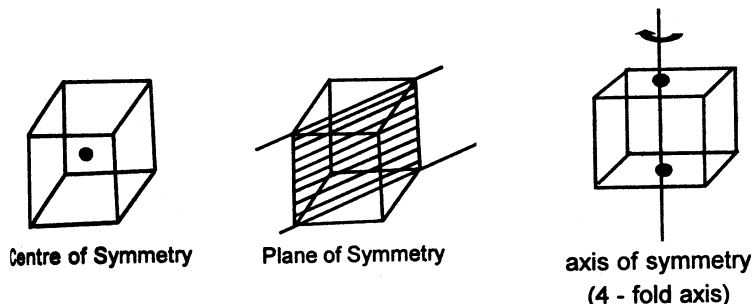
For a cubic crystal, there are two types of planes of symmetry (i) three rectangular plans of symmetry, since there are six faces (ii) six diagonal planes of symmetry, since there are twelve edges.

c) Axis of symmetry :

It is an imaginary axis around which if the crystal is rotated through 360^0, the crystal presents, exactly the same appearance more than one time. There are two types of axis of symmetry.

i) n – fold axis of symmetry :

n – fold axis of symmetry is an imaginary line (axis) around which if the crystal is rotated through $360^0 C$ the crstal presents exactly the same appearance 'n' times. If n = 2,3,4 or 6 it is called 2,3,4 or 6 fold axis of symmetry respectively.

ii) n-fold axis of rotation-inversion :

n-fold axis of rotation inversion is an imaginary line (axis) through which if the crystal is rotated through $360^0 C$ and then inverted through the centre the crystal presents the same appearance. If n = 2 or 4 it is called 2 or 4 fold axis of rotation-inversion respectively.

Symmetry elements of a cube :

There are 23 elements of symmetry in a simple cubic crystal. They are as follows

Centre of symmetery	I	
	___	1
Planes of symmetry		
Rectangular planes of symmetry	3	
Diagonal planes of symmetry	6	9

Axis of symmetry   ___

    Two fold axis of symmetry   6

    Three fold axis of symmetry   4

    Four fold axis of symmetry   3   13

                                                  ___   ___

                                                      23

                                                    ____

X-RAY DIFFACTION BY CRYSTALS

Principle :

    X-rays are electromagnetic radiations with wave lengths of about 0 – 1 nm of A°. X rays can be prepared by producing cathode rays in highly evacuated discharge tube and allowing them to fall on a metal target called an anticathode.

    Laue suggested that the distance between the lattice planes in the crystals are in the order of a few angstroms. Therefore he suggested that the crystal should act as a diffraction grating for the X-rays since the wave length of X-rays are also in the order of 1 A° Bragg suggested that crystal's can act as reflection grating also. He developed a simple equation to determine the structure of a crystal using the X-rays. This equation is known as the Bragg's equation or Bragg's law.

Derivation of Bragg's Equation :

    Equation : nλ = 2d sin θ

Explanation of the terms:

    n = order of refletion : λ = wavelength of the X-ray used ; d = Inter planar distance; θ = glancing angle of the incident X-ray.

Derivation :

    The figure shows, the reflection of monochromatic X-rays with wavelength I by the planes of atoms or ions with inter planar distance 'd' (BE). Let all the incident rays be in phase. Let the glancing angle be θ. If the reflected rays are in phase they reinforce. If they are out of phase they will cancel out each other. Let us consider two waves, 1 and 2 failing on planes XX' and YY' respectively at an angle q. Let the two waves be in phase with each other. The wave 2 travels, a longer distance before and after it is reflected by the plane YY' than wave I is reflected by the plane XX'. The path difference d of the two waves is got by drawing BG $\perp$ DE and BH $\perp$ EF.
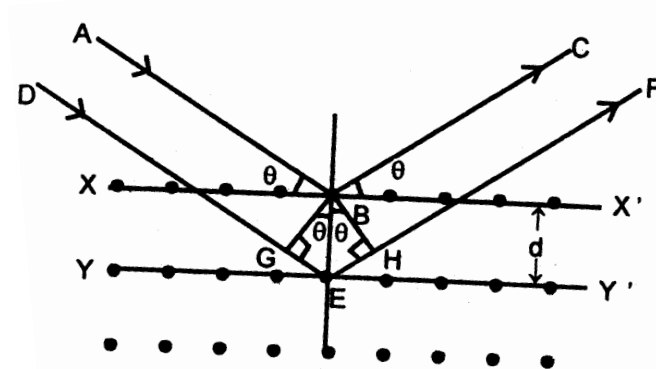
Then $\delta = GE + EH$ (1)

If the reflected waves are to be in phase the condition is

$GE + EH = \lambda$ or $n\lambda$

Where 'n' is an interger

i.e., $n\lambda = GE + EH$

From figure

$\angle GBE = \angle ABX = \theta (=90 - \angle XBG)$ (2)

Similarly $\angle HBE = \angle CBX' = \theta$

∴ Triangles BGE and BHE are congruent

∴ GE=EH(3)

∴ $n\lambda = 2GE$(4)

(5) $\boxed{\therefore \; n\lambda = 2d \sin\; \theta}$

$$\left\{ \therefore \frac{GE}{BE} \;=\; \frac{GE}{d} = \sin\theta \right\}$$

When n=1,2,3…

'n' is known as the order of reflection. The equation (5) is known as the Bragg's equation or the Bragg's Law.

Uses :

i) We know from Bragg's equation $n\lambda = 2d \sin\theta$. By knowing λ and θ we can find the ratio $d\lambda$. From this we can calculate 'd' if λ is known and vice versa.

ii) From Bragg's law we can determine the crystal structure [Refer the heading " crystal structures of NaCI, KCI and CsCI is subsequesnt pages.]

iii)we can determine the Avogadro's number using Bragg's law.

1. LAUE'SMETHOD:

Principle : we know from Bragg's equation

$$n\lambda = 2d \sin \theta$$

In this method, the angle of incidence (θ) is fixed and X-rays with the whole range of wave lengths are used. A certain set of planes which fulfil the condition given by Bragg's Law gives a spot. The various sets of planes present in the crystal give several such spots. We get the Laue pattern of spots.

Procedure :

The apparatus is shown in figure 16.X-ray from the X-ray tube, 'A' are passed through slits S_1,S_2 and converted into a beam. It is allowed to fall on ZnS sheet and then fall on a crystal 'C'. The various atoms in various planes of the crystal satisfying the Bragg's Law scatter or deflect some of the X-rays
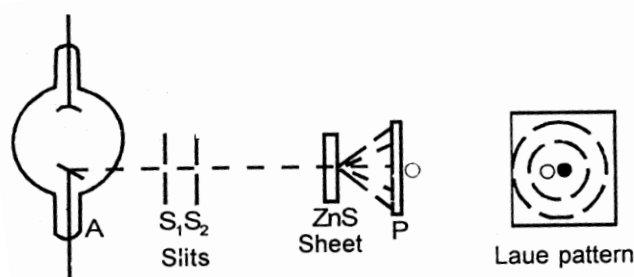
from the original path. These X-rays are photographed and developed. We get the Laue patern 'D'. From a study of the Laue patterns crystal structure is determined.

2. Bragg's Mothod :

Principle:

In the Bragg's method 'I' the wavelength of the X-ray is fixed and θ is varied by rotating the crystal about it's axis. The angles for which reflections are maximum give the 'θ' values which are substituted in the equation.
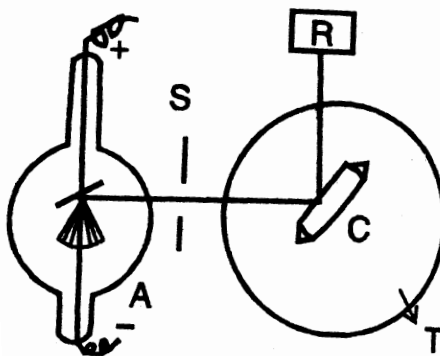
$$n \lambda = 2d \sin \theta$$

The lowest angle at which the maximum reflection occurs corresponds to n = 1. This is called the first order reflection. The next higher angle at which the maximum reflection occurs corresponds to n=2. Similarly, we can explain other orders of reflections also. This is called the second order reflection and so on. The process in carried out for each plane of crystal.

Procedure :

X-rays are generated in the X-rays tybe 'A'. They are passed through a focussing slit 'S'. A narrow beam is got. It is allowed to strike a single crystal 'C; mounted on a turn table T'A particular face is exposed to the X-ray. The crystal is rotated gradually and the glancing angle θ at which the reflections are maximum is determined using a recording device 'R'. The experiment is repeated for n=1,2……Similarly different faces are exposed to the X-rays and the θ values are determined from which d values for various planes are calculated. From these values we can determine the crystal and the crystal class to which the crystal belongs.

Powder Method : (Debye – Scherre)

Principle : In Laue's method and the Bragg's method we require well-formed single crystals which are difficult to get. In debye-Scherrer method we use very fine powder. In the powder the crystal planes are oriented at all possible angles to the beam of X-rays i.e., some particles will have their (100) planes properly oriented to the X-rays: some will have (110) planes and some others will have (III) planes correctly oriented for reflection.

Procedure:

X-rays are generated in the X-ray tube 'A'. (figure 18). They are passed through a focussing slit S_1 and S_2 and 'B'. A narrow beam is got. It is allowed to strike the powdered crystals in a glass caplillary "C". The

diffratad X – rays strike a photographic film strip D' which is placed in the from of a circular are. We get a bright spot at the centre and arcs appear on either side of the bright spot. Each pair of arc is equi-distant from the centre. They correspond to a particular order of diffraction for a set of planes. q can be calculated from

$$2\theta = \frac{s}{r}$$

Where   S = the distance of an arc from the central spot and

r = distance from the powder to the film.

θ will be in radians. To convert into degree the q' is multiplied by 180/p. From θ we can calculate 'd'. From'd' the ratios of d_{100};d_{110}:d_{111} are calculated. From these values we can determine the crystal system and the crystal class to which the, crystal belongs.
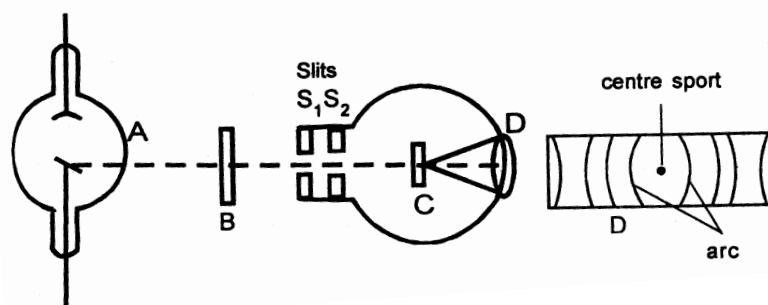
4.2. Colloidal State

SIZE OF COLLOIDAL PARTICLES

When a salt is dissolved in water we get a homogenous mixture which is called a solution, When this is allowed to stand nothing happens.

When finely ground clay is mixed with water we get a heterogenous mixture. When this mixture is allowed to stand the clay particles settle down. Such heterogenous mixture are called suspensions.

When soap is mixed well with water we get a heterogenous mixture. This is neither a solution nor a suspension. We call it a colloid. When this is allowed to stand soap does not settle down.

The size of the particles present in colloids is smaller than the size of particles in suspensions but larger than the particles in the solutions.

Thus the size of the particles play an important role in determining whether a mixture of two substances is a solution or colloid or suspension.

The size of colloidal particles is between 1 mm and 100 nm ($1nm-10^{-9m}$)

If the particles are larger than 100 nm the system is called a suspension. If the particles are smaller than 1 nm the system is called a solution.

PEPTISATION

Peptisation is a process by which a precipitate is converted into a colloid. This can be done in two ways i) By adding suitable ions or ii) by adding the dispersion medium. The substance added for this purpose is called the peptizing or *dispersing agent.*

Peptisation by ions:

In this method a small concentration of an electrolyte is added to a precipitate in presence of the dispersion medium. The ions persent in the electrolyte act as peptising agent. We get a colloid. In this process the precipitate particles adsorb suitable common ions from the added electrolyte. Their boundary potentials are raised, So they are dispersed into the medium as a result of the electrostatic repulsion of the adsorbed ions. (E.g.,) Freshly precipitated silver chloride is peptised by a solution containing chloride ions, say NaCl.

Peptisation by dispersion medium:

In this method a precipitate is converted into a sol by simply shaking it with the dispersion medium. By this method we can prepare Iyophilic sols, E.g., Gelation is peptised by water.

Thus peptisation is used for preparing both lyophobic and lyophilic sols.

STABILITY OF COLLOIDS

A true colloidal solution is stable. Its particles do not come close and separate out. The stability of sols is mainly due to two factors.

1. Presence of like charge on sol – particles – Origin of charge:

The dispersed particles of a lyophobic sol posses like electrical charges, all positive or all negative, on their surfaces due to preferential adsorption of positive or all negative ions from the electrolyte which is present in the colloid. Since like chatges repelone another, the particles push away one another and resist joining together. However, when an excess of electrolyte is added to a hydrophobic sol, the particles are discharged and coagulated.

2. Solvation of the sol particles:

The lyopnilic sols are stable of two reasons. Their possess a charge and in addition have a layer of the solvent around them. Thus a hydrosol of protein does not coagulate simply by addition of an electrolyte although its particles are discharged. But when a dehydrating substance such as ethanol is added, the water particles are removed. Then the sol is coagulated. Thus lyophilic sols are more stable than lyophobic sols.

COAGULATION

The conversion of colloids into precipitates is called coagulation Lyophilic sols are not easily coagulated, whereas, the lyophobic sols are easily coagulated.

Coagulation of lyophobic colloids:

Coagulation of lyophobic colloids may be done as follows:

1. By mutual coagulation:

When oppositely charged colloids are mixed in equal proportions, their charges are neutralised and the dispersed phases of both the sols are coagulated. This is called mutual coagulation. E.g., $Fe(OH)_3$ and As_2S_3.

2. By continued electrophoresis:

During electrophoresis the dispersed phase moves towards the oppositely charges electrode. If electrophoresis is continued for a longer time the colloidal particles reach the electrodes, lose their charge and are coagulated.

3. By the addition of electrolytes:

Lyophobic sols may be coagulated by the addition of electrolytes. E.g., HCI, NaCI etc., coagulate sols like ferric hydroxide sol and gold sol.

When electrolytes are added to clolloids the ion in the electrolyte which has a charge opposite to that of the colloid neutralises the charge on the colloid. The colloidal particles some together and coagulate. E.g., i)Sd_2S_3 sol is negatively charged. It's coagulated by K^+ of KCl and Na^+ of NaCl (u) $Fe(OH)_3$ Sol is positively charged. It is coagulated by CI of KCI and Br of KBr.

Hardy – Schulze law :

The quantity of the electrolyte required to coagulate a given amount of a colloid depends on the valency of the ion which bears a charge opposite to that of the colloidal particles.

165

E.g., To coagulate a negatively charged colloid like aresenious sulphide sol, the required quantities of ions with valencies +1,+2 and +3 will be in the ratio 500 : 70:1.

Floculation value:

The minimum concentration of an electrolyte which is able to coagulate of flocculate a sol is called its flocculation value. It is expressed in milli moles/litre.

4. By continued dialysis:

We know that a small quantity of electrolyte is always necessary to make the colloids stable. Also we know that the colloids are purified by dialysis. By dialysis we remove excess ions that are present in colloids. So if dialysis is continued for a longer time the electrolytes are completely removed and the colloid is ultimately coagulated.

Coagulation of Lyophilic Colloids:

It is very difficult to precipitate lyophilic colloids. This is because the dispersed phase is highly solvated. The degree of solvation must be decreased significantly before a lyophilic colloid could be coagulated. This is done usually by the following methods.

i. By adding large quantities of soluble salts:

The ions present in these soluble salts get solvated heavily. Thus the solvation of colloidal particles is reduced and they are converted into lyophobic colloids. These are easily coagulated by the ions present in the dispersion medium.

ii. By adding a second solvent which is miscible with dispersion medium:

By this method also the lyophilic colloid is converted into lyophobic colloid which would be subsequently coagulated by adding a small quantity of an electrolyte. For example, if alcohol is added to agar agar in water, it is easily precipitated by adding a small quantity of an electrolyte.

PROTECTION

Definition/What is it? The process of adding a suitable lyophilic sol to a lyophobic sol so that the latter is not precipitated by the addition of electrolytes is known as protection to a colloid.

Explanation: If a stable organic colloid such as gelatin is added to a metal sol, the metal sol is stabilised. The addition of a lyophilic sol to a lyophobic sol usually stabilises the lyophobic sol. Such a lyophilic sol is called the *protective colloid*. Gelatin, albumin, agar, casein, gum arabic, glue and starch are some of the protective colloids. It is beleived that the

lyophilic colloid forms and envelope around, the particles of the dispersed phase of the lyophobic sol and thus protects the latter from precipitation by the addition of electrolytes.

Zsigmondy introduced the term **gold number** to measure the protective action of colloids.

Gold number is the weight in milligrams of a protective colloid which prevents the coagulation of 10 ml of a given gold sol on adding 1 ml of a 10% solutions of sodium chloride.

