PERIYAR INSTITUTE OF DISTANCE EDUCATION (PRIDE)

PERIYAR UNIVERSITY

SALEM - 636 011.

B.Sc. BOTANY

SECOND YEAR

ALLIED – II : CHEMISTRY

Prepared by :
A.N.S. VASUDEVAN
Department of Chemistry
Thiruvalluvar Govt. Arts College
Rasipuram
Namakkal Dt.

B.Sc. BOTANY
SECOND YEAR
ALLIED – II : CHEMISTRY

UNIT - I

Chemical Bonding

1.1. Molecular Orbital Theory-bonding, antibonding and nonbonding orbitals.

M.O. diagrams of Hydrogen, Helium, Nitrogen, Fluorine and Nitric Oxide - discussion of bond order and magnetic properties.

1.2. Hydrides-classification and characteristics - preparation, properties and uses of Borazole, $NaBH_4$ and $LiAlH_4$.

1.3. Carbonyls-mononuclear and polynuclear carbonyls - Examples. Preparation, properties and structure of $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$.

Co-ordination chemistry

1.4. Definition of terms-classification of ligands-Nomenclature- Chelation - Examples. Chelate effect-explanation.

1.5. Werner’s theory-conductivity and precipitation studies. Sidgwick’s theory-Effective Atomic Number concept.

1.6. Pauling’s theory-postulates-Application to octahedral, square planar and tetrahedral complexes. Pauling’s theory and magnetic properties of complexes. Merits and demerits of Pauling’s theory.

1.7. Biological role of Haemoglobin and Chlorophyll (Elementary idea of structure and mechanism of action).

1.8. Application of coordination compounds in qualitative and quantitative analysis-separation of Copper and Cadmium ions, Nickel and Cobalt ions-identification of metal ions like Cu, Fe and Ni. Quantitative estimation of Ni using DMG, Aluminium using Oxine.EDTA and its application.

UNIT - II

2.1. Covalent Bond-Orbital Overlap-Hybridisation – Geometry of Organic molecules-Methane, Ethylene, Acetylene and Benzene.

2.2. Electron displacement Effects: Inductive, Resonance, Hyper conjugative & steric effects. Their effect on the properties of compounds.

2.3. Stereoisomerism: Symmetry-elements of symmetry- cause of optical activity, Tartaric acid. Racemisation. Resolution. Geometrical isomerism of Maleic and Fumaric acids-Keto-enol tautomerism of Acetoacetic ester-conformers of n-butane with brief explanation

2.4. Aromatic compounds-Aromaticity-Huckel's rule

2.5 Electrophilic substitution in Benzene-Mechanism of Nitration, Halogenation-Alkylation, Acylation.

2.6. Isolation, preparation, properties and structure of Naphthalene Haworth's synthesis.

2.6. Heterocyclic compounds:- Preparation, properties and uses of Furan, Thiophene, Pyrrole and Pyridine.

UNIT - III

3.1 **Carbohydrates**: Classification, preparation and properties of Glucose and Fructose-discussion of open chain and ring structure of Glucose. Mutarotation. Preparation and properties of Sucrose. Structure (detailed discussion of structure not necessary) Properties of Starch, Cellulose and derivatives of Cellulose. Inter conversion of Glucose to Frutose and vice versa.

3.2. **Amino Acids**-classification, preparation and properties of Glycine. and Alanine. Preparation of peptides (Bergmann method only).

3.3. **Proteins:** classification according to composition, biological function and shape. Denaturation of proteins.

3.4. **Chemotherapy:** Preparation, uses and mode of action of sulpha drugs-prontosil, sulphadiazine and sulphafurazole. Uses of penicillin, chloramphenicol and streptomycin, Definition and one example each for-analgesics, antipyretics, tranquilizers, sedatives, hypnotics, local anaesthetics and general anaesthetics

UNIT - IV

Nuclear Chemistry

4.1. Fundamental particles of Nucleus – nuclide, isotopes, isobars and isotones

4.2. Natural radioactivity-radioactive series including Neptunium series-Group displacement law.

4.3. Nuclear Binding energy, mass defect-Calculations.

4.4. Nuclear Fission and Nuclear Fusion-differences – Stellar energy.

4.5. Applications of radioistopes-C-14 dating, rock dating,isotopes an tracers, study of Reaction mechanism (ester hydrolysis) radiodiognosis and radiotherapy

4.6. **Photochemistry**: Grotthus-Draper law and Stark-Einstien's law of photochemical equivalence. Quantum yield. Example for photochemical reactions- Hydrogen-Chlorine reaction (elementary idea only) photosynthesis.