The smaller the gold number value of a protective colloid, the greater is its protective action.

REVERSE OSMOSIS:

The osmosis taking place from solution to pure water by application of a pressure greater than the osmotic pressure of the solution, on the solution is called reverse osmosis.

Explanation: When a solution is seperated from the pure solvent by a semi permeable membrane, the solvent difusses into the solution side   . This is called *osmosis.*

Whenever the solution is seperated from the pure solvent by a semi permeable membrane, at equilibrium, the solution experiences an excess of pressure called osmotic pressure π. The solvent is under atmospheric pressure P. The solution is under a pressure $P + \pi$. Due to this difference of pressure π, the chemical potential of the solvent in the solution becomes equal to chemical potential of pure solvent. Due to osmotic pressure the solvent flows from the pure solvent side to the solution side.

This osmosis can be stopped by applying a pressure equal to the osmotic pressure of the solution, on the solution. If a pressure greater than the osmotic pressure of the solution is applied on the solution, flow of solvent occurs in the reverse direction in which osmosis occured. i.e, solvent difusses from the solution side to the solvent side. This is called *reverse osmosis*.

If a pressure, which is more than the osmotic pressure of the solution, is applied on the solution, then the solvent starts flowing from the solution side to the solvent side. This is called reverse osmosis.

Application: The principle of reverse osmosis is applied in getting pure water from sea water. This method is called desalination of sea water.

Desalination of Sea Water:

The process of obtaining pure water from sea water by removing the salts dissolved in it, is called **desalination of sea water.**

Principle: The principle of reverse osmosis is applied for this purpose.

Procedure: The sea water if fed into the top of the reverse osmosis cell under pressure. The middle part of the consist of a unit of millions of hair like hollow fibres whose walls acts as semi permeable membrane. Nylon, cellulose acetate etc., are used as hollow fibres. Reverse osmosis takes peace. Desalinated water is obtained from inside of the fibres.
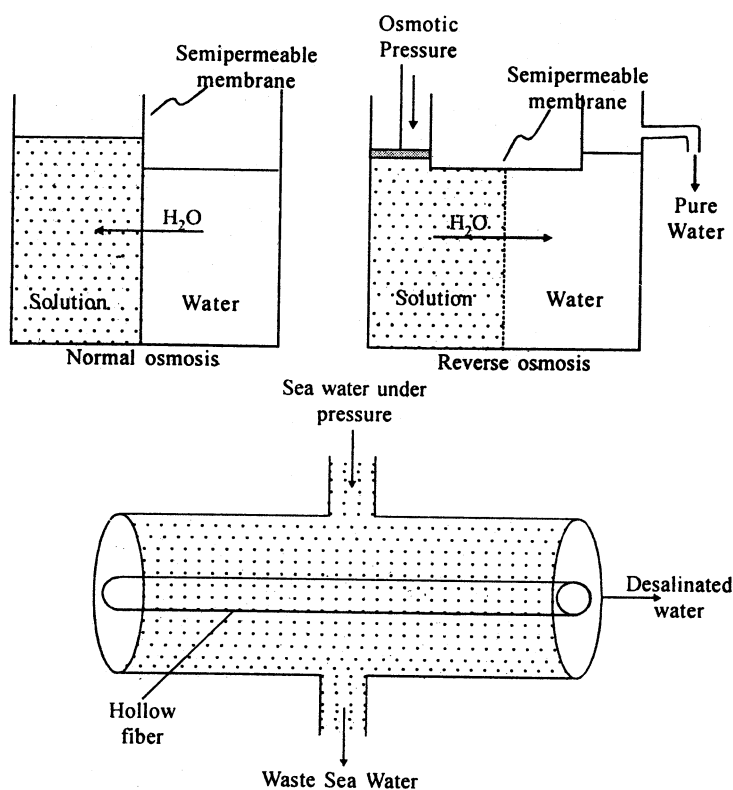
Donnon – Membrane Equilibrium:

It is an equilibrium which occurs when large, non diffusible, charged ions like protein anions, congored anions etc. are separted by a semi permeable membrane from a diffusible electrolyte.

Explanation: When two solutions containing electrolyte are seperated by a semi permeable membrane which are impermeable to one of the ions of the electrolyte, then, at equilibrium there is an unequal distribution of the permeable ion on the both sides of the semi permeable membrane. Such an equilibrium is called **Donnon membrane equilibrium.** Further, at such an equilibrium, the osmotic pressure of the two solutions seperated by the membrane will be different. If two reference electrodes

such as, calomel electrodes are introduced into these two solutions, then a potential difference is developed between them.

The molar masses of charged macromolecules like proteins determined by osmotic pressure measurements in electrolytic media are considerably smaller than those determined by other methods. This is a direct consequence of the presence of **Donnon membrane equilibrium** in the system. So molar masses of such macro molecules should be determined by osmotic pressure measurements by using a high concentration of salt (diffusible electrolyte) in the solution. Under these conditions the effect of Donnon membrance equilibrium on osmotic pressure would be eliminated.

ELECTROPHORESIS:

When a colloidal solution is placed in an electric field, the particles move in one direction or the other showing that they are electrically charged. *The migration of colloidal particles under the influence of an electric field is called electrophoresis(or cataphoresis).* Positive charged particles move towards the cathode while negatively charged particles move towards the anode.

Experiment:

The colloidal solution is placed in a U-Tube. A coloured layer of dispersion medium is also placed in each limb (coloured layers) above the colloidal solution. On applying the potential (EMF) to the platinum electrodes, the (coloured) boundries of the colloidal solution are seen to move in one direction. The direction of migration depends on the sign of the electric charge on the particles. In the case of negatively charged AS_2S_3 sol, the boundry on the cathode side is seen to move down and that on the anode side moves up. The opposite happens in the case of positively charges sols like $Fe(OH)_3$. By means of electrophoresis, using water as the dispersion medium, we can find out the charge on the colloidal particles.

Electrophoresis
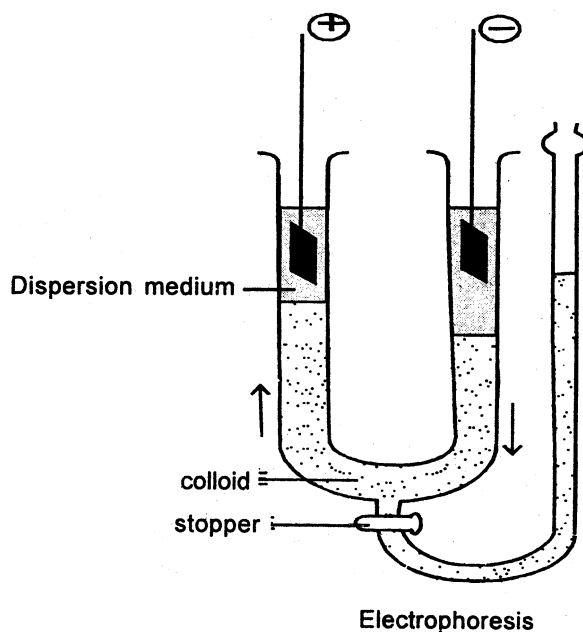
Negatively charged	1. Positively charged
1. Arsenic sulphide, AS_2S_3	1. Metallic oxides e.g., TiO_3
2. Acide dyes, e.g., Eosin	2. Ferric hydroxide, $Fe(OH)_3$
3. Starch, gums. Brown	3. Aluminium hydroxide, $Al(OH)_3$
4. Clay	4. Basic dyes e.g., Bismark
5. Metals e.g., Au, Ag, Pt.	5. Haemoglobin
6. Silicic acid	

Applications:

Electrophoresis is an important industrial process. It is useful.

1. To classify colloids as positive or negative colloids.
2. For the removal of smoke from chimney gases.
3. For removal of suspended impurities.
4. Electro – deposition of rubber on metal surfaces from latex (a sol).

SEPERATION OF PROTEINS

1. By adjusting the pH of a solution containing a mixture of proteins:

Principle: The solubility of a protein depends upon the pH of the solution. At a particular pH, known as isoelectric point, a protein has a minimum solubility . So it is precipitated. This principle is used to separate proteins.

Procedure: The pH of the solution containing a mixture of proteins is adjusted to the isoelectric points of each protein in turn. Each of these is precipitated in turn.

2. By salting out:

Principle: The solubility of a protein depends on the presence or absence of salts. This principle is used to separate proteins.

Procedure: The solubilities of many proteins increase with an in the concentration of added neutral salts, reaches a maximum and then decrease. Thus at sufficiently high concentrations of salts, the proteins are precipitated i.e., are salted out one after another. Thus they are separated.

3. By controlled electrophoresis:

Principle: Different proteins get discharged at different potentials during continued electrophoresis.

Procedure: A Solution of the mixture of proteins is subjected to continued electrophoresis. The applied potential is increased slowly. Different proteins are precipitated at different potentials. Thus they are separated.

4. By column chromotography:

Principle: Different proteins are adsorbed to different extents in the column. This principle is used to separate proteins.

Procedure: A long column is packed with suitable adsorbent. A solution containing a mixture of proteins in a suitable solvent is added to the top of the column. The solution percolates down the column. Different proteins are adsorbed at different places in the column. Now the column is eluted with a suitable eluent. The proteins come out one after the other. Thus they are seperated.

GOLD NUMBER

The lyophilic colloids widely in their powers of protection. The protection action of different colloids is measured in terms of the 'Gold Number' introduced by Zsigmondy. The gold number is defined as ***the number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10 percent sodium chloride solution.***

The onset of the precipitation of the gold solution is indicated by a colour change from red to blue when the particle size just increases.

The gold numbers of a few protective colloids are given in table. The smaller the gold number of a hydrophilic colloid, the greater is its protective power. Gelatin has a small gold number and is an effective protective colloid. Starch has a very high value, which shows that it is an interactive protective colloid.

Table – Gold numbers of some hydrophilic colloids

Lyophilic colloid	Gold number
Gelatin	0.005 – 0.01
Egg albumen	0.08 – 0.10
Gum arabic	0.10 – 0.15
Potato Starch	25

The use of protective colloids to stabilise colloidal systems is widespread. In the preparation of ice cream, gelatin is added to act as a protecting agent to the colloidal particles of ice. If the ice particles coagulate, the smooth texture of ice cream is lost. Argyrol, used in the eye drops, is a solution of silver protected by organic materials.

Origin of charge on solution particles

All the dispersed particles of a particular sol carry a positive or a negative charge. They acquire this charge by

A. Adsorption of ions from the aqueous medium.

B. Ionisation of surface groups.

EMULSIONS

What are they? An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids. An emulsion may be defined as a dispersion of finely divided liquid droplets in another liquid.

Eg. : Milk, Butter, etc.,

Types:

The emulsion may be classified into two types.

Oil – in – water emulsions (O/W):

An oil can be dispersed In water to give O/W emulsion.

Example: Milk.

In milk, fat globules which are liquid droplets are dispersed in water with casein as emulsifier.

Water (dispersion medium)

Oil (dispersed phase)
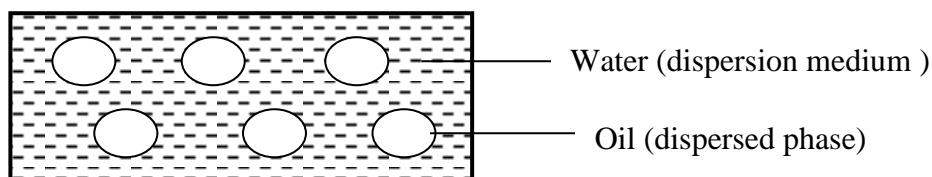
Water-in-oil emulsion(W/O):

If a Little water is shaken with an excess of oil an emulsion of water in oil (W/O emulsion) type is formed.

Example: Butter

In butter fine water droplets are dispersed in liquid fat.

Oil (dispersion medium)

Water (dispersed phase)
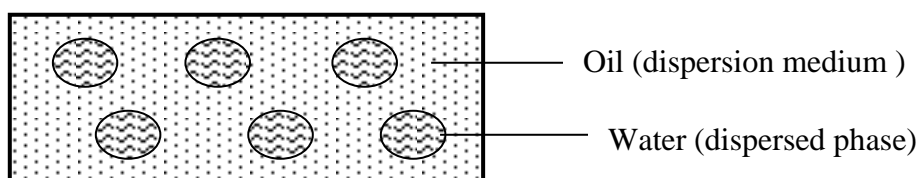
Identification water of the type of emulsion:

To find the type of a give emulsion the following methods are adopted.

i.   A small amount of an oil-soluble dye is added to the emulsion under examination. Water in oil emulsion will take up the colour of the dye but an oil in water emulsion will not mix with the dye and so the emulsion will remain colour less.

ii.   The electircal conductivity of the emulsion under examination is measured If the conduction is appreciable than it is and oil in water emulsion . If the conductivity is negligible then it is a water in oil emulsion.

The type of emulsion formed in a given case depends largely upon the relative proportions of the constituent liquids. The constituent which is in excess forms the dispersion medium. Thus, if water is in excess we get oil in water emulsion On the other hand if oil is in excess we get a water in oil emulsion.

Preparation: When the concerned liquids are mixed and shaken vigorously a dispersion of very droplets of one liquid in the other will result.
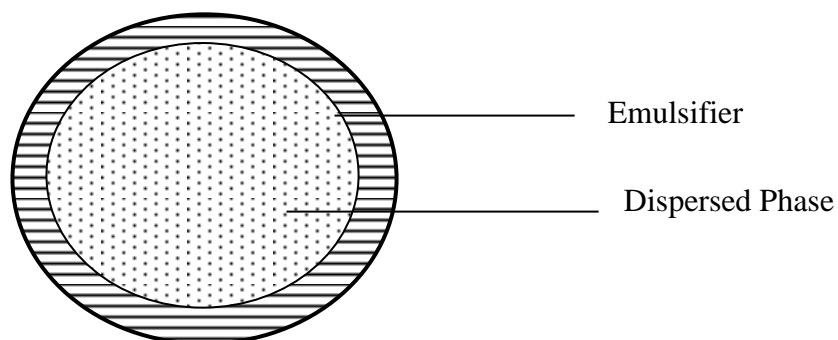
Such emulsions are not stable and separate and into two layers on standing. To stabilize and emulsion the addition of a third substance known as emulsifying agent or emulsifier is essential The emulsion forms a thin film around every drop of the dispersed phase and hence prevents drops from coming together (in other words it reduces the interfacial tension between the two liquids). In milk the emulsifying agent is casein. Soapsgum and gelatin are useful emulsifiers.

Properties:

1) Emulsion show all the properties of sols. The particle size of the dispersed phase is larger than those in sols.

2) They usually carry negative charges and are coagulated by positively charged ions.

3) Emulsions show Tyndall effect and Brownian movement .They also exhibit electrophoresis.

4) The electrical conductivity of aqueous emulsion (o/w emulsion) is higher than that of an oily emulsion (w/o emulsion)

5) **De-emulsification:** The process of breaking of emulsion in two components is known as de emulsification. This can be achieved by methods like heating, freezing, centrifuging, electrophoresis or by destroying the emulsifier chemically.

Applications:

Emulsions play an important role in our everyday life. They have many important applications in industry medicine and cosmetics.

1) Milk is an emulsion it is colloidal system in which fat globules are dispersed in water with casein as emulsifier.

2) Butter crude petroleum etc., are also emulsions.

3) A variety of emulsion are used in leather industry to make the leather soft.

4) The detergent (cleaning) action of soap is due to emulsification of oily or greasy materials. The soap is more strongly adsorbed at the fibre water inter face the grease is displaced from the fibre and the globule is detached into water to be emulsified by the soap.

5) Numerous medicines and phamaceutial preparation are emulsions Eg., Cod-liver oil.

6) Vanishing creams, hair creams are emulsions

7) Phenol and Lysol give emulsion which act as disinfectants

8) Many paints and distempers are applied in the form of emulsion.

9) Oild emissions are added to finely divided ores in the concentration of ores by oil-floatation process.

10) Many spraying liquids are used in the form of emulsion in agriculture.

GELS:

A gel is a jelly like colloidal system in which a liquid is dispersed in a solid medium. When a hot solution of gelatin is cooled it sets to a semi solid mass(gel) Thecolloidal (gelatin) molecules grow progressively bigger until they touch each other and form a kind of network which can enclose the entire dispersion medium.

Example:

Jellies, gelatin, agar-agar, aluminium hydroxide etc.,

Preparation:

1. By cooling:

Gels of agar agar , gelatin etc., are prepared by dissolving them in hot water and allowing the solution to cool.

2. By coagulation:

Many colloidal solution can be changed into gels by coagulation Adding a coagulating agent into the colloidal sol gives a gel. Gels of $Al(OH)_3$ and $Fe(ON)_3$ may be prepared by adding salts as coagulating agents to their sols.

3. By double decomposition:

When dilute acid is added to solium silicate, silicic acid gel is obtained.

$$Na_2SiO_3 + 2HCl \longrightarrow H_2SiO_3 + 2NaCl$$
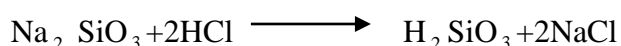
4.   By exchange solvent:

Gels may be formed by changing suddenly the solvent in which the substance is insoluble. For example when pure alcohol is added to an aqueous solution of calcium acetate the sol first of formed sets in the form of a gel.

Classification:

Dry gels are called xerogels. Examples gelatin: sheets and cellophane. Depending upon the dispersed phase the gels are named as follows: 'hydrogel' when water is dispersed phase 'alcogel' when alcohol is used and 'benzogel' when benzene is the dispersed phase.

Gels are broadly classified into types : elastic and non elastic.

i. Elastic gels:

Elastic gel are those which possess the property of elasticity.They changed they shaped on applying force and return to orginal shape when the force is moved. Gelatin starch and soaps are examples of substances which form elastic gels. Partial dehydration of an elastic gel(eg., gum) gives elastic solid from which from the gel can be obtained by the addition of water.

ii. Non – elastic gels:

Non-elastic gels (or irreversible gels) are those which are rigid e,g., silica gel. On dehydration it gives a glassy powder which cannot be reconverted into gel by adding the solvent (Distinction from elastic gels)

Properties:

1. Hydrations:

A completely dehydrated elastic gel can be regenerated by addition of water. But once a non elastic gel is freed from moistures addition of water will not bring about gelatin.

2. Swelling (Imbibition):

Partially dehydrated elastic gels imbibe water when immersed in the solvent. This causes the increase in the volume of the gel and the process is called "swelling (or imbibition) of gel"

3. Syneresis:

Many inorganic gels on standing may shrink and lose (exude) the liquid held by it. This process is termed 'syneresis" (or weeping)

4. Thixotropy:

Some gels are semi solids when at rest but revert to liquid sol on agitation. (some gels liquify on shaking an reset when allowed to stand)

This sol-gel transformation is know as "thixotropy". Iron oxide and silver oxide gels exhibit this property.

Applications:

1. Silica gel is used to absorb moisture and hence used as a dehydrating agent.

2. Gelatin and agar-agar gels are used in laboratories for making liquid junctions in electrochemistry.

3. Curd and eatable jellies are forms of gels.

4. Protected gels are used in food preparations such as ice creams, halva etc.,

5. Boot polishes and animal tissues have gel structures. The setting of cement is due to the formation of gels.

6. Dyeing fabrics like cotton, silk, wool, etc., takes place by gel formations.

4.3. Polymer Chemistry

4.3.1. Basic concepts :-

Polymers : -

Polymers are large molecules formed by repeated linking of small molecules (called monomers).

Polymers are made by sequential addition of many monomer molecules to each other.

$$nA \longrightarrow A - A - \equiv .... A -(A)_{n-2} - A$$
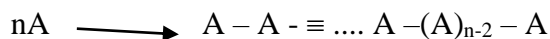
Eg : - Polyethylene is a polymer formed by linking together large number of ethylene molecules (monomers) .

$$nCH_2 = CH_2 \longrightarrow -(CH_2 - CH_2)_{\overline{2}}$$

Ethylene   Polyethylene
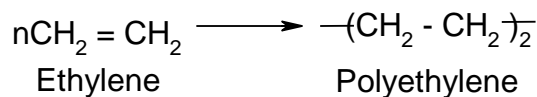
Monomers : -

Monomers (meaning, single part) are simpler and smaller molecules (micro molecules) of similar (or) different types, which react with each other to form a polymer. Monomer should contain a double bond or two or more functional groups.

Some monomers and the repeating units in the polymers : -

Sl. No	Monomer	Repeating unit in the polymer.
1.	Ethylene, $CH_2=CH_2$	$-(CH_2-CH_2)_n$ polyethylene

2.	Vinnylchloride, $CH_2=CH$
	          |
	          Cl
		$-CH_2-CH-$ polyvinylchloride (PVC)
		          |
		          Cl

3.	Styrene, $CH_2=CH$
	        |
	        C_6H_5
		$-CH_2-CH$ polystyrene (Ps)
		       |
		       C_6H_5

4.	Methyl CH_3
	             |
	 methacrylate $CH_2=C$
	             |
	             $COOCH_3$
		CH_3
		        |
		 $-CH_2-C-$ Polymethyl
		      | methacrylate (PMMA)
		      $COOCH_3$

5.	$CF_2=CF_2$ Tetrafluoroethylene	$-CF_2-CF_2-$ polytetrafluora ethylene (PTFE).

Bi functional monomer :-

i)   Linear (or) straight chain molecule.
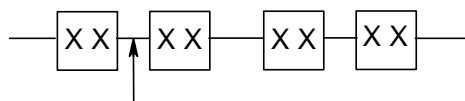
Strong Covalent bond

ii)   Branched – Chain moldcule.

Weak Vanderwall's forces

Strong Covalent bond
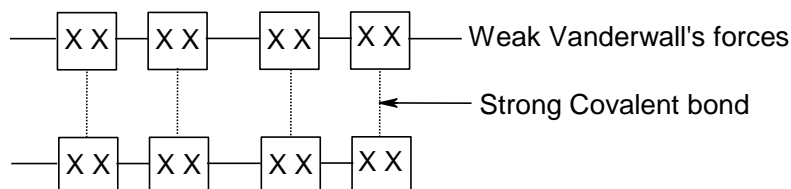
Poly functional monomer:-

Primary bonds
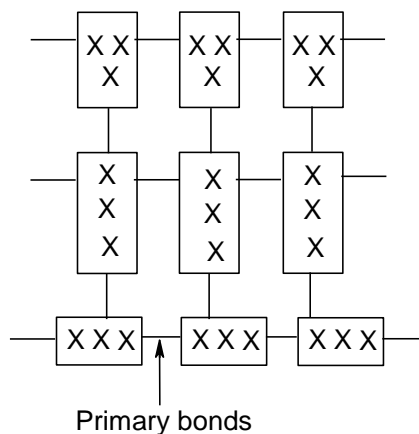
Addition polymers : -

They are obtained by the addition of several structural units of the monomer without the elimination of any of product molecules. Eg : - In polyethylene, the monomer is ethylene $(CH_2 = CH_2)$ but the structural unit is (- CH_2 – CH_2 -). So there great difference in structural unit and the monomer. The length of the polymer molecule depends upon the number of structural units in the chain. This is known as the degree of polymerization (DP). The properties of a polymer depends on its D.P.

The polymers of different D.P. may now be manufactured to suit the specific requirements. PVC sheets can be made with a D.P. of 500, while a D.P. of 1000 is required to manufacture PVC pipes and fittings. Eg : - polyethylene, polyvinyl chloride, polystyrene, PMMA.

Condensation polymers : -

This type of polymers are formed by the process of condensation ploymerisation. They are formed from monomers bearing two or more reactive groups of such a character that they may condense intermolecularly with the elimination of a bye product, often water.

X Ho – R – COOH $\rightarrow$ Ho (- R – Coo -) (X –I) R – (OOH + (X –I)H_2O

Eg : - Bakelite (phenol – formaldehyde)

urea – formaldehyde, melamine, polyesters, polyoxides, epoxy resins.

Polymer Structure

A polymer may consist of identical monomers (or) monomers of different chemical structure and accordingly they are called homopolymers and copolymers respectively. Thus

…….M – M – M – M – M ………

Homopolymer

……..M_1 – M_2 – M_1 – M_2 – M_1 – M_2 ……..
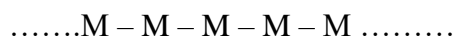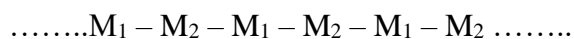
co – polymer.

The monomeric unit in a polymer may be present in linear, branched, and cross linked (three – dimensional) structure.

i) Linear structure (or) polymer : -

It is one in which the repeating units are similar to the links in a very long chain.

Eg : -   …….M – M – M – M – M – M ……..
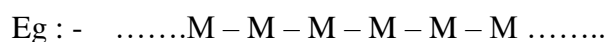
Linear homo polymer

………..$M_1 - M_2 - M_1 - M_2 - M_1 - M_2$ ………..

Linear co – polymer.

Branched structure (or) polymer : -

It is one in which some of the molecules are attached as side chains to the linear chains.

Back bones : -

Eg :

M - M - M - M - M **. . . . .**
|
Branching of ⟶ M
same monomer |
M
|
M

(Branched chaind home polymer)

Eg : M_1 ⟵ Branching
          |
          M_2 ↓ Bact Bone
          |
. . . . $M_1 - M_2 - M_1 - M_2 - M_1 - M_2 - M_1 - M_2 -$
                          |
                          M_1
                          | ⟵ Branching of Comonomers
                          M_1
                          | Comonomers
                          M_2
                          |

(Branched Copolymer)
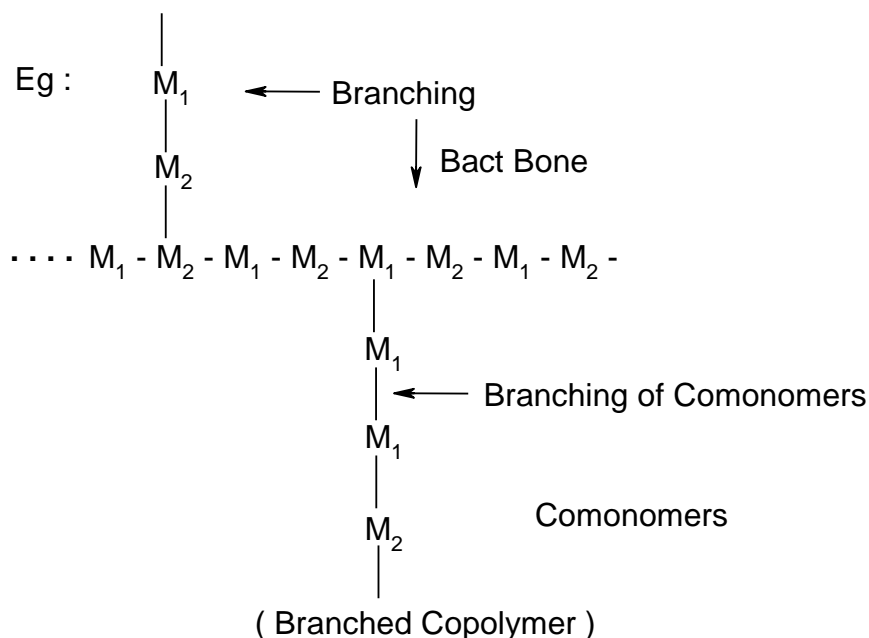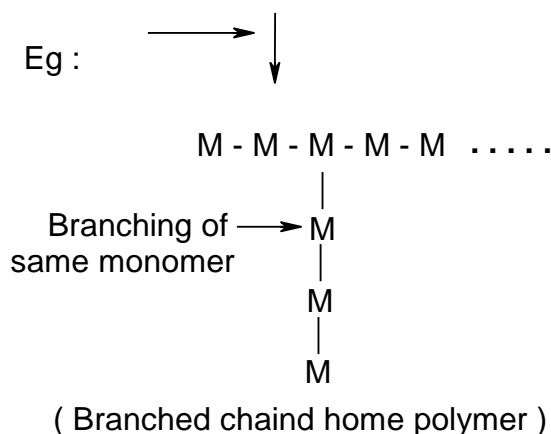
iii) Cross – Linked structure (or) polymer : -

It is one in which more branching at random points connecting many chains give rise to network or cross – linked polymers.

```
                    | Monomer Unit
                    ↓
Eg :-   · · · · · M - M - M - M - M - M - M  · · · · ·
                          |                 |
                          M ←— Cross Link —→ M ←— Cross Link        Cross Linked Polymet
                          |                 |
· · · · · M - M - M - M -      M —        M - M - M · · · · ·
                          |                 |
                          M                 M
                          | ←— Cross Link   | ←— Cross Link
                          M                 M
                          |                 |
                          M                 M
                          |                 |
          · · · · · M —— M —— M —— M —— M —— M —— M —— M · · · · ·
```
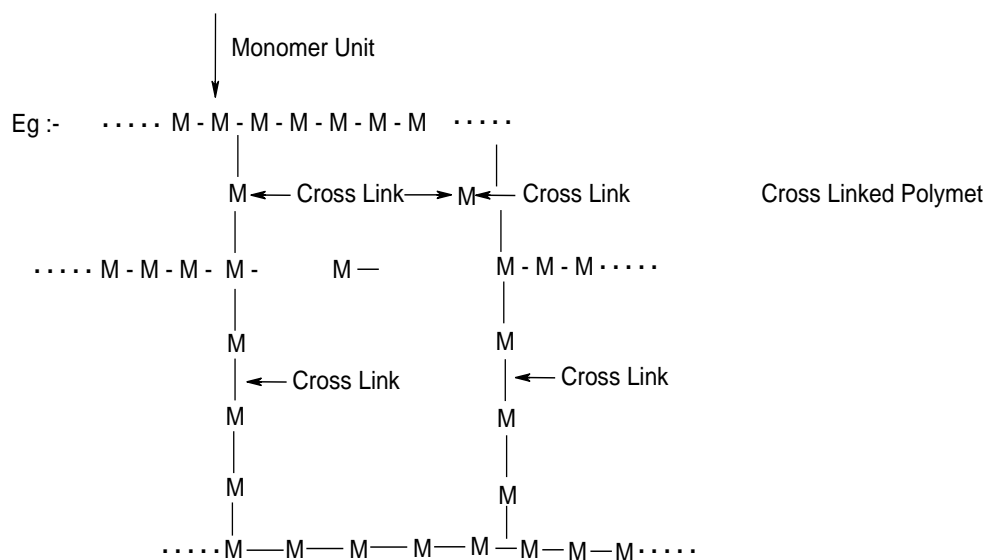
4.3.3 Mechanism and kinetics of free radical and addition polymerisation.

Polymerisation through multiple bonds chain growth or addition or polymerisaction :-

The term addition polymerisation was given by carothers (1929) was moidified by H.F. Mark (1950) as chain polymerisation. This type of polymerisation involve the self addition of normal unsaturated molecules of one or two monomers without loss of any small molecule to give a single gaint molecule. Reactions of this type involve the successive stages of initiation, propogation and termination common to chain reaction in general. This process of chain polymerization can be brought of chair polymerization can be brought about by a free radical (or) coordination mechanism.

No by product is formed. The product has the same elemental composition as that of the monomer. The bifunctionality is provided by the double bond present in the monmenr. Compounds containing reactive double bonds can undergo this type of reactions.

Typical examples are vinyl compounds ($CH^2 = CHX$), allyl compounds ($CH_2 = CH\ CH_2X$), olefins ($CH_2=CHR$) and dienes ($CH_2 = CR-CH=CH_2$). Since most of these monomers can be classified as 'Vinyl', chain polymerization is known as 'vingl polmerisation'.

Eg :-

1.
$$nH_2 C = CH \longrightarrow (CH_2 - CH)_n$$
|　　　　　　　　　　|
Cl　　　　　　　　　Cl

Vinyl Chloride　　　Poly vinyl Chloride (PVC)

2.
$$n \, CH - CH_2 \longrightarrow \left[\begin{array}{c} CH - CH_2 \end{array} \right]_n$$

Sty rene　　　　　　Poly Styrene (PS)

3.
$$n \, CH_2 = CH \longrightarrow \left[CH_2 - CH \right]_n$$
|　　　　　　　　　　　　|
CN　　　　　　　　　　CN

Acrylonitrile　　　　Poly acrylonitrile (PAN)
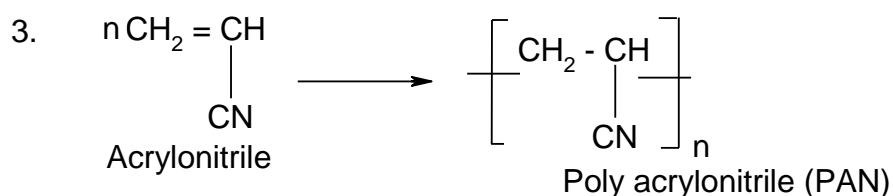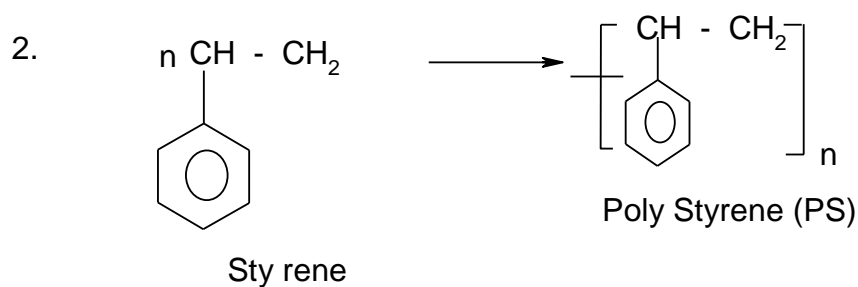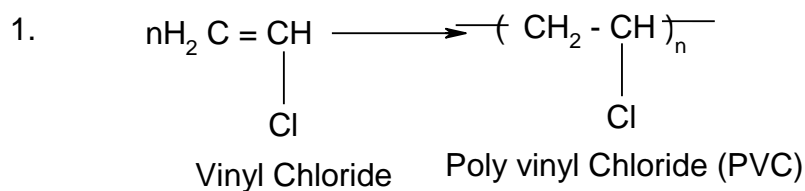
Mechanism of free radical polymerisation reaction:-

　　　In free radical polymerisation, monomer is activated by its transformation into radical by the action of light, heat, ionzing radiations, catalysts etc., Initiators are decompoxsed into free radicals so that monomer molecule can interact with these free radicals for their activation.