4.8. **Phase Rule:** Phase rule and the definition of terms in it. Application of phase rule to water system. Reduced phase rule and its application to a simple eutetic system (Pb-Ag) Freezing mixtures.

UNIT - V

5.1. Solutions: Liquid in liquid type-Raoult's law for ideal solutions. positive and negative deviation from Raoult's law-Reasons and examples, Fractional distillation and Azeotropic distillation.

5.2. Colligative properties: Review of colligative properties of dilute solutions-lowering of V.P, elevation of B.Pt and depression of F.Pt and osmotic pressure. Reverse osmosis. Abnormal molecular weights-van't Hoff factor-degree of dissociation and association-problems.

5.3. Chromatography: principle and application of column, paper and thin layer chromatography.

5.4. Electro Chemistry: Kohlrausch law -measurement of conductance, pH determination. Conductometic titrations. Hydrolysis of salts.

Derivation of K_h. pH and buffer action in living system. Galvanic cells-EMF-standard electrode potentials, reference electrodes, electrochemical series and its applications. Principle of electroplating, pH determination

UNIT – I

Chemical Bonding

Molecular Orbital Theory:-

According to MOT, Put forward by Hund and Mullikan all the atomic orbital’s of the atoms participation in the formation of the molecule approach nearer to each other and get mixed up to give an equivalent number of new orbital’s that now belong to the molecule as a whole these new orbital’s are called molecular orbital’s (MOs).

Formation of Bonding and Anti bonding Molecular orbital’s.

Molecular orbital’s of a molecule are obtained by the bonded atoms. The linear combination of two AO ware Functions is brought about either by adding or by subtracting the two wave functions of two AOs . Thus is Ψ is the wave function of the MO obtained from two AOs of two Atoms. A and B having Ψ_A and Ψ_B respectively as their wave function.

$$\Psi = \Psi_A I \Psi_B \qquad - 1$$

Equation (1) clearly shows that the linear combination of Ψ_A and Ψ_B gives two MO_S. one of these is represented as Ψ_b and the other as Ψ^* . These are thus given by :

$$\Psi^* = \Psi_A - \Psi_B \quad \textbf{Repulsion (or) Substraction}$$

Ψ^b → **one bonding**
Ψ^* → **one antibonding**

The MO, Ψ_b, has lower energy than that of either of the AO_S from which it is formed. The MO thus leads to the formation of a stable molecule, AB and is, therefore, called a bonding molecular orbital. The other MO namely Ψ^* has higher energy than that of Ψ_A and Ψ_B and is, therefore, called an antibonding molecular orbital’s. The superscript b used is Ψ_b indicates that the molecular orbital is bonding molecular orbital while * used in Ψ^* indicates that the molecular orbital is antibonding. The number of molecular orbital’s is always equal to the number of atomic orbital’s involved in the formation of molecular orbital.

The plus sign in equation (2) indicates that the Ψ^b MO_s is obtained when the regions of AO_s marked with positive sign overlap with each other. In this case it is said that the two AO_s have been added on the other hand is equation.

3) Negative sign indicates that Ψ^* is obtained when the region of positive sign of one AO (say of Ψ_A) overlaps with the region of negative sign of the other AO(say of Ψ_B) . In this case we say that the two AO_s have been subtracted.

Difference Between Bonding and Anti-bonding Molecular orbital's.

Bonding	**Anti-Bonding**
i) A bonding MOs is formed by the combination of electron wave of the same sign, ie, by the addition overlap of atomic orbitals.	i) Anti bonding MOs is formed by the combination of electron waves of the opposite sign, ie. by the subtraction overlap of atomic orbitals.
ii) Bonding MOs possesses lower than the atomic orbitals from which it is formed.	ii) Anti bonding MOs possesses higher energy than the atomic orbitals from which it is formed.
iii) The electron density in between the nuclei is high and hence the attraction between the nuclear is high. This explains the formation of a bond between the atoms.	(iii) The electron density is between the nuclear is low and hence the repulsion between the nuclear is high. This explains the non-formation of the bond between the atoms.
(iv) $\Psi=\Psi_A+\Psi_b$	(iv) $\Psi^*=\Psi_A-\Psi_b$

Energy level Dragran of Molecular orbitals:

The order of energy of the molecular orbitals has been determined experimentally by spectroscopic measurements. The energy of these molecular orbitals increases as we move from left to right in the following list.