Eg :-

1.
$$H_3 C - C - N - N - C - CH_3 \xrightarrow{Heat} 2 \, H_3 C - C^o + N_3 \uparrow$$

Azobis Iso butyro nitrile　　　　　Cyanopropyl radical

2. Benzoyal Peroxide

$$\xrightarrow{Heat} 2 \, \bigcirc - C - O^o$$

$$2 \, \bigcirc^o + 2 \, CO_2$$
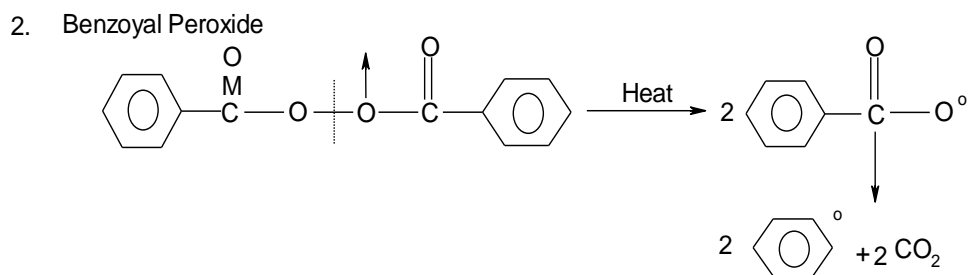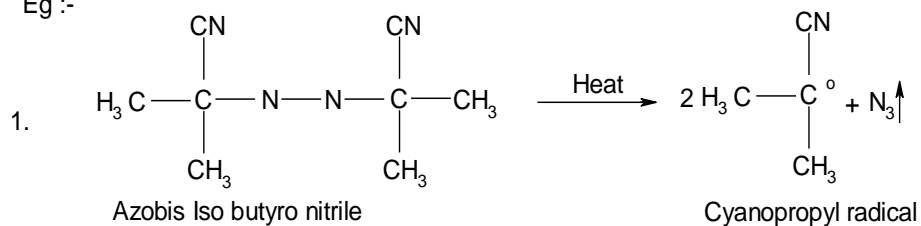
Free radical polymerisation involves addition of free radicals to the double bond of the monomer, addition, first of the free radical generates from the initiator, and then of the growing polymer module.

Initiation step:-

Chain initiation involves two steps:-

  i.   Production of free radicals (R^o) by the hemolytic dissociation of an initiator (R-R).

$$R:R \longrightarrow 2R^o$$

  ii. The second step involves the addition of this free radical (R^o) to the first monomer molecule (M) to produce the chair initiation species M^o

$$R^o + M \longrightarrow M^o_1$$
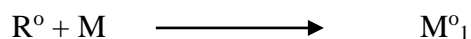
Free radical monomer chain initiating molecule.

Propogation step:-

Chain propogation is accomplished by the addition of monomer molecule to M^o leading to the formation of macro – radicals.

$$M^o_1 + M \longrightarrow M^o_2$$
$$M^o_2 + M \longrightarrow M^o_3$$
$$M^o n + M \longrightarrow M^o_{n+1}$$
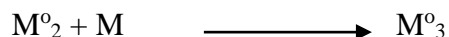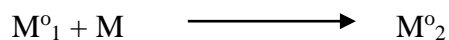
Termination step:-

In this step the resultion macro-adical may be converted into inactive polymer molecule by any one of the following ways.

i)   Recombination of primary radicals:-

$$R^o + R^o \longrightarrow R - R$$

ii) Combination of macro radicals:-

$$M^o_{n+I} + M^o n+I \longrightarrow M - M$$
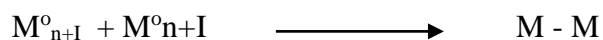
iii) Combination of a macro radical with primary radical

$$M^o_{n+I} + R^o \longrightarrow M - R$$
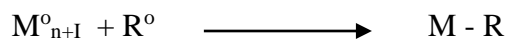
vi) Disproportionation:-

Trans of a hydrogen atom of one radical centre to another radical center resulting in the formation of a saturated and an unsaturated polymer,

$$M^o_n + M^o_m \longrightarrow M_n - M_m$$

There is yet another method of chain termination which takes place by the chain transfer and / or by the addition of inhibitors.

Molecular weight of a polymer:-

When we speak of molecular of a polymer, pt is however quite different from that applied to small sized compounds. Polymers are poly disperse and Quite heterogenous in molecular – mass. In other words, polymers are mixtures of molecular of different molecular masses. Three type of molecular – mass of polymers have ben recognized:

i)   Number - Average molecular mass

$\overline{M}_n$ is determined by measurement of colligative properties [such as freezing point depression [cryoscopy], boiling point elevation [ebullimetry], usmotic presseure and lowering of vapour pressure]. $\overline{M}_n$ is defined as the total mass (w) of all the molecules in a polymer sample divided by the total number of molecules present. Thus, the number average molecular mass is

Where Ni is the number of molecules of mass Mi,

The number – average molecules – weight is a good index at physical propersties such as input and tensile strength, but is not a good index at other properties such as flow.

Weight – Average Molecular Mass (Mw)

$\overline{Mw}$ is obtained from light – scattering and ultra – centrifugation technique, which measure molecular size.

It is defined as,

$$\overline{Mw} = \frac{w}{\sum N} \frac{\sum W_i M_i}{W_i}$$

$$\overline{Mn} = \frac{\sum N_i M_i}{N_i}$$

Where w_i is the weight fraction of molecules, whose mass is

Mi

M_w can also be defined as,

$$\overline{Mw} = \frac{\sum C_i M_i}{C_i} = \frac{\sum C_i M_i}{C} = \frac{\sum N_i M_i^2}{N_i M_i}$$

Where (C_i = weight – concentration of Mi molecules,

C= total- weight concentration of all polymer molecules.

4. 3. 2. Co – Polymerisation

Co – polymerisation is the process in which a mixture of two or more monomers gets polymerised to yield product. The product obtained is known as co – polymer. A co – polymer product contains some units of each type of monomer and is different from a physical mixture of individual polymer molecules formed by different monomers.

Example :

Vinyl chloride and vinyl acetate can be mixed to give mixture and then mixed polymerised to give a poly (vinyl chloride – vinyl acetate)

$$CH_2 - CH - CH_2 - CH - CH_2 - CH - CH_2 - CH$$
$$\qquad | \qquad\qquad | \qquad\qquad | \qquad\qquad |$$
$$\qquad Cl \qquad\qquad Cl \qquad\quad OCOCH_3 \qquad Cl$$
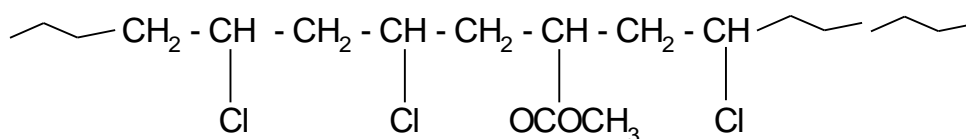
Classification of copolymers : -

Copolymers are classified into four types depending upon the nature of the distribution of different monomer in the polymer chain.

1. Random copolymers.
2. Alternating copolymers.
3. Block copolymers.
4. Graft copolymers.

1. Random copolymers : -

Random copolymers are obtained by the random arrangement of monomer units in the chain.

- A – B + A – A – B – A – B – B – A – A – B –
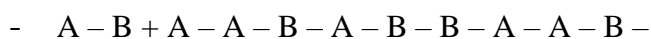
Random copolymers are produced under specific polymerization conditions.

2. Alternating copolymers : -

In alternating copolymers the monomers are produced alternately along the copolymer chain.

- A – B – A – B – A – B – A – B –
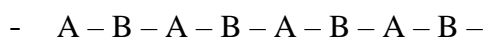
Alternating copolymers are produced during condensation polymerization when two different types of monomers like diacid and diols are used.

3. Block copolymers : -

Block copolymers is a linear copolymer that contains long chain of one monomer with another monomer in the polymer chain.

$$-A – A – A – A – B – B – B – B – A – A – A – A –$$
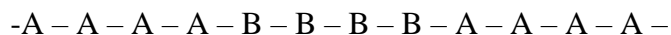
The block copolymer sometimes are made up of two or three long blocks of each type of unit giving a material with interesting properties. In block co – polymerisation, the macromolecules is made up of block of considerable length consisting entirely of one type monomer.

4. Graft polymer : -

Graft polymer are branched molecules where main chain is made entirely where the main is made entirely of one repeat unit, while the branch – chains are made of another repeat unit.

Graft co – polymers through co – polymerisation : -

In this method, one dissolves an unsaturated polymer in the monomer to be grafted on and polymer in the monomer to be grafted on and allows the monomer to polymerize the double bond of the polymer is then incorporated into the growing chain of the polymerizing monomer. An important example is the graft polymerization of an unsaturated polyester costing resin.

$$\sim\!\!\!\sim OC - CH = CH - CO - OCH_2 - CH_2 - OCO - CH = CH - CO - OCH_2\, CH_2O \sim\!\!\!\sim$$

Unsaturated Poly coster)

$$\sim\!\!\!\sim CH - C_6H_5$$
$$|$$
$$CH_2 \quad \backslash$$

$$\sim\!\!\!\sim OC - CH - CH - CO - OC - H_2\, CH_2O - CO - CH - CH - CO \sim\!\!\!\sim$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_2 \qquad\qquad\qquad\qquad\qquad\qquad CH_2$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH - C_6H_5 \qquad\qquad\qquad\qquad\quad CH - C_6H_5$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH - C_6H_5 \qquad\qquad\qquad\qquad\quad CH - C_6H_5$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_2 \qquad\qquad\qquad\qquad\qquad\qquad CH_2$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\sim\!\!\!\sim OC - HC - CH - CO - CH_2 - CH_2O - CO - CH - CH - CO \sim\!\!\!\sim$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$

Cross Linked polycester) resin.

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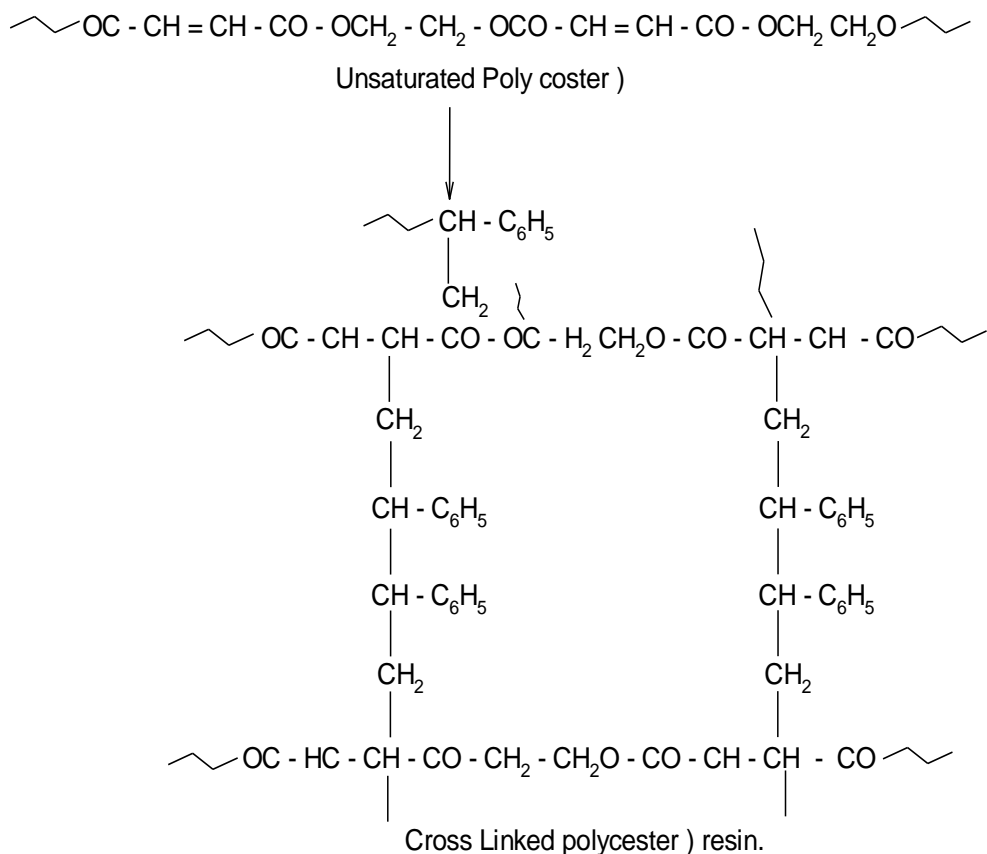
4.3.6 Application of polyethylene :-

Poly ethylene can be used as pipes for piping hot liquids and also as corrosion resistant lignin for chemical plants.

❖ There are two varieties of polyethylene. These are low density and high density polyethylenes. Low density poly ethylene consists of molecules with branches. High density polyethylene is essentially lineas.

❖ Low density polyethylene is produced by the high pressure polymenisation of ethylene, making use of oxygen as an initiator, In addition to oxygen, other initiators such as peroxides, hydroperoxides and azo compounds can also be used.

❖ No solvent can dissolue low density polyethylene at room temperature. But it is soluble is many solvents at high temperatures. Some of these solvents are toluene, carbon tetra chloride, xylene, trichloro ehhyle etc., The disso wed polymer precipitates out as the solution is woled at room temperature.

❖ High density polyethylene is much stiffer than low density poly ethylene and has a higher tensile strength and hardness. Chemically it is more resistant than low density polyethylene and has a significantly lower gas permeability.

❖ High density polyethylene is prepared by coordination polymerization of ethylene monomer by tricthyl aluminium and titanium tetrachloride $[(C^2H^5)_3Al.Ticl_4]$ (Zeigler's Nana catalyst).

Poly vinyl resins:-

The poly vinyl resins are synthetic polymers made from compounds having the vigyl ($-CH = CH_2$) group. The polymerization reactors for these polymers is the free radical ploymerisation os the alkene group. The most important members of this class are poly vinyl acetate, poly vinyl chloride, poly vinyl alcohol and co-polymers of vinyl chloride with vinyl acetate and vinylidene chloride.

The monomer vinyl chloride, vinyl acetate and vinylidene chloride are used in the production of nor only the fibres but also the rubber like and brittle resbn is also, The resins are thermo plastic because the monomers are biofunctional and double bonds of the vinyl group give rise to polymer growth in two directions.

Application of biomedical polymers for contact causes & dental uses:-

1. Phosphorus – Based like, the sodium maddrell's salt is used as a polishing agent in dental surgery & the borophosphate glasses are used for manufacturing optical lenses.

Maddnell's salt :-

Sodium polymetal phosphates $NaPo_3$-II & $NaPo_3$-III are known as Maddnell's salt.

NOTES

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UNIT- V
THERMO CHEMISTRY

Kirchoh's equation :

Enthalpy of a reaction depends upon the temperature. The temperature dependence can be obtained by expressing the enthalpy of the reaction.

The enthalpy change for the reaction

$$aA + bB \longrightarrow cC + dD \longrightarrow \qquad (1)$$

$$\Delta H = \Sigma H \longrightarrow \Sigma H$$

Product reactant

$$\Delta H = (cHC + dHD) - (aHA + bHB) \longrightarrow (2)$$

Differentiating with temperature at constant pressure (P) we get

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left[c\left(\frac{\partial HC}{\partial T}\right)_P + d\left(\frac{\partial HD}{\partial T}\right)_P\right]$$

$$- \left[a\left(\frac{\partial HA}{\partial T}\right)_P + b\left(\frac{\partial HB}{\partial T}\right)_P\right] \longrightarrow (3)$$

Since $\left(\frac{\partial H}{\partial T}\right)_P = C_P$

$$(3) \Rightarrow \Delta Cp = [cCp, C + d C p, D] - [aCp, A + b Cp, B] \longrightarrow (4)$$

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta Cp \longrightarrow \qquad (5)$$

This is show that variation of ΔH of a reaction with temperature at constant pressure is equal to ΔCp of the system.

Similarly for the ethalpy of the reaction at constant volume, we have

$$\left(\frac{\partial(\Delta E)}{\partial T}\right)_V = \Delta C_v \longrightarrow \qquad (6)$$

This is shown that the variation of ΔE of a reaction with temperature at constant volume is equal to Δ CV of the system.

Where Δ CP and Δ CV equal to sum of heat capacities of products – sum of heat capacities of reactions.

From equations (5) a (6) show that " the rate of change of enthalpy of a reaction with temperature is equal to the difference in the heat capacities of the products and the reactions."