Bond Order:

The stabilizes of various species may be compared in terms of band strengths which is turn are measured by means of quantity called bond order.

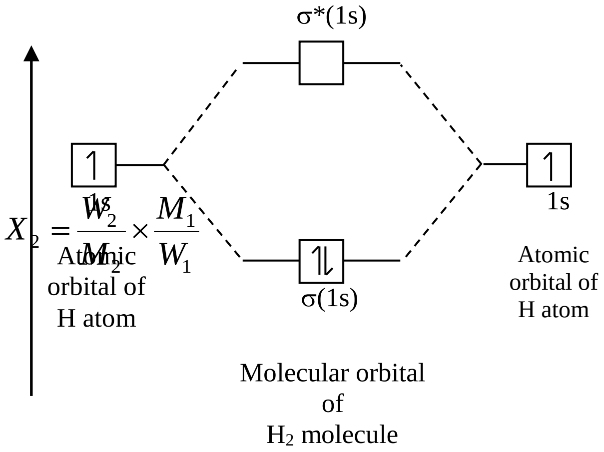
$$\text{Bond Order} = \tfrac{1}{2}\begin{pmatrix}\text{Number of } e^- \text{ in}\\ \text{bonding MOs}\end{pmatrix} + \begin{pmatrix}\text{Number of } e^- \text{ in}\\ \text{Antibonding MOs}\end{pmatrix}$$

M.O diagrams of Hydrogen :

The electronic configuration of H is $1s^1$. Each atom contributes 1 valence electrons. The H_2 molecule would have two molecular orbitals. Two electrons have to be accommodated in them. The electrons are filled following aufbau principle. 2 electrons go to the bonding molecular orbital. The σ*(1s) orbital is empty.

The number of bonds in H_2 molecule = ½ (2-0) = 1.

This represents one σ bond. Since there is no unpaired electrons, H_2 molecule is diamagnetic.



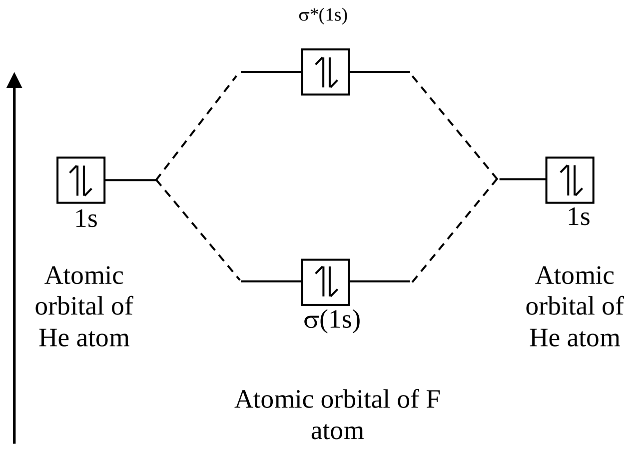
$$X_2 = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

M.O diagram of Helium :

The electronic configuration of He is $1s^2$. Each atom contributes 2 valence electrons. The He_2 molecule would have two molecular orbitals. Ten electrons have to be accommodated in them. The electrons are filled following aufbau principle. 2 electrons go to the bonding molecular orbital, 2 electrons to σ*(1s) antibonding molecular orbital.

The number of bonds in He_2 molecule = ½ (2-2) = 0.

This means that the molecule does not exist. Since bonding energy of the σ(1s) orbital is more than cancelled by the antibonding σ*(1s) orbital. This is because the effect of antibonding e^-s is somewhat stronger than that of bonding electrons.