On intergration of equation (5) between the two temperatures (T, & T_2) gives,

$$(5) \Rightarrow \left(\frac{\partial(\Delta H)}{\partial T} \right)_P = \Delta CP$$

$$\int_{H1}^{H2} d(\Delta H) = \int_{T1}^{T2} \Delta Cp \, dT \longrightarrow \qquad (7)$$

$$\left[\Delta H \right]_{H1}^{H2} = \Delta Cp \left[T \right]_{T1}^{T2}$$

$$\Delta H_2 - \Delta H_1 = \Delta Cp \left[T_2 - T_1 \right] \longrightarrow (8)$$

If Δ Cp is not a constant, it can be expressed as function of temperature in the form.

$$Cp = a + bT + CT^2 + \ldots \ldots \ldots \longrightarrow \qquad (9)$$

Where a, b and C are constants for a given species, Hence

$$\Delta Cp = \Delta a + \Delta bt + \Delta CT^2 + \ldots \ldots \longrightarrow (10)$$

Where, $\quad a_{pdt} - a_{\text{reactant}}$

$$\Delta a = apdt - a \text{ reactant} \longrightarrow \qquad (11)$$

$$\Delta b = bpdt - b \text{ reactant} \longrightarrow \qquad (12)$$

Equations (10) substituted in eqn (7)

$$\int_{H1}^{H2} d(\Delta H) = \int_{T1}^{T2} \left(\Delta a + \Delta bT + \Delta CT^2 \right) dt \longrightarrow \qquad (13)$$

$$\Delta H_2 - \Delta H_1 = \int_{T1}^{T2} (\Delta a) dT + \int_{T1}^{T2} (\Delta bT) \, dT + \int_{T1}^{T2} \left(\Delta CT^2 \right) dT \longrightarrow (14)$$

$$\Delta H_2 - \Delta H_1 = \Delta a \left[T \right]_{T1}^{T2} + \Delta b \left[\frac{T^2}{2} \right]_{T1}^{T2} + \Delta C \left[\frac{T^3}{3} \right]_{T1}^{T2}$$

$$\Delta H_2 - \Delta H_1 = \Delta a \left[T_2 - T_1 \right] + \frac{\Delta b}{2} \left[T2^2 - T1^2 \right] + \frac{\Delta C}{3} \left[T2^3 - T1^3 \right] \longrightarrow (15)$$

This eqn is known as integrated kirchoff's equation.

Eqns (5) & (6) also known as kirchoff's eqn.

Flane & Explosion temperatures:

The combustion of a gaseous fuel in air takes place so that the heat produced during combustion doesn't get any opportunity to be dusipated to the surroundings.

So the combustion process in equivalent to an adiabatic process.

Maximum flame temperature :

The maximum temperature attained in the combustion of hydrocarbons (fuel) under adiabatic condition at constant pressure in the presence of air or orygen is known as the maximum flame temperatures.

Calculation for the flame temperatures:

For an adiabetic process the maximum flame temperature can be calculated using the kirchaff's equation.

$$\frac{\partial(\Delta H)}{\partial T} = \Delta Cp \longrightarrow \qquad (1)$$

On integration

$$\int_{H1}^{H2} d(\Delta H) = \int \Delta Cp\, dT \longrightarrow \qquad (2)$$

$$\Delta H_2 - \Delta H_1 = \Delta Cp\ (T_2 - T_1) \longrightarrow (3)$$

Hence, knowing ΔH, ΔCp and the initial temperature T, the final temperature T_2 can be calculated .

Air contains about 20% by volume of oxygen and 8% by volume of hydrogen, the combustion reaction involving. One mole of oxygen is associated with four moles of unreacted nitrogen in the products.

Thus the combustion of hydrogen gas in air can be represented as,

$$2H_2\ (g) + O_2\ (g) + 4N_2\ (g) \longrightarrow 2H_2O\ (g) + 4\ N_2\ (g)$$
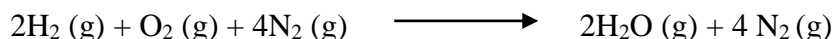
Hence ΔCp is considered as equal to the sum of the products plus the four moles of unreacted nitrogen pre mole of oxygen gives during combustion.

Hence,

$$\Delta Cp = \Sigma Cp + 4Cp\ N2 \longrightarrow (2)$$

Accordingly for determined flame temperature, ΔCp in eqn (1) is neplaced by ΣCp.

Where ΣCp is the heat capacities of products of combustion & the unreacted nitrogen.

Maximum explosion temperature.

If the combustion is carried out under adiabatic condition at constant volume, the maximum temperature attained is called maximum explosion temperature.

Calculation for the explosion temperature:

The calculation of explosion temperature is similar to that of the flame temperature except that ΔH is replaced by ΔU. The pressure required for the system at the explosion temperature is called the maximum explosion temperature.

5.2 Second law of thermodynamics

5.2.1. Limitations of the first law (or) need for second law

    i.   The Ist law gives the relationship between Internal energy (E), heat absorbed (g) and work done (w).

$\Delta E = q - W$

But it does not gives the direction of flow of heat i.e., heat flows from hotter end to colder end only. The reverse process is not possible but the Ist law says both the process are possible.

    ii.   The Ist law says the energy of a system always remains constant and it doesn't says anything about feasibility of a reaction.

        Some reaction occurred in its own accord. [Natural process (or) spontanious process]

    iii.   The Ist law says one form of the energy is completely converted to another form in equiuvalent amount.

But the complete conversion of heat (g) into work (W) is not possible i.e, $q \neq W$

Because of these limitations we need second law.

To predict the direction of flow of heat, feasibility of a reaction and fraction of heat is converted into work.

Statement of second law:

Classius Statement :

    i.   One form of the energy is converted into another form where as complete conversion of heat energy into any other form is impossible.

    ii.   Entropy of the universe is always increases.

i.e, $\Delta S > O$ (or) $\Delta S = + Ve$

Kelvin's Statement :

Heat cannot be transform from colder end to hotter end without the help of some external energy.

It is impossible to construct a machine which convert the complete heat energy.

Spontaneous Process (or) Natural process (or) Irreversible process:

The process which occurs on the own nature is called spontaneous process.

eg:

    i.   Flowing of river from hills.

    ii.   Gases flow from high pressure region to low pressure region.

    iii.   Heart beat and blood circulation

Criteria for sportaneous process:

    i.   We need not to supply any energy

    ii. $\Delta H = - Ve$

    iii. $\Delta S = + Ve$

Cyclic Process:

When a system after completing a serious of changes returns to original state.

It is said to be have completed the entire process in known as cyclic process.

Since the internal energy of a system depends only upon its state is follows, that in a cyclic process, the net change of internal energy is zero.

i.e. $\Delta E = O$

According to the Ist low,

$\Delta E = q - w$

$O = q - w$

$$\boxed{q = w}$$

These are three types of cycles in a cyclic process.

    i.   Iso thermal cycle

    ii.   Reversible cycle

    iii.   Carnot cycle

(i) Iso thermal cycle:

If the serious of changes in a cycle are conducted at constant temperature, the cycle is said to be an isothermal cycle.

(ii) Reversible cycle:

If the changes are carried out reversibly the cycle is said to be a reversible cycle.

(iii) Cannot cycle:

The most important well known cyclic process is cannot cycle.

Cannot is 1824 design a hypothetical heat engine called cannot cycle.

The carnot engine, the working substance is one mole of an ideal gas, the engine works reversible in cyclic process ($\Delta E - O$). Let the temperature of the source will be T_2 and the temperature of the sink will be.
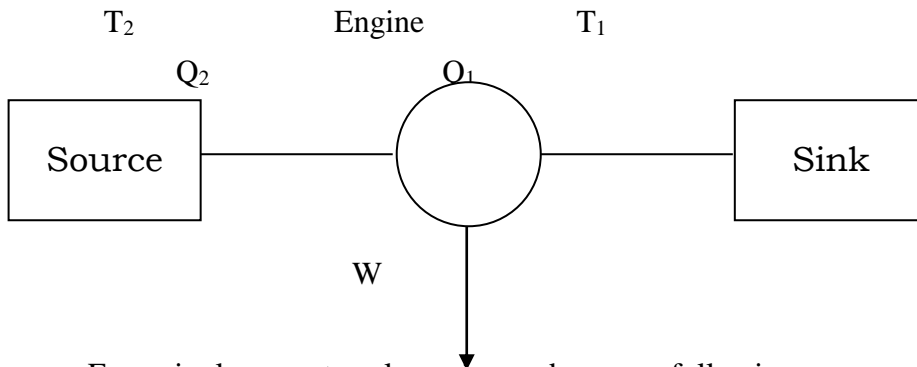
For a single cannot cycle engine undergoes a following process.

   i.   Isothermal reversible expansion

   ii.   Adiabetic reversible expansion

   iii. Isothermal reversible compression

   iv. Adiabetic reversible compression

$$Efficiency\left[\eta\right] = \frac{Work\ done}{heat\ absorbed}$$

$$\eta = \frac{W}{Q_2} \longrightarrow \qquad (1)$$

(i) Isothermal reversible expansion :

Let 1 mole of an ideal gas absorbed [Q_2] from source [T_2] and expands isothermally. The volume of the gas changes from V_1 to V_2 and the pressure changes form P_1 to P_2.

An isothermal process.

$\Delta E = O$

$\Delta E = Q_2 - W_1$

$O = Q_2 - W_1$

$$Q2 = W_1 = RT_2 \ln\left(\frac{V2}{V1}\right) \qquad \longrightarrow \qquad (2)$$

(ii) Adiabefic reversible expansion:

When the gas expands adiabatically [suddenly] the volume changes from V_2 to V_3. And the temperature reduces from T_2 to V_1. An adiabatic process,

$Q = 0$

$\Delta E = Q - W_2$

$\Delta E = -W_2 = C_v dT$

$$-W_2 = C_v \int_{T_2}^{T_1} dT$$

$= -Cv (T_1-T_2)$

$W_2 = -Cv (T_1-T_2) \qquad \longrightarrow \qquad (3)$

(iii) Isothermal reversible compression:

Now the gas is compressed isothermally the volume decreases from V_3 to V_4 and the heat is given to sink [T_1]

$$Q_1 = W_3 = RT_1 \quad \ln \frac{V_4}{V_3} \qquad \longrightarrow \qquad (4)$$

(iv) Adiabatic reversible compression:

The gas is compressed adiabatically and the temperature rises from T_1 to T_2 and the volume decreases from V_4 to V_1.

$W4 = Cv (T_1-T_2) \qquad \longrightarrow \qquad (5)$

The total work done,

$W = W_1 + W_2 + W_3 + W_4$

$$W = RT_2 \ln\left(\frac{V_2}{V_1}\right) - C_v(T_1 - T_2) + RT_1 \ln\left(\frac{V_4}{V_3}\right) + C_v(T_1 - T_2)$$

$$W = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right) \quad\longrightarrow\quad (6)$$

For an adiabatic expansion,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad\longrightarrow\quad (7)$$

For an adiabatic compression,

$$\frac{T_2}{T_1} = \left(\frac{V_4}{V_2}\right)^{\gamma-1} \quad\longrightarrow\quad (8)$$

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\frac{V_1}{V_2} = \frac{V_4}{V_3} \quad\longrightarrow\quad (9)$$

Put equation (9) in equation (6) we get,

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_1}{V_2}\right) \quad\longrightarrow\quad (10)$$

$$W = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_1}{V_2}\right)$$

$$W = R \ln\left(\frac{V_2}{V_1}\right)(T_2 - T_1) \quad\longrightarrow\quad (11)$$

Substitute the equations (11) and (2) in equation (1),

$$\eta = \frac{R \ln\left(\frac{V_2}{V_1}\right)(T_2 - T_1)}{RT_2 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\eta = \frac{T_2 - T_1}{T_2}$$

$$\eta = 1 - \frac{T_1}{T_2} \quad\longrightarrow\quad (12)$$

CARNOT'S THEOREM

Statements:-

i. All reversible heat engines are working between the two given temperature has same efficiency.

ii. No engine is more efficient than Carnot engine ($\eta = 1$)

Explanation:-

Efficiency is independent of nature of working substance.

It is depends only on source [T_2] and sink [T_1] efficiency

$$(\eta) = \frac{T_2 - T_1}{T_2}$$

The work done is minimum in carnot engine

i.e., T_1 = o [sink]

$$\eta = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - 0}{T_2}$$

$$\eta = 1$$

But in other engines spontaneous process occurs.

i.e., $T_1 \neq 0$

$$\eta < 1$$

Proof:

Let E_1 & E_2 be the two reversible engines working between the source (T_2) and sink (T_1). Let E_1 be the more efficient than E_2, when E_1, E_2 are coupled then it's a cyclic forces.

The engine (E_1) takes heat (Q_2) from source and performs work (W_1) rejects heat (Q_1) to sink.

The engine (E_2) takes heat (Q_1) from sink and performs work (W_2), rejects heat (Q_2) to source.

Hence source hasn't lost any heat after completion of a cycle.

Hence the net result is,

Work done = W_1, - W_2 = Q_2 – Q_1

Significance :

Carnot's theorem helps to the working condition for getting maximum efficiency to the given engine.

Thermodynamic scale of temperature (or) kelvin scale of temperature :

Statement :

It's a scale which is independent of working substance and depends on temperature of source and sink.

Explanation :

It is consider a reversible engine working between the two temperatures source, sink. Let the engine takes heat (Q_2) and converse into work. And there is no heat liberated to sink. i.e. T_1 is minimum $T_1 = O$

By definition

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \longrightarrow \quad (1)$$

(or)

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \longrightarrow \quad (2)$$

Sub eqn (2) from eqn (1) on both sides

$$1 - \frac{Q_2}{Q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \longrightarrow \quad (3)$$

We know that the work done (W) = $Q_2 - Q_1$ sub this value is eqn (3)

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - T_1}{T_2} \longrightarrow \quad (4)$$

Case :1

In carnot engine (Q_2) heat is completely converted into the work and $T_1 = O$

$$\eta = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 = O}{T_2}$$

$$\boxed{\eta = 1}$$

Case -2

For the other engine $T_1 \neq O$

$\therefore \quad \eta < 1$

Case – 3

When T1 =T2

$$\eta = \frac{T_2 - T_2}{T_2}$$

$$\boxed{\eta = O}$$

i.e, the engine cannot work (or) No heat is converted into work.

Significance :

In thermodynamic scale [T_1=O] which measures the maximum conversion of heat into work. In an ideal gas of temperature also $\eta = 1$

$\therefore$ Both the scale of temperatures are same.

5.2.2. Concept of entropy

Efficiency of carnot engine is given as

$$\eta = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} \longrightarrow \qquad (1)$$

Since $W = Q_2 + Q_1 \longrightarrow \qquad (2)$

$$\eta = \frac{Q_2 + Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{Q_2}{Q_2} + \frac{Q_1}{Q_2} = \frac{T_2}{T_2} - \frac{T_1}{T_2}$$

$$1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \longrightarrow \qquad (3)$$

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \longrightarrow \qquad (4)$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = O \longrightarrow \qquad (5)$$

This shows that is a reversible process, the sum of Q/T term is equal to zero.

This is stated as,

$$\oint \frac{Qrev}{T} = O \qquad\qquad\longrightarrow \qquad (6)$$

Every cyclic integral is a an act differential hence,

$\dfrac{Qrev}{T}$ denoted as entropy (Δ S)

$$\Delta\,S = S_2 - S_1 = \frac{Qrev}{T} \qquad\qquad\longrightarrow\qquad (7)$$

Entropy is a state function

$S_1 \rightarrow$ initial state

$S_2 \rightarrow$ Final state

$\Delta\,S \rightarrow$ Entropy change

$$\Delta S = \int_1^2 \frac{Qrev}{T} \quad .. JK^{-1}Mole^{-1}$$

Definition :

Entropy is an integral of the ratio of heat change in a reversible process with absolute temp during small change.

Entropy change in reversible process :

Let us consider an isothermal reversible expansion of an ideal gases. In this volume changes from V_1 to V_2.

From the Ist law of thermodynamics,

$$\Delta\,E = q - w \qquad\qquad\longrightarrow\qquad (1)$$

For an insothermal process

$$\Delta\,E = O$$

$$q = W$$

$$Q = W = P\Delta\,V = P\,(V_2 - V_1) \qquad\longrightarrow (2)$$

Hence, $\Delta S = \dfrac{Qrev}{T}$

Entropy of the system increases

$$\Delta S\,(system) = \frac{Qrev}{T} \qquad\qquad\longrightarrow\qquad (3)$$

Entropy of the surrounding decreases,

$$\Delta S\,(Surroundings) = \frac{-Qrev}{T} \qquad\qquad\longrightarrow\qquad (4)$$

Over all entropy change in reversible process is,

$\Delta S = \Delta S$ (system) + ΔS (Surroundings)

$$= \frac{Qrev}{T} - \frac{Qrev}{T}$$

$$\boxed{\Delta S = O} \qquad \longrightarrow \qquad (5)$$

The entropy including both the system and surroundings are zero.

Entropy change in irreversible process:

Let us consider an isothermal irreversible expansion of an ideas gas at constant temp, change in volume from V_1 to V_2.