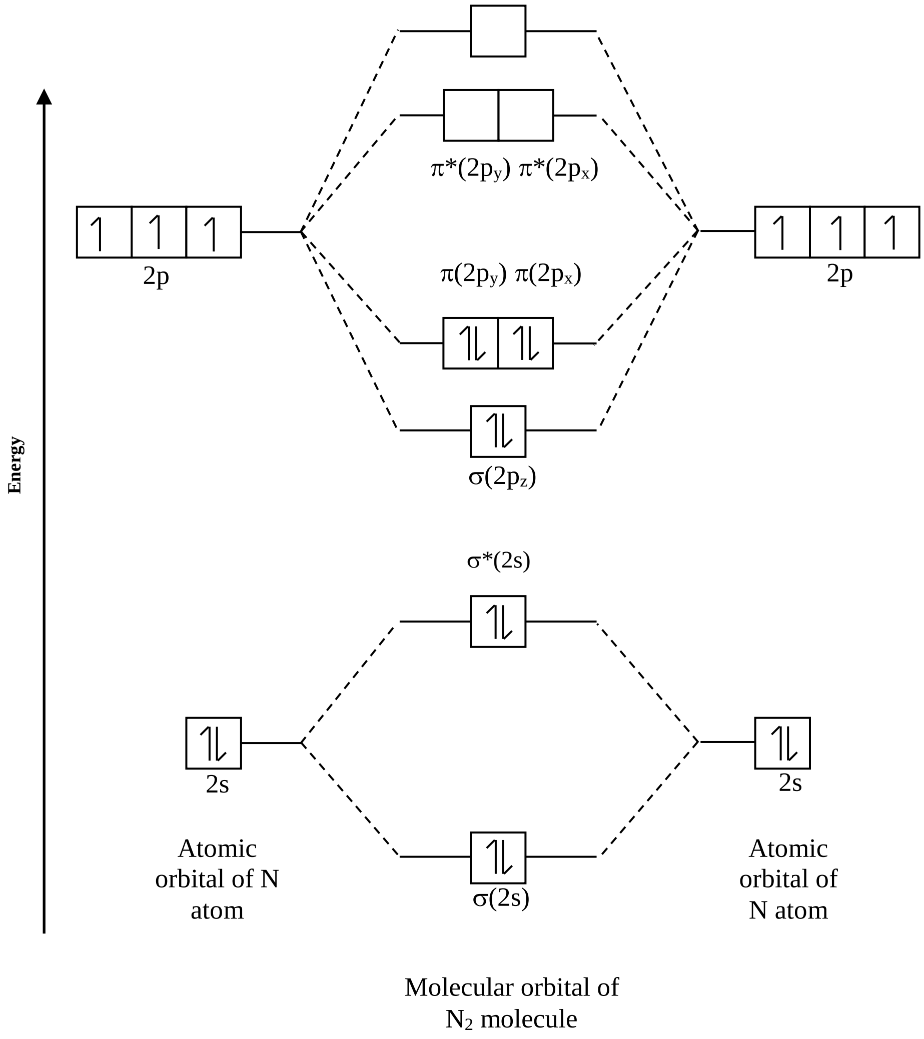


M.O diagrams of Nitrogen :

The electronic configuration of N is $1s^2$, $2s^2$, $2p^3$. Each atom contributes 5 valence electrons (2+1+1+1). The N_2 molecule would have eight molecular orbitals. Ten electrons have to be accommodated in them. The electrons are filled following aufbau principle. 8 electrons go to the bonding molecular orbitals, 2 electrons to σ*(2s) antibonding molecular orbital.

The number of bonds in N_2 molecule = ½ (8-2) = 3.

This represents one σ bond and two π bonds. Since there is no unpaired electrons, N_2 molecule is diamagnetic.



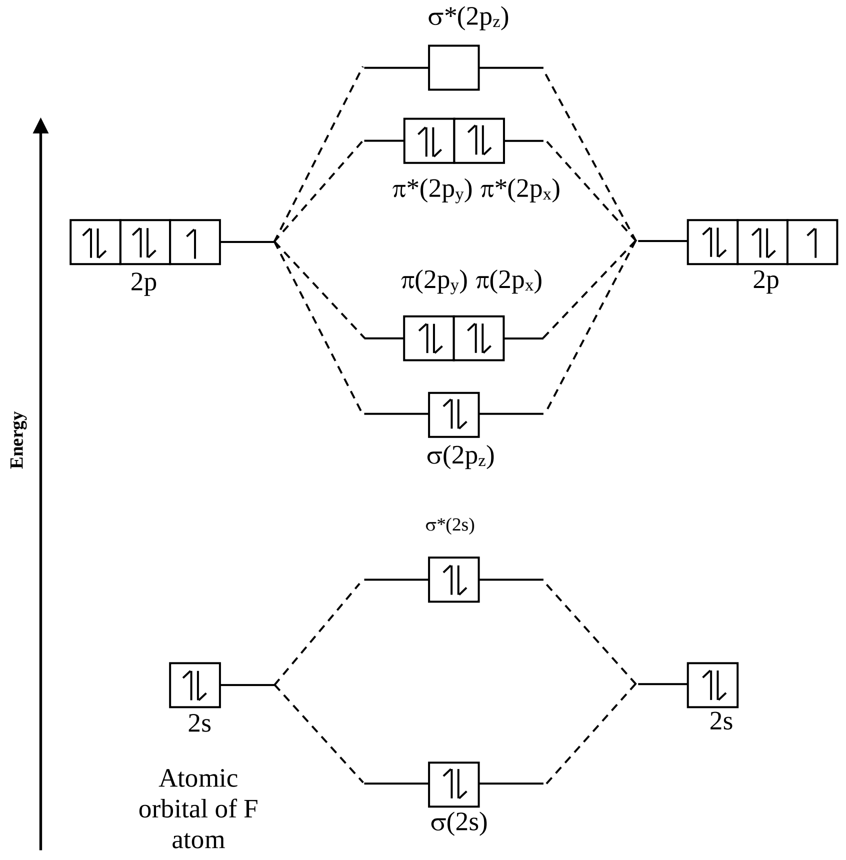
Molecular orbital of N_2 molecule

M.O diagram of F_2 molecule :

The electronic configuration of F is $1s^2$, $2s^2$, $2p^5$. Each atom contributes 7 valence electrons (2+2+2+1). The F_2 molecule would have eight molecular orbitals. Fourten electrons have to be accommodated in them. The electrons are filled following aufbau principle. 8 electrons go to the bonding molecular orbitals, 6 electrons to antibonding molecular orbitals.

The number of bonds in F_2 molecule = ½ (8-6) = 1.

This represents one σ bond. Since there is no unpaired electrons, N_2 molecule is diamagnetic.



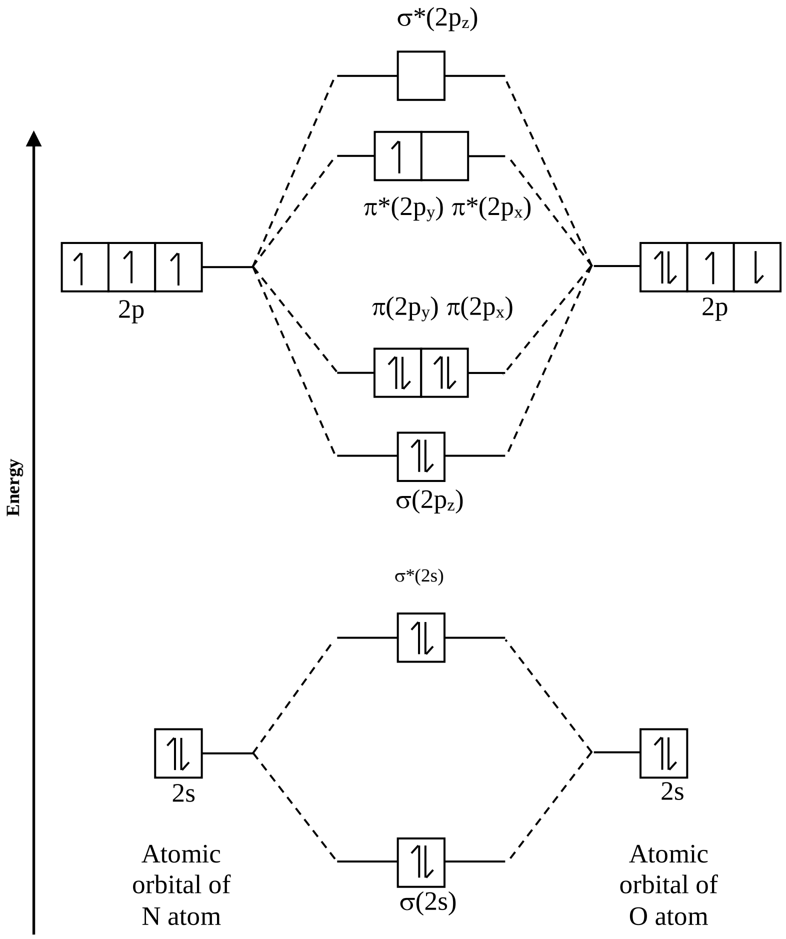
Molecular orbital of
F_2 molecule

M.O diagram of NO (Nitric oxide)

This molecule has one nitrogen atom and one oxygen atom. Their electronic configurations are $1s^2$, $2s^2$, $2p^3$ and $1s^2$, $2s^2$, $2p^4$ respectively. 5 and 6 = 11 electrons in their valency shell. So its molecular electronic configuration will be $KK(\sigma 2s)^2$ $(\sigma sp)^2$ $(\sigma sp)^4$ $(\pi sp)^1$.