From the Ist law of thermodynamics,

$$\Delta E = Q - W$$

for an isothermal process

$$\Delta E = O$$

$$Q = W \qquad \longrightarrow \qquad (2)$$

In an irreversible process [natural process] work done by the system is zero.

$$Q = O \qquad \longrightarrow \qquad (3)$$

This shows that an entropy of surroundings has no changes,

$$\Delta S \text{ (Surrounding)} = O \qquad \longrightarrow \qquad (4)$$

No heat is removed or supplied to the surroundings.

Entropy of the system is given as

$$\Delta S \text{ (system)} = RT \, Ln \left(\frac{V_2}{V_1} \right) \qquad \longrightarrow \qquad (5)$$

The totel entropy $= \Delta S$ (system) + ΔS (Surroundings)

$$\Delta S = RT \, Ln \left(\frac{V_2}{V_1} \right) + O$$

$$\Delta S = RT \, Ln \left(\frac{V_2}{V_1} \right) \qquad \longrightarrow \qquad (6)$$

This shows that entropy is positive Hence,

$$\boxed{\Delta S \; > \; O} \qquad \longrightarrow \qquad (7)$$

So that entropy of the universe is always maximum.

Clausious inequality :

We know that isothermal reversible expansion on a cycle is,

$$\oint \frac{dqrev}{T} = O \quad \longrightarrow \quad (1)$$

And isothermal irreversible expansion of the cycle,

$$\oint \frac{dqirr}{T} < O \quad \longrightarrow \quad (2)$$

Consider a system go from state (A) to state (B) irreversibly and returns back to initial state B to A reversibly. It is given as A = B.

$$A = B$$

$$\oint_A^B \frac{dqirr}{T} + \oint_B^A \frac{dqrev}{T} > O \quad \longrightarrow \quad (3)$$

$$\oint_A^B \frac{dqirr}{T} - \oint_A^B \frac{dqrev}{T} > O \quad \longrightarrow \quad (4)$$

We know that $ds = \dfrac{dq}{T}$

$$\oint_A^B dsirr - \oint_A^B dsrev > O \quad \longrightarrow \quad (5)$$

In this eqn the Ist term is the entropy change in irreversible process and 2nd term is the entropy change in reversible process.

For a small change, it is given as

$ds_{irr} - dsrev > O$

Hence, $dsirr > dsrev$ $\quad \longrightarrow \quad$ (6)

The eqn (6) is called clausious inequality i.e., entropy change in irreversible process is greater than entropy change in reversible process. So that, entropy of universe is always maximum.

Physical significance of entropy :

i) Entropy – A measure of unavailable energy :

According of the second law heat cannot be completely converted into work. i.e, some amount of heat is not available for the conversion of work.

Hence entropy is a measure of heat that unavailable energy.

ii) Entropy – A measure of disorderness in a system:

In a spontaneous process like diffusion of a gas from high pressure region to low pressure region and flow of heat from hotter end to colder end and is accompanied increase in disorder in a system.

Hence, entropy is a measure of disorder ness.

eg. entropy of a water is more than ice.

iii) Entropy – A measure of probablity :

A spontaneous process occurs from a less propable state to more propable state, Hence entropy always increase in a spantaneous process. Let the thermodynamic probability be 'W' then the relation with entropy is given as,

$S = kln\ W$

K – Boltzmann constant

This equation is called Boltzman entropy equation.

Entropy change in an isothermal expansion of an ideal gas :

In an isothermal expansion of an ideal gas carried out reversibly, there will be no change in internal energy.

ie. $\Delta E = O$

Hence, from the I^{st} equation

$\Delta E = q-W$

$qrev = W \longrightarrow$ (1)

In such a case the work done in the expansion at 'n' moles of a gas from volume V_1 to V_2 at constant temperature (T), is given by,

$$W = n\ RT\ Ln \left(\frac{V_2}{V_1}\right) \longrightarrow \text{(2)}$$

(1) in (2) $\Rightarrow qrev = nRT\ Ln \left(\frac{V_2}{V_1}\right)$

We know that,

$$\frac{qrev}{T} = \Delta S$$

$$\frac{qrev}{T} = nR\ln \left(\frac{V_2}{V_1}\right)$$

$$\boxed{\Delta S = n\ Rln \left(\frac{V_2}{V_1}\right)}$$

Entropy change accompanying change of phase :

1. Entropy change from solid phase to liquid phase:

Consider 1 mole of a substance changes from solid state to liquid state reversibily and its fusion point.

If, under a constant pressure, then the entropy change accompanying the process will be given by

$$\Delta Sf = \frac{\Delta Hf}{Tf} \quad \Delta s_f = \frac{\Delta H_f}{T_f}$$

Where, ΔH_f is the molar heat of fusion.

ii) Entropy change from liquid to vapour phase:

Consider 1 mole of a substance change from liquid to vapour phase reversibly and its boiling point T_b, under a constant pressure. Then the entropy change accompanying, the process will be given by,

$$\Delta S_v \frac{\Delta Hv}{T_b}$$

Here, ΔH_v is the molar heat of vapourisation

iii) Entropy change from one crystalline state to another crystalline state :

Consider 1 mole of a substance changes from one crystalline form [Rhormbic form] to another crystalline from [Monoclnic from] at the transistion temperature 'T' is given by.

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T}$$

Here,

ΔH_{tr} is the molar heat of transistion.

Calculation of entropy changes of an ideal gas with changes in PVT:

i) When T,V are the two variables [Entropy change T,V]

From the Ist law of thermodynamics equation,

$\Delta E = q-W \longrightarrow$

(1)

According to Ist law, entropy change is given by

$$ds = \frac{dqrev}{T} \longrightarrow \qquad (2)$$

Eqn (1) written as,

$dE = dq - dw$

dq = dE + dW $\qquad\longrightarrow$ (3)

We know that,

dw = Pdv $\qquad\longrightarrow$ (4)

Eqn (4) in (3)

dqrev = dE + Pdv $\qquad\longrightarrow$ (5)

Sub 'dE' value from $Cv = \left(\dfrac{dE}{dT}\right)_v$

dE = CvdT $\qquad\longrightarrow$ (6)

Sub eqn (6) in (5)

dqrev = Cv dT + Pdv $\qquad\longrightarrow$ (7)

For 1 mole of an ideal gas equation,

PV = RT

$P = \dfrac{RT}{V}$

Sub the 'P' value in eqn $\qquad$ (7)

$dq_{rev} = CvdT + \left(\dfrac{RT}{V}\right) dv \qquad\longrightarrow$ (8)

Sub the eqn (8) in eqn (2)

$ds = \dfrac{CvdT + \left(\dfrac{RT}{V}\right) dv}{T}$

$= \dfrac{CvdT}{T} + \dfrac{RT}{VT} dv$

$ds = Cr\, \dfrac{dT}{T} + R\dfrac{dv}{v}$

On integration

$\Delta S = S_2 - S_1 = Cv \int\limits_{T1}^{T2} \dfrac{dT}{T} + R\int\limits_{V1}^{V2}\dfrac{dv}{v}$

$\Delta S = Cv\, Ln\, (T_2 - T_1) + R\, Ln\, (V_2 - V_1)$

$$\boxed{\Delta S = Cv\, Ln \left(\dfrac{T_2}{T_1}\right) + R\, Ln\left(\dfrac{V_2}{V_1}\right)}$$

ii) When T,P are the two variables [Entropy change on T.P]

If 'P$_1$' is the pressure of the ideal gas in the initial state and 'P$_2$' is the pressure of the ideal gas in the final state.

'V$_1$' is the volume of ideal gas in initial state and 'V$_2$' is the volume of the ideal gas in final state.

T$_1$, T$_2$ are the temperature of an ideal gas in initial and final state respectively.

According to ideal gas equation,

$$P_1V_1 = RT_1 \longrightarrow \quad (1)$$

For 1 mole of the gas in the final state (1) ÷ (2)

$$\frac{P_1V_1}{P_2V_2} = \frac{RT_1}{RT_2}$$

$$\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

$$P_1 V_1 T_2 = P_2 V_2 T_1$$

$$\boxed{\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}}$$

$$\Delta s = Cv \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

$$= Cv \ln\frac{T_2}{T_1} + R \ln\left(\frac{P_1T_2}{P_2T_1}\right)$$

$$= Cv \ln\frac{T_2}{T_1} + R \ln\frac{P_1}{P_2} + R \ln\frac{T_2}{T_1}$$

$$\Delta s = Cv \ln\frac{T_2}{T_1} - R \ln\frac{P_2}{P_1} + R \ln\frac{T_2}{T_1}$$

$$= \ln\left(\frac{T_2}{T_1}\right)(Cv + R) - R \ln\frac{P_2}{P_1}$$

$$\Delta s = Cp \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

Ebtropy change in different process :

i) Isothermal process : ['T' remains Constant T₁=T₂]

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$T_1 = T_2$$

$$\Delta S = C_v \ln \left(\frac{T_2}{T_2} \right) + R \ln \left(\frac{V_2}{V_1} \right)$$

$$= C_v \ln (1) + R \ln \left(\frac{V_2}{V_1} \right)$$

$$= O + R \ln \left(\frac{V_2}{V_1} \right)$$

$$\boxed{\Delta S = R \ln \left(\frac{V_2}{V_1} \right)}$$

$$\Delta S = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$= C_p \ln \left(\frac{T_2}{T_2} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$= C_p \ln (1) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$\boxed{\Delta S = - R \ln \left(\frac{P_2}{P_1} \right)}$$

ii) Isobaric Process : ['P remains constant P₁-P₂]

$$\Delta S = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_1} \right)$$

$$P_1 = P_2$$

$$= C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{P_2}{P_2} \right)$$

$$= C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln (1)$$

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$$= Cp \ln \left(\frac{T_2}{T_1} \right)$$

$$\boxed{\Delta S = Cp \ln \left(\frac{T_2}{T_1} \right)}$$

iii) Isochoric Process : ['V' remains constant $V_1=V_2$]

$$\Delta S = Cp \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$= Cp \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_2}$$

$$= Cp \ln \left(\frac{T_2}{T_1} \right) + O$$

$$\boxed{\Delta S = Cp \ln \left(\frac{T_2}{T_1} \right)}$$

Entropy of a minture of Ideal gases :

We know that for one mole of an ideal gas equation,

$$ds = Cv \frac{dT}{T} + R \frac{dV}{V} \longrightarrow (1)$$

On integrating the above equation, we get

$$\int ds = Cv \int \frac{dT}{T} + R \int \frac{dV}{V}$$

$$S = Cv \ln T + R \ln V + C \longrightarrow (2)$$

C – is an integration constant

put $V = \dfrac{RT}{P}$ *in* (2)

$$S = Cv \ln T + R \ln \left(\frac{RT}{P} \right) + C$$

$$= Cv \ln T + R \ln RT - R \ln P + C$$

$$= Cv \ln T + R \ln R + R \ln T - R \ln P + C$$

$$= (Cv + R) \ln T + R \ln R - R \ln P + C$$

$$(Cv + R) = C_p$$

$$= Cp \ln T + R \ln R - R \ln P + C$$

$$S = C_p \ln T - R \ln P + C_o$$

Now, consider Ideal gases placed in a separate vessel using partition. Let entropy of this is 'S$_A$' and for n moles of Ideal gas is given as,

$$S_A = \sum{}_n \left(C_p \ln T - R \ln P + C_o \right) \longrightarrow \quad (3)$$

The partial pressure of an Ideal gas (P) is given by the expression.

$$p = xP \longrightarrow \quad (4)$$

p = partial pressure

P = total pressure

x = mole fraction

When the partition is removed and gases mixed with each other. Let the entropy be 'S$_B$' [without partition].

$$S_B = \sum{}_n \left(C_p \ln T - R \ln xP + C_o \right) \longrightarrow \quad (5)$$

$$= \sum{}_n \left(C_p \ln T - R \ln x - R \ln P + C_o \right) \longrightarrow \quad (6)$$

This equation gives the entropy of a mixture of an Ideal gas.

Entropy mixing:-

Entropy mixing is given as,

$$\Delta_s(mix) = (S_B - S_A) = \sum{}_n \left(C_p \ln T - R \ln x - R \ln P + C_o \right) - \left[\sum{}_n \left(C_p \ln T - R \ln P + C_o \right) \right]$$

$$= \sum{}_n \left(-R \ln x \right)$$

$$\Delta_s(mix) = -R \sum{}_n \ln x$$

$$\Delta_s(mix) = -R \sum{}_{ni} \ln x_i$$

Where, n$_i$ is the number of moles

x$_i$ is the mole fraction

Hence, the quantity on right on side is always positive.

This shows that entropy during isothermal mixing always increases (or) +Ve.

$$\Delta_s(min) > 0.$$

Second law of thermodynamics – II

Maxwell's relationship:-

From the first law of thermodynamics,

$$\Delta E = q - w$$

$$q = \Delta E + w$$

$$q = dE + w \longrightarrow (1)$$

If the process is reversible and the work is restricted to work of expansion alone.

By definition,

$$W = Pdv \longrightarrow (2)$$

Equation (2) sub in equation (1)

$$q_{rev} = dE + Pdv$$

Divide the above eqn by 'T'

$$\frac{q_{rev}}{T} = \frac{dE + Pdv}{T} \longrightarrow (3)$$

By definition,

$$\frac{q_{rev}}{T} = dS$$

So that, $dS = \dfrac{dE + Pdv}{T}$

$$TdS = dE + Pdv$$

$$dE = TdS - Pdv \longrightarrow (4)$$

It's a fundamental equation of thermodynamics,

At constant 'V'

$$dE = TdS$$

$$\left(\frac{dE}{dS}\right)_v = T \longrightarrow (5)$$

Differentiate the eqn with respect ot 'V' at constant 'S'

$$\frac{\partial^2 E}{(\partial S)(\partial V)} = \left(\frac{\partial T}{\partial V}\right)_s \longrightarrow (6)$$

At constant 'S' eqn (4)

$$dE = - Pdv$$

$$\left(\frac{\partial E}{\partial V}\right)_s = -P \longrightarrow (7)$$

Differentiate the eqn with respect ot 'S' at constant 'V'

$$\frac{\partial^2 E}{(\partial V)(\partial S)} = -\left(\frac{\partial P}{\partial S}\right)_v \longrightarrow (8)$$

Compare the equations (6) and (8),

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$$

This equation is known as the Maxwell's relationship equation.

The relation between different thermodynamic functions can be obtaining during the definition of the composite functions.

$$H = E + PV \longrightarrow (1)$$
$$A = E - TS \longrightarrow (2)$$
$$G = H - TS \longrightarrow (3)$$

On differentiating the above equations we get,

$$dH = dE + PdV + VdP \longrightarrow (4)$$
$$dA = dE - TdS - SdT \longrightarrow (5)$$
$$dG = dH - TdS - SdT \longrightarrow (6)$$

From the equation (4), eqn (6) will be rearranged,

$$dH = dE + PdV + VdP - TdS - SdT \quad (7) \longrightarrow$$

Now the value of dE is substituted in equation (4),(5) and (6) equations,

$$(4) \Rightarrow dH = Tds - Pdv + Pdv + Vdp$$

$$\boxed{dH = Tds + Vdp}$$

$$(5) \Rightarrow dA = TdS - PdV - TdS - SdT$$

$$\boxed{dA = -PdV - SdT}$$

$$(6) \Rightarrow dG = TdS - PdV + PdV + Vdp - TdS - SdT$$

$$\boxed{dG = Vdp - SdT}$$

(1.)dH = TdS + VdP at constant 'p'

$$dH = TdS$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \longrightarrow (1)$$

Differentiate the equation with respect to 'P' at constant 'S'

$$\frac{\partial^2 H}{(\partial S)(\partial P)} = \left(\frac{\partial T}{\partial P}\right)_S \longrightarrow (2)$$

At Constant 'S'

$$\partial H = V \partial P$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \longrightarrow (3)$$

Differentiate the equation with respect to 'S' at constant 'P'

$$\frac{\partial^2 H}{(\partial P)(\partial S)} = \left(\frac{\partial V}{\partial S}\right)_P \longrightarrow (4)$$

Compare equations (2) and (4)

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

(2.) $dA = - PdV - SdT$

At constant 'T'

$$dA = - PdV$$

$$\left(\frac{\partial A}{\partial V}\right)_T = \text{-P} \longrightarrow (1)$$

Differentiate with respect to 'T' at constant 'V'

$$\frac{\partial^2 A}{(\partial V)(\partial T)} = \text{-}\left(\frac{\partial P}{\partial T}\right)_V \longrightarrow (2)$$

At constant 'V'

$$dA = \text{- } SdT$$

$$\left(\frac{\partial^2 A}{\partial T}\right)_V = \text{-S} \longrightarrow (3)$$

Differentiate with respect to 'V' at constant 'T'

$$\frac{\partial^2 A}{(\partial V)(\partial T)} = \text{-}\left(\frac{\partial S}{\partial V}\right)_T \longrightarrow (4)$$

Compare equations (2) and (4)

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$

3. dG = Vdp – SdT

At constant 'T'

dG = VdP

$$\left(\frac{\partial G}{\partial P}\right) = V \longrightarrow (1)$$

Differentiate the equation with respect to 'T' at constant 'P'

$$\frac{\partial^2 G}{(\partial P)(\partial T)} = \left(\frac{\partial V}{\partial T}\right)_P \longrightarrow (2)$$

At constant 'P'

dG = – SdT

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \longrightarrow (3)$$

Differentiate the equation with respect to 'P' at constant 'T'

$$\frac{\partial^2 G}{(\partial T)(\partial P)} = -\left(\frac{\partial S}{\partial P}\right)_T \longrightarrow (4)$$

Compare equations (2) and (4)

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$$

Gibb's – Helmholtz equation:-

The thermo dynamic function equation

dG = VdP – SdT $\longrightarrow$ (1)

At constant 'P'

dG = - SdT $\longrightarrow$ (2)

When the system is in its initial state, its free energy is given by G, at the temp 'T', suppose the temperature rises to T+dT, where dT is infinitesimally small.