Bond order = ½ (8-3) = 2 ½

Since the molecular orbital structure of NO contains an unpaired electron, the molecule is paramagnetic.



Molecular orbital of NO molecule

HYDRIDES

Classification :

The hydrides are divided into three groups .

1. Ionic (or) salt – like hydride
2. Covalent (or) molecular hydrides.
3. metallic (or) interstitial hydrides.
4. Polymeric hydrides.

1. Ionic or Salt like hydrides:

They are also called electrovalent hydrides. Only elements with very low electronegativity values can transfer electrons to the hydrogen atom and form salt-like hydrides. The elements of IA, IIA and IIIA form hydrides of this type having the composition MH_x. Where, x is the group valency of the metal.

Example: LiH, NaH, CaH_2

2. Volatile or Covalent hydrides:

These hydrides are formed by the highly electronegative elements by sharing of electrons with hydrogen. They have the general formula $XH_{(8-n)}$. Where n is the group number of the element. The metals belonging to IIB, IVB, VB, VIB and VIIB groups form this type of hydrides.

Example: HF, CH_4, NH_3..

3. Metallic hydrides or interstitial hydrides:

The transition elements and rare-earth metals combine with hydrogen to produce hydrides, which are metallic in appearance. They do not possess definite composition. In these hydrides the hydrogen atoms seem to occupy the interstities of the metals. Hence they are called as interstitial hydrides.

4. Polymeric hydrides:

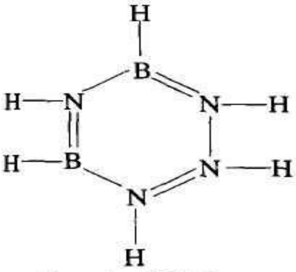
In polymeric hydrides two or more metal atoms are linked by hydrogen bridges.

Examples: $LiAlH_4$, $LiBH_4$.

Borazole :

Borazole or borazine, also known as the inorganic benzene has the molecular formula $B_3N_3H_6$

Structure of Borazole :



Borazine, $B_3N_3H_6$

Preparation :

i) **By Stock's method :**

Borazole was prepared by the action of NH_3 on diborane, B_2H_6. The adduct (B_2H_6 . $2NH_3$) is formed first., which then gets decomposed by heating in a closed tube at 200^0.

$$2B_2H_6 + 6NH_3 \longrightarrow 3[B_2H_6.2NH_3] \xrightarrow{200^0C} 2B_3N_3H_6 + 12H_2$$

i) By heating the mixture of $LiBH_4$ and NH_4 Cl:

$B_3N_3H_6$ can be prepared in the laboratory by heating a mixture of $LIBH_4$ and NH_4Cl in vacuum at 230^0C.

$$3HN_4Cl \quad 3LiBH_4 \longrightarrow B_3N_3H_6 \quad 3LiCl \quad 9H_2$$

Properties :

- It is a colourless mobile volatile liquid.
- It freezes at -58^0 C.
- It boils at 64.5^0 C and melts at -58^0 C.
- It undergoes addition reactions.

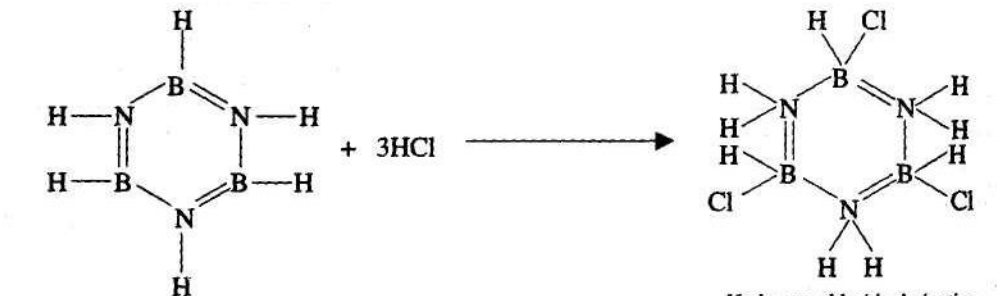
Similarities with benzene:

Since borazine is isoelectronic with benzene, some of its physical properties ar similar to those of benzene. This is shown below.

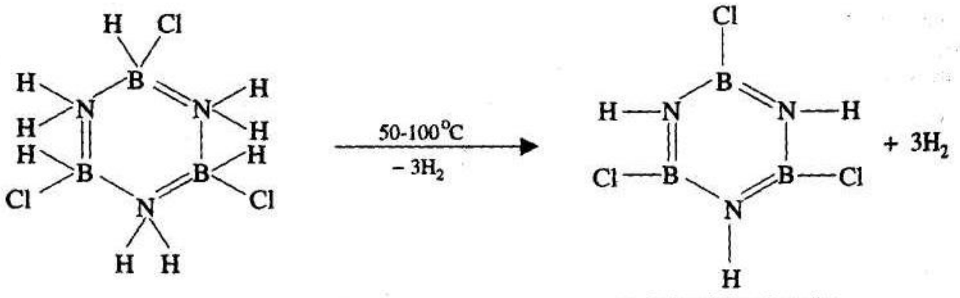
	Mol. Wt.	**M.Pt.**	**B.Pt**	**ΔH_{vap} (KJ/mole)**	**Trouton's Constant**
Borazine ($B_3N_3H_6$)	80.6	-58	64.5	39.3	21.4
Benzene (C_6H_6)	78.0	+6	80.0	31.0	21.0

Chemical Properties:

i Addition Reactions:



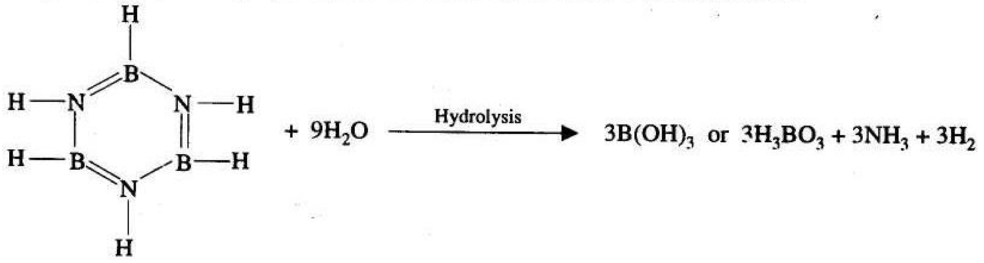
Hydrogen chloride derivative



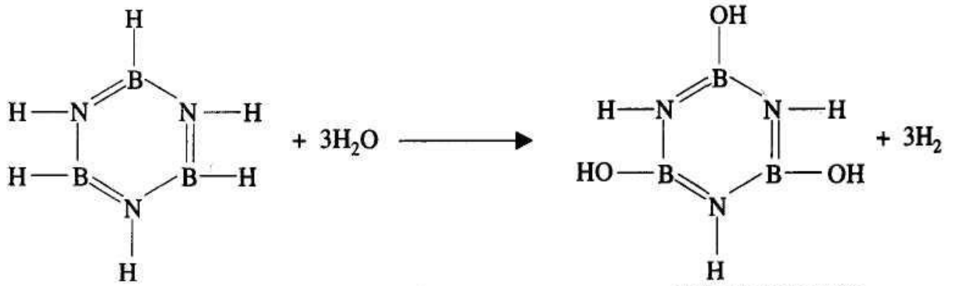
B, B, B-trichloroborazine

ii) Hydrolysis:

Borazine gets slowly hydrolysed by water to produce boric acid $B(OH)_3$ or H_3BO_3, NH_3 and H_2.



Borazine reacts with three molecules of water and gives B-trihydroxyl borazine, $B_3N_3H_3(OH)_3$.