So that,

$d_1G = -S_1dT \longrightarrow$ (3)

$d_2G = - S_2dT$ $\longrightarrow$ (4)

Where S_1 and S_2 are the initial and final states of the system.

Substitute the equation (3) and (4)

$d (G_2 - G_1) = (- S_2 - S_1) dT$ $\longrightarrow$ (5)

$d(\Delta G) = - \Delta SdT$ $\longrightarrow$ (6)

$\left(\dfrac{\partial(\Delta G)}{\partial T}\right)_P = - \Delta S$ $\longrightarrow$ (7)

Since the free energy equation,

$G = H - TS$ $\longrightarrow$ (8)

If G_1, H_1 and S_1 are the initial states of the system and G_2, H_2 and S_2 are the final states of the system, the temp remaining constant at 'T'.

We have,

$G_1 = H_1 - TS_1$

$G_2 = H_2 - TS_2$

$G_2 - G_1 = H_2 - H_1 - (TS_2 + TS_1)$

$\Delta G = \Delta H - T\Delta S$ $\longrightarrow$ (9)

$\Delta G - \Delta H = -T\Delta S$

$\dfrac{\Delta G - \Delta H}{T} = -\Delta S$ $\longrightarrow$ (10)

Substitute equation (10) in equation (7)

$\dfrac{\Delta G - \Delta H}{T} = \left(\dfrac{\partial \Delta G}{\partial T}\right)_P$

$\Delta G - \Delta H = T\left(\dfrac{\partial \Delta G}{\partial T}\right)_P$

$\Delta G = \Delta H + T\left(\dfrac{\partial \Delta G}{\partial T}\right)_P$ $\longrightarrow$ (11)

This equation is known as the Gibb's Helmholtz equation.

Gibb's – Duhem Equation:

If a system has a definite composition having $n_1, n_2, \ldots n_J$ moles of constituents $1, 2, \ldots J$ respectively and the chemical potential are $\mu_1, \mu_2, \ldots \mu_J$ moles of constituents $1, 2, \ldots j$ respectively, then we have,

$G = n_1\mu_1 + n_2\mu_2 + \ldots\ldots\ldots + n_j\mu_j$ $\longrightarrow$ (1)

Differentiate the equation,

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + ...n_j d\mu_j + \mu_j dn_j \text{———— (2)}$$

But according to the first term on the right hand side is equal to dG at constant 'P' and 'T'

$$dG = \left(\mu_1 dn_1 + \mu_2 dn_2 + ...+ \mu_j dn_j \right) + \left(n_1 d\mu_1 + n_2 d\mu_2 + ...+ n_j d\mu_j \right)$$

$$dG = dG + \left(n_1 d\mu_1 + n_2 d\mu_2 + ...+ n_j d\mu_j \right)$$

$$0 = \left(n_1 d\mu_1 + n_2 d\mu_2 + ...+ n_j d\mu_j \right)$$

$$0 = \sum n_i d\mu_i$$

$$\sum n_i d\mu_i = 0$$

This equation is known as the Gibb's Duhem equation.

For a system having only two components the above equation reduces to,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$d\mu_1 = -\left(\frac{n_2}{n_1} \right) d\mu_2$$

The above equation shows that the variation in chemical potential of one component affects the value for the other component as well.

Thus if $d\mu_1$ is positive i.e., if μ_1 increases, then $d\mu_2$ must be negative i.e., μ_2 must decreases.

Duhem – Margulus Equation:

Consider a binary solution of components A and B at constant temperature and pressure. If n_A and n_B are the numbers of moles of components A and B respectively.

According to Gibb's Duhem equation,

$$n_A d\mu_A + n_B d\mu_B = 0 \longrightarrow (1)$$

Where, μ_A and μ_B are chemical potentials of A and B respectively.

Dividing equation (1) by $n_A + n_B$,

$$\frac{n_A}{n_A + n_B} d\mu_A + \frac{n_B}{n_A + n_B} d\mu_B = 0$$

Since,

$$x_A = \frac{n_A}{n_A + n_B} \quad ; x_B = \frac{n_B}{n_A + n_B} \longrightarrow (2)$$

So that,

$$x_A d\mu_A + x_B d\mu_B = 0 \longrightarrow (3)$$

Where, x_A and x_B are the components of A and B respectively.

Thermodynamically the chemical potential of any constituent of a liquid mixture is represented by the equation.

$$\mu_i = \mu_0 i + RT \ln f_i \longrightarrow (4)$$

Where f_i represents the fugacity of the given constituent $\mu_0 i$ is a constant for the substance at constant temperature.

Differentiating the above equation at constant temperature, we have

$$d\mu_i = RT \ln f_i \longrightarrow (5)$$

For components A and B, the above equation becomes,

$$d\mu_A = RTd \ln f_A \longrightarrow (6)$$

$$d\mu_B = RT \, d \ln f_B \longrightarrow (7)$$

The equations (6) and (7) are substituted in equation (3),

$$x_A RTd \ln f_A + x_B RT \, d \ln f_B = 0 \longrightarrow (8)$$

Dividing through out by dX_A we get,

$$\frac{x_A RTd \ln f_A}{dX_A} + \frac{x_B RTd \ln f_B}{dX_B} = 0 \longrightarrow (9)$$

We have that the mole fraction on $x_A + x_B = 1$

Differentiate this equation we get,

$$dX_A + dX_B = 0$$

$$dX_A = - dX_B \quad (10) \longrightarrow$$

Substitute the equation (10) in equation (9),

$$\frac{x_A RTd \ln f_A}{dX_A} + \frac{x_B RTd \ln f_B}{- dX_B} = 0 \longrightarrow (11)$$

$$\frac{d \ln f_A}{d \ln X_A} - \frac{d \ln f_B}{d \ln X_B} = 0$$

$$\frac{d \ln f_A}{d \ln X_A} = \frac{d \ln f_B}{d \ln X_B} \longrightarrow (12)$$

If the vapour behaves as an ideal gas, the fugacity can be replaced by vapour pressure. So that the equation (12) becomes,

$$\frac{d \ln P_A}{d \ln X_A} = \frac{d \ln P_B}{d \ln X_B}$$

This equation is known as Duhem – Margulus Equation.

Clausius Clapeyon Equation:

According to thermodynamic equation

$dG = VdP - SdT$ $\longrightarrow$ (1)

For phase 'A' the above equation will be

$dG_A = V_AdP - S_AdT$ $\longrightarrow$ (2)

For phase 'B' the above equation will be

$dG_B = V_BdP - S_BdT$ $\longrightarrow$ (3)

Where V_A and V_B are the molar volumes for the phase A and B.

G_A and G_B are the free energy for the phase A and B.

S_A and S_B are the free entropy for the phase A and B.

Since the two phases are still in equilibrium.

Hence, $dG_A = dG_B$

$V_AdP - S_AdT = V_BdP - S_BdT$

$S_BdT - S_AdT = V_BdP - V_AdP$

$(S_B - S_A) dT = (V_B - V_A) dP$

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}$$ $\longrightarrow$ (4)

Where $(V_B - V_A)$ represents the change in volume, so we put as ΔV.

Where $(S_B - S_A)$ represents the change in entropy, so we put as ΔS.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$ $\longrightarrow$ (5)

The change of entropy in this process is given by,

$$\Delta S = \frac{q}{T}$$ $\longrightarrow$ (6)

Where, q – is heat exchange reversibly for mole of the substance.

Substitute equation (6) in equation (5),

$$\frac{dP}{dT} = \frac{q}{T\Delta V}$$

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)}$$ $\longrightarrow$ (7)

This equation is known as Clausius Clapeyon Equation.

Suppose the system consists of water in the two phases. i.e., liquid and vapour.

$$Water_{(liq)} \Longleftrightarrow Water_{(vapour)}$$
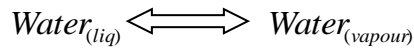
According to Clapeyron equation,

q – Molar heat of vaporization = ΔH_V

V_B – Volume of 1 mole of water in the vapour state (V_g)

V_A – Volume of 1 mole of water in the liquid state (V_l)

The Clapeyron equation becomes,

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_g - V_l)} \longrightarrow (8)$$

Comparing V_g, V_l – V_l is the very small so it will be neglected.

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_g)} \longrightarrow (9)$$

The gas equation is applied in above equation,

PV = RT

$$V = \frac{RT}{P} \longrightarrow (10)$$

Equation (10) in equation (9)

$$\frac{dP}{dT} = \frac{\Delta H_V}{T\left(\dfrac{RT}{P}\right)} \longrightarrow (11)$$

$$\frac{dP}{dT} = \frac{P\Delta H_V}{T^2 R}$$

$$\frac{dP}{PdT} = \frac{\Delta H_V}{RT^2}$$

$$\frac{d \ln P}{dT} = \frac{\Delta H_V}{RT^2} \longrightarrow (12)$$

The above equation can also be integrated between the limits of P_1 and P_2 corresponding to temperature T_1 and T_2.

Thus,

$$\int_{P_1}^{P_2} d \ln P = \frac{\Delta H_V}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_V}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad\longrightarrow\qquad (13)$$

This integrated form of the Clapeyron equation is known as Clausius Clapeyron equation.

$$\ln = 2.303 \log$$

$$2.303 \log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Work and Free energy constants:

The work and free energy constants are represented by A and G respectively.

These are given by the following equation

$$A = E - TS \qquad\longrightarrow\qquad (1)$$

$$G = H - TS$$

Where,

E – Internal energy

H – Enthalpy

S – Entropy

Work Function:

Consider an isothermal function change at temperature T from the initial state and Final state i.e.,

$$A_1 = E_1 - TS_1 \qquad\longrightarrow\qquad (2)$$

$$A_2 = E_2 - TS_2 \qquad\longrightarrow\qquad (3)$$

Where,

A_1, E_1 and S_1 represent the thermodynamic function for the system in the initial state.

A_2, E_2 and S_2 represent the thermodynamic function for the system in the final state.

Subtracting equation (2) from equation (3)

$$A_2 - A_1 = E_2 - E_1 - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \longrightarrow \quad (4)$$

Where,

ΔA is the change in the work function.

ΔE is the change in the internal energy.

ΔS is the change in the entropy of a system.

Since from the first law of thermodynamics,

$$\Delta S = \frac{q_{rev}}{T} \longrightarrow \quad (5)$$

Where, q_{rev} is heat taken at constant temp in a reversible manner.

Substitute equation (5) in equation (4)

$$\Delta A = \Delta E - T\left(\frac{qrev}{T}\right)$$

$$\Delta A = \Delta E - qrev \longrightarrow \quad (6)$$

According to the Ist law of hermo dynamics,

dE = qrev – Wrev

$$\Delta E = qrev = - wrev \longrightarrow \quad (7)$$

Sub eqn (7) in eqn (6) we get,

ΔA = - Wrev

-Δ A = Wrev

The above eqn is clear that decrease in the function (i,e,- Δ A) gives the maximum work that can be done by the system during the given change.

Free energy function :

It is defined as

G = H-TS $\longrightarrow \quad (1)$

Where,

G – Fee energy

H – Entholpy

S – Entropy

consider a system which under goes a changes of state from initial to final at constant temp we have,

$$G_1 = H_1 - TS_1 \longrightarrow \quad (2)$$

$$G_2 = H_2 - TS_2 \quad\longrightarrow\quad (3)$$

Sub eqn (2) from eqn (3)

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \quad\longrightarrow\quad (4)$$

We know that the following eqn

$$\Delta H = \Delta E + P\Delta V \quad\longrightarrow\quad (5)$$

Sub (5) in (4)

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad\longrightarrow\quad (6)$$

We know that

$$\Delta A = \Delta E - T\Delta S$$

$$\Delta G = \Delta A + P\Delta V \quad\longrightarrow\quad (7)$$

Since ΔA is equal to $(-W)$ hence we have

$$\Delta G = -W + P\Delta V$$

$$-\Delta G = W - P\Delta V \quad\longrightarrow\quad (8)$$

Therefore $-\Delta G$ gives the maximum work abtainable from a system other then that due to change of volume at constant temperature & pressure.

The work other than the due to change of volume is called the network.

So that, network $= W - P\Delta V = -\Delta G$

$$\boxed{W - P\Delta V = -\Delta G}$$

Criteria for reversible and irreversible process :

The criteria for reversibily and irreversibily interms of change of entropy of a system is given by the equation.

$$ds = \frac{dqrev}{T} \quad\longrightarrow\quad (1)$$

If the change is brought about reversibly then the above eqn becomes.

$$ds = \frac{dE + pdV}{T}$$

$$Tds = dE + Pdv \quad\longrightarrow\quad (2)$$

Suppose the change of state is brought about irreversibly. Now the heat absorbed by the system will be less [qirrev <qrev], reprsent the entropy change ds will have the same value.

Hence for an irreversible process,

$Tds > dq_{rev}$

$Tds > dE + Pdv$ ──────────────→ (3)

Compaing the eqn (2) & (3) we have

$Tds \geq dE + Pdv$ ──────────────→ (4)

The equal sign refers to a reversible process while the greater than sign refers re to an irreversible process.

(i) Criterion interms of changes entropy :

If V & E remains constant, for an isothermal process.

$ds \geq O$

The equal sign refers the reversible process while that greater than sign refers in irreversible process.

ii) Criterion interms of change of Internal energy :

If S & V remains constant, then for an isothermal process (i.e, T = constant)

$dE \leq O$

The equal sign refers to reversible process while the greater than sign refers to an irreversible process.

iii) Criterion interms of changes of entholpy :

If S & V are kept constant, the expresion

$Tds \geq dE + Pd V$

May be written as

$dE + Pdv \leq O$

But we know that,

$dE + Pdv = dH$

$dH \leq O$

The '=' sign refers to reversible process. The '>' sign refers to an irreversible process.

Partial molar free energy [Concept of chemical protential]

The most important partial molar quantity is the partial molar free energy designed as chemical protential and represented as.

$$\left(\frac{\partial G}{\partial ni}\right) \text{ T, P, n, } \dots\dots\dots\dots \text{ nj} = \overline{G,} = \mu \, i \longrightarrow (1)$$

The free energy 'G' most be a function of 'T' 'P' & the number of moles of various constituents.

i.e, $G = f$ (T,P, n_1, n_2 .... nj)

For a small free energy change in 'T' 'P' & the no of moles of the components, the energy change dG will be given by the expression.

$$dG = \left(\frac{dG}{dT}\right) P, \overset{dT}{N} + \left(\frac{dG}{dP}\right)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots\dots\dots + \mu_j dn_j \longrightarrow (2)$$

Where,

$\mu_1 \mu_2$ .... μ_j are chemical protentials of comproments 1,2, ... j respectively.

If P & T remain constant, then

$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \dots\dots\dots \mu_j dnj \longrightarrow (3)$

On intergrating the above equation, we have

$(G)_{T,P} = \mu_1 n_1 + \mu_1 n_2 + \dots\dots\dots \mu_j nj \longrightarrow (4)$

From the above eqn the chemical protential may be defined as the constituent of the mixture to the totel free energy of the system under condition of constant T & P.

If readily follows the for a totel of one mole of a pure substance, $G = \mu$.

i.e, free energy is identical with chemical protential.

Chemical protential in the system of a Ideal gas :

Consider a system consiting of a number of ideal gases. Let $n_1, n_2 \dots$ be the number of moles of various constituents present in the mixture.

Then the ideal gas eqn

$PV = nRT$

$$V = n \left(\frac{RT}{P}\right) \longrightarrow (1)$$

In the above eqn the total number of moles (n) may be replaced by $(n_1 + n_2 + \dots)$.

Hence,

$$V = (n_1 + n_2 + \dots)\left(\frac{RT}{P}\right)_{n_i} \quad \left(\frac{RT}{P}\right) \longrightarrow \qquad (2)$$

Diff the eqn (2) with respect to ni at constant T & P, we have,

$$\left(\frac{\partial V}{\partial ni}\right)_{T,P,N} = \frac{RT}{P} \longrightarrow \qquad (3)$$

$$\overline{Vi} + \frac{RT}{P} \longrightarrow \qquad (4)$$

The partial molar volume of the component 'i' is given by the following eqn.

$$\left(\frac{\partial \mu i}{\partial P}\right)_{T,N} + \overline{Vi} \longrightarrow \qquad (5)$$

Sub the value of $\overline{Vi} = \dfrac{RT}{P}$ in eqn (5), we have,

$$\left(\frac{\partial \mu i}{\partial P}\right)_{T,N} = \frac{RT}{P} \longrightarrow (6)$$

For a constant composition of the gas and at the gas and at constant temperature the above eqn may be expressed in the form.

$$d\mu_i = \frac{RT}{P} \cdot dP$$

$$d\mu_i = RTd\ LnP \longrightarrow (7)$$

The partial pressure of the ideal gas eqn,

$$P_iV = n_i\ RT$$

Divide by the Ideal gas eqn $PV = nRT$

$$\frac{P_iV = n_iRT}{PV = nRT}$$

$$\frac{Pi}{P} = \frac{n_i}{n}$$

$$Pi = \left(\frac{n_i}{n}\right)P \longrightarrow (8)$$

Since n_i & n are constants.

On taking log and differentiation the eqn we get.

$$dLn\ P_i = dlnP \longrightarrow (9)$$

Sub eqn (9) in eqn (7)

$d\mu_i - RTd \ln P_i$ $\longrightarrow$ (10)

On integrating the eqn

$\mu_i = RT \ln P_i + \mu_i$

$\mu_i = \mu_i (P) + RT \ln P_i$ $\longrightarrow$ (11)

Where, μ_i is the integrated constant.

If the partial pressure of the constituent 'i' is unity i-e, $P_i = 1$

$\mu_i = \mu_i (P)$ $\longrightarrow$ (12)

According to the eqn $P_i V = n_i RT$

$$P_i = P_i = \left(\frac{n_i}{V}\right)^{n_i} RT \longrightarrow (13)$$

Now, $\left(\dfrac{n_i}{V}\right)^{n_i}$ represents molar concentration, if this concentration is

represented by C_i . So the above eqn becoems.

$P_i = C_i RT$

Sub this value in eqn (11)

$\mu_i = \mu_i + RT \ln (C_i RT)$

$\mu_i = \mu_i + RT \ln RT + RT \ln C_i$

Where $RT \ln RT$ is a constant

$\mu_i = \mu_i + RT \ln C_i$ $\longrightarrow$ (14)

If $C_i = 1$ then $\mu_i = \mu_i (c)$

According to eqn (8)

$$Pi = \left(\frac{ni}{n}\right)P$$

Since $\dfrac{ni}{n}$ represents the mole fraction μ_i of the constituent 'i' in the

mixture, the above eqn represents by.

$Pi = niP$

Sub this value of pi in eqn (11),, we get

$\mu_i = \mu_i + RT \ln (n_i P)$

$\mu_i = \mu_i + RT \ln n_i + RT \ln P$

Where,

$RT \ln P$ is a constant term, so

$\mu_i = \mu_i (n) + RT \ln \mu_i$

If ni = 1

μi = μi (n)

Where, μ_i, μ_i (G) and μ_i (n) represents the chemical protential of the constitnent i.

Application of classius clapeyom equation :

    i. Caculation of molar heat of vaporsisation.

    The molar heat of vapourisation of a liquid can be calculated if its vapour pressure two different temperatures are known.

    ii.Effect of temperature vapour pressure of a liquid:

    If vapour pressure of a liquid at 1 temp is known, that at another temp can be calculated.

    iii. Effect of pressure of boiling point

    If the boiling point of a liquid at 1 pressure is known, that at another 'P' can be calculated.

Concept of fugacity:

    Consider a system composed of liquid water and its vapour. Liquid water has a tendency to escape into the vapour phase while the vapour tends to escaped the gaseous state and come into the liquid phase condensation.

    When the system is in equilibrium, there two escaping tendencies become equal and we observe a constant vapour pressure at constant temperatures.

Definition:

    Fugacity may be stated that each substance in a given state has a tendency to escape from the state and this escaping tentendcy denoted by 'f' is called fugacity.

    Lewis introduced the new concept of fugacity for representing the actual behaviour of real gases which is distinctly different from the behaviour of ideal gas.

    Variation of free energy with pressure at constant 'T' is given by the eqn.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \longrightarrow \quad (1)$$

An ideal gas eqn

PV = nRT

For a one mole of a system the above eqn becomes,

PV = RT

$$V = \frac{RT}{P} \quad\longrightarrow\quad (2)$$

The value of 'V' sub in eqn (1)

$$\left(\frac{\partial G}{\partial P}\right)_T \quad \frac{RT}{P} \quad\longrightarrow\quad (3)$$

$$\partial G = \frac{RT}{P}\, dP$$

$$\partial G = RT\, d\ln P \quad\longrightarrow\quad (4)$$

This eqn is only for ideal gases, not for real gases. Now lewis function fugacity 'f' is sub by eqn (4)

$$dG = RT\, d\ln f \quad\longrightarrow\quad (5)$$

This eqn is for real gases only.

On integration the eqn (4) & (5) at constant 'T'

$$G = G^o\, RT \ln \frac{P_2}{P_1}$$

$$G = G^o + RT \ln \frac{f_2}{f_1}$$

Where, G^o is the free energy of real gas. When its fugacity happens to be 1.

Fugacity at low pressure:

The fugacity function at low 'P' may be defined as

$$\mathrm{Lt}\ \frac{f}{P} = 1$$

$$P \to O$$

$$\mathrm{Lt}\ \frac{f}{P} = 1$$

$$P \to O$$

The ratio f/p approaches unity. When 'P' approaches zero. Since i that real gas appropriate to ideal behaviour.

Evidently at low pressure, fugacity is equal to pressure. These two terms are differ at high pressure.

Determination of fugacity of a gas:

Variation of free energy with 'P' at constant 'T' is given by the eqn.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \longrightarrow \quad (1)$$

$$\partial G = V \partial P \longrightarrow \quad (2)$$

The free energy change of one mole of a real gas,

$$\partial G = RTd\, \ln f \longrightarrow \quad (3)$$

Comparing (2) & (3)

$$V\partial P = RT\partial \ln f \longrightarrow \quad (4)$$

The ideal gas molar volume $\dfrac{RT}{P}$, It is given by the eqn.

$$\propto = \frac{RT}{P} = V \longrightarrow \quad (6)$$

Multiply by dP through out, we get

$$\propto dP \frac{RT}{P}\, dP - VdP \longrightarrow \quad (7)$$

According to eqn $\quad (4)$

$$\propto dP = \frac{RT}{P} . dP - RTd\, \ln f$$

$$\propto dP = RTd\, \ln P - RTd\, \ln f$$

$$RTd\, \ln f = RTd\, \ln P - \propto dP$$

$$d\, \ln f = \frac{RTd\, \ln P - \alpha dP}{RT}$$

$$d \ln f = d\, \ln P - \frac{\alpha dP}{RT}$$

$$d\, \ln f = d\, \ln P - \frac{\alpha dP}{RT}$$

$$\int_{o}^{f} d\, \ln f = \int_{O}^{P} d\, \ln P - \frac{1}{RT} \int_{O}^{P} \alpha dP \longrightarrow \quad (8)$$

On $\int$ the eqn (8)

$$\ln f = \ln P - \frac{1}{RT} \int_{O}^{P} \alpha dP$$

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_{P}^{P} \alpha\, dP \longrightarrow \quad (9)$$

The above graph is plotted by $\propto$ Vs P for the determination of fugacity of the gas.

Now, $\propto$ as given the eqn (9) can be determind experimentally at different pressure.

At low pressure:

The value of integration of $\int\limits_{O}^{P}(\alpha)$ dP as illustrated by the shaded protion show in the graph. Then the fugacity of the gas would be less than the pressure (P) at low pressure.

At high pressure:

The value of integration of $\int\limits_{O}^{P}(\alpha)$ dP as illustrated by the shaded portion show in the graph. Then the fugacity of the gas would be greater than the pressure (P) at high pressure.

Example:

The data given in the table for ideal gas at various pressure at O°C.

Pressure (atm)	Fugacity (atm)
50	48.9
100	96.7
200	194.2
400	424.4
800	1191
1000	1834

Fugacity of a liquid component in a liquid mixture:

Consider a liquid 'i' in equilibrium with its vapour. The chemical potential of the liquid (μ_i) l is equal to the chemical potential of its vapour (μ_i) g

$$(\mu_i)_l = (\mu_i)_g$$

According to fugacity of a real gas eqn. The chemical protential of a vapour may be written as,

$(\mu_i)_g = (\mu_i^*)_g + RT \ln f_i$

Where, $(\mu_i)^*_g$ is the chemical protentials of the vapour. Then fugacity = 1

Chemical protential of a liquid may be written as,

$(\mu_i^*)_l = (\mu_i^*)_2 + RT \ln f_i$

Where $(\mu_i^*)_l$ is the chemical protential of the liquid, then fugacity = 1.

So that, the fugacity of a pure liquid would be the same as that of its vapour in equilibrium with it, at a given temperature.

Concept of activity and activity Co-efficient :

Consider a system having the chemical protential (μ_i) of a substance 'i' inpure stage and f_i, be the fugacity in the same state, then

$\mu_i = \mu_i + RT \ln f_i$

Let 'μ_i' be the chemical protential of the same substance in some other stage [Stage]

$$\mu^o_i = \mu_i^* + RT \ln f_i^o \xrightarrow{\hspace{3cm}} (2)$$

The difference between chemical potential of a substance in any state an that in a pure state is given by

$$\mu_i - \mu_i = RT \ln \frac{f_i}{f_i^o} \xrightarrow{\hspace{2cm}} (3)$$

We may introduce a new term hear, activity

$$(a) = \frac{f}{fo} \xrightarrow{\hspace{2cm}} (4)$$

For a Substance 'i' as

$$a_i = \frac{f}{fi} \xrightarrow{\hspace{1.5cm}} (5)$$

The above eqn sub in eqn (3)

$$\mu_i - \mu^o_i = RT \ln a_i \xrightarrow{\hspace{2cm}} (6)$$

Definition :

So that, activity is defined as the ratio of the fugacity of the substance in that substance in that state to the fugacity of the same substance in the pure state.

Let a system consisting of 1 mole of a substance change from a state in which its chemical protential is (μ_i) to another state in which its chemical protential is (μ_2).

The change in chemical protential ($\Delta\mu$) is then given by,

$\Delta\mu = \mu_2 - \mu_1$

from (6) $\Rightarrow \mu_1 = \mu^o_1 + RT \ln a_1$

$\mu_2 = \mu^o_2 + RT \ln a_2$

$\Delta\mu_1 = \mu^o_2 + RT \ln a_2$

$\Delta\mu_1 = (\mu^o_2 + RT \ln a_2) - (\mu^o_1 + RT \ln a_1)$

$= \mu^o_2 + RT \ln a_2 - \mu^o_1 + RT \ln a_1$

$= RT \ln (a_2 - a_1)$

$\Delta\mu = RT \ln \dfrac{a_2}{a_1}$

$\Delta\mu = \Delta G$

Activity Co-efficent :

For an ideal gas activity is numerically equal to its pressure i.e,

a=P

For a real gas activity is only proportionall to its pressure i.e.

a α P

a = δ P

Where δ is known as the activity Co-efficient.

Reference states (or) standard state :

It may emphasised again that there is no means of finding absolute values of free energy (G) or chemical protentials (μ) of any substance.

It's necessary, therefore to make such measuments with reference to the value obtain for some convinient though orbitary reference state called standard state.

The standard state for a gas :

It is defined as the state in which the fugacity of the gas is equal to unity.

Since activity $a = \dfrac{f}{f^o}$

if $f^o = 1$

$a = f$

Evidently the standard state for a gaseous component is such that,

$f_i - a_i = 1$

Standard State for Liquid :

The standard state for a liquid is the pure state of a liquid at 1 atm pressure at any given temperature.

In this state $f = f^o$

$a = \dfrac{f^o}{f^o}$

$a = 1$

The standard state for a liquid component is such that $a_i = 1$

Standard state for solid :

The standard state for a solid is the pure state of the solid at 1 atom pressure at any given temperature.

In this state is activity $a = 1$

Third law of thermodynamics statement :

At absolute zero temp, entropy of perfects crystalline solid is zero.

Explanation :

In a perfect crystal, a crystal lattice will have lowest energy at absolute zero temperature, hence there will be disorder or random less so its entropy will be zero.

Nernst heat theorem

Consider Gibb's helmoltz equation,

$$\Delta G = \Delta H + T \left(\dfrac{\partial \Delta G}{\partial T} \right) \longrightarrow (1)$$

At absolute Zero (T=O)

Therefore the above eqn becomes,

$$\Delta G = \Delta H \longrightarrow (2)$$

i,e, As the temp is lower, ΔG & ΔH approach closely and becomes equal at absolute zero.

A graph is ploted temp V$_s$, ΔG & ΔH

The mathermatical expression is

$$\lim_{T \to O} \left(\frac{\partial \Delta H}{\partial T}\right)_P = \lim_{T \to O} \left(\frac{\partial \Delta H}{\partial T}\right)_P = O \longrightarrow (3)$$

We know that,

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = -\Delta S \longrightarrow (4)$$

$$\Delta CP = \left(\frac{\partial \Delta H}{\partial T}\right)_P \longrightarrow (5)$$

Sub eqns (4) & (5) in eqn (3)

$$\lim_{T \to O} (\Delta CP) = \lim_{T \to O} (-\Delta S) = O$$

Nernst heattheorem holds good for solids i,e, It is mostly applicable for solids.

ΔS – entropy change

ΔCP – Difference between heat capacity of product and reactant at constant prensure.

Definition :

From the above explanation the value of $\frac{\partial \Delta G}{\partial T}$ becomes zero gradunally at the temp is lower towards absolute zero kelvin.

Evaluation of absolute entropy from heat capacity measurments:

We know that for an infinitesimally small change of a system, the entropy change is given by,

$$ds = \frac{dq}{T} \longrightarrow (1)$$

At constant pressure,

$$(ds)_P = \frac{(dq)P}{T} \longrightarrow (2)$$

Divide by dT

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial q}{\partial T}\right)_P \times \frac{1}{T} \longrightarrow (3)$$

We know that

$$\left(\frac{\partial \Delta H}{\partial T} \right)_P = CP$$

$$\partial S = Cp \times \left(\frac{\partial T}{T} \right) \longrightarrow (4)$$

For a perfect crystalline substance absolute entropy S-O at temperature T =O

$$\int_{S=O}^{S=T} ds = Cp \int_{T=O}^{T=T} \frac{dT}{T} \longrightarrow (5)$$

$$[S]_O^T \quad Cp \int_{T=O}^{T=T} \frac{dT}{T}$$

$$S_T - S_o = CP \int_O^T \frac{dT}{T} \longrightarrow (6)$$

At absolute zero $S_o = O$

$$S_T = Cp \int_O^T \frac{dT}{T} \longrightarrow (7)$$

$$S_T = Cp \int_O^T \frac{dT}{T} + Cp \int_T^T \frac{dT}{T} \longrightarrow (8)$$

Where

$10 < T \; V 15 \; K$

The first integral is evaluated with debye theory of heat capacity which says that at very low temperature.

$$Cp \approx Cv \approx aT^3 \longrightarrow (9)$$

Where,

a is an empiricale constant

The above equation is known as debye T^3 law.

eqn (9) sub in eqn (8)

$$S_T = aT^3 \int_O^{T^*} \frac{dT}{T} + Cp \int_{T^*}^T \frac{dT}{T}$$

$$= a \int_O^{T^*} \frac{dT}{T} X T^3 + Cp \int_{T^*}^T \frac{dT}{T}$$

$$= a \int_{O}^{T^*} dT(T^2) + Cp \int_{T^*}^{T} \frac{dT}{T}$$

$$= a \left[\frac{T^3}{3} \right] + Cp \int_{T^*}^{T} \frac{dT}{T} \longrightarrow \qquad (10)$$

The second integral is evaluated by experiments of heat capacity.

The graph is drawn between Cp & Ln T

Area under the graph gives the value of absolute entropy.

At lower temperature the value of Cp is obtained by extra polation.

Test for third law [Experimental Verification]

The third law is verify using two different crystalline forms.

Let us the crystalline tranistiom $\propto \rightarrow \beta$

$$\Delta S = S_\beta - S_\propto = \frac{\Delta H_{tr}}{T_{tr}}$$

Where,

ΔH_{tr} entholpy of transistion

T_{tr} Transistion temperature

Where ΔH_{tr} & T_{tr} are experimentally determined To verify third law we should prove that

$S_\beta - S_\propto$

i,e. both crystalline forms as equal entropies at OK.

The third law is verified experimentally incase of sulphea, tin and phospine.

For phosphine calculated entropy as the following values.

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}} = \frac{185.7}{49.43} = 15.73 \, TK^{-1} \, mole^{-1}$$

Experimental values is found to be 15.96 JK^{-1} mole^{-1} i,e, J/K/ mole.

The comparision of two values we should be the thrid law of phosphine.

Exceptions to third law:

CO, NO, H_2O doesn't obey the third law. i.e, they doesn't have definite structure. Hence they have some disorder at OK and the entropy is not zero, $(\Delta S \neq O)$.

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