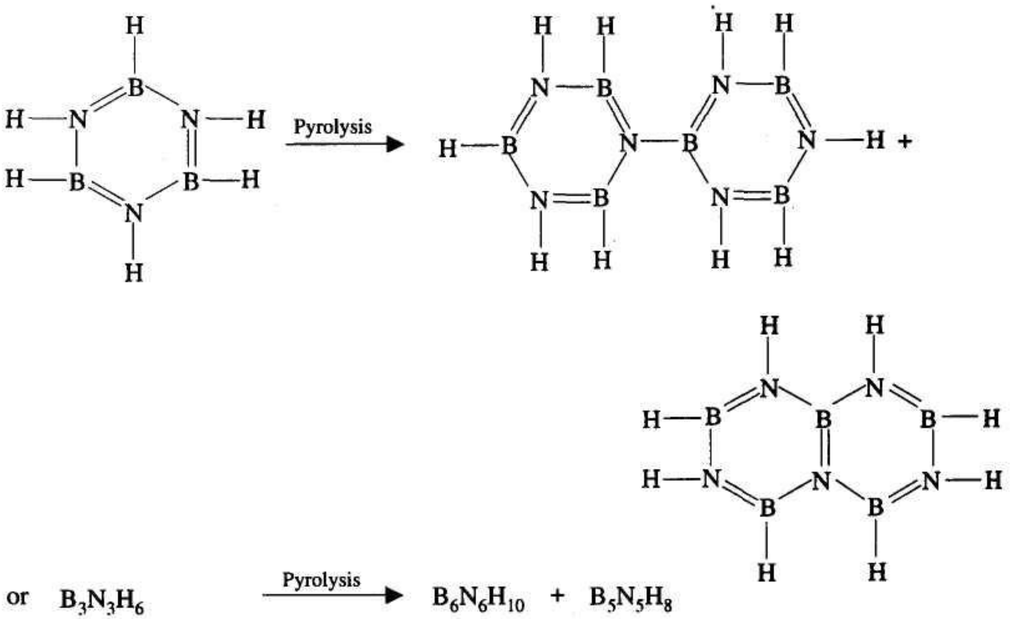


B-trihydroxyl borazine

or $B_3N_3H_6 + 3H_2O \longrightarrow B_3N_3H_3(OH)_3 + 3H_2$

iii) Pyrolysis:

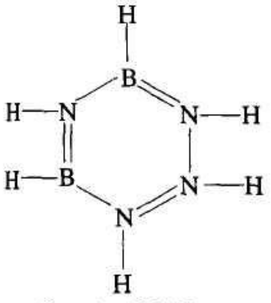
When borazine is pyrolysed above 340^0C, $B_6N_6H_{10}$ and $B_5N_5H_8$ are produced. These products are boron-nitrogen analogus of diphenyl and naphthalene respectively.

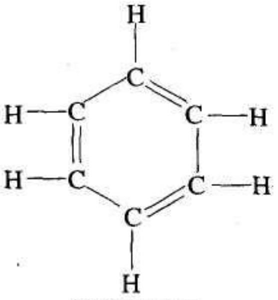


or $B_3N_3H_6 \xrightarrow{\text{Pyrolysis}} B_6N_6H_{10} + B_5N_5H_8$

Structure:

Various chemical reactions and electron diffraction study of borazine molecule have shown that this molecule is isoelectronic with benzene and hence its structure is the same as that of benzene. Thus like benzene, borazine has a planar hexagonal structure, containing six-memebered ring, in which B and N atoms are arranged alternately. It is because of the similarity between the structures of borazine and benzene that borazine is called inorganic benzene.


Borazine, $B_3N_3H_6$


Benzene, C_6H_6

In borazine, B-N bond length is equal to 1.44A^0, which is between the calculated singly B-N bond (1.54A^0) and double bond B=N (1.36A^0) distances. The angles are equal to 120^0. In benzene, C-C bond length is equal to 1.42A^0.

Sodium Borohydride :

Preparation :

1) It may be prepared by reacting sodium hydroxide with methyl borate $B(OCH_3)_3$ using tetrahedron furan (THF) as the solvent.

$$4NaOH + B(OCH_3)_3 \longrightarrow 3CH_3ONa + NaBH_4$$

2) It can also be prepared by the action of B_2H_6 on NaH (in either)

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4$$

Properties:

- It is a solid stable up to 397^{o}c.
- It does not decompose water is the cold.
- It is soluble in water and other polar solvents.
- It reacts with HCl and BF_3.

It is a good reducing agent. It does not reduce carbon –carbon double bonds. Not even those conjugated with carbonyl groups and so is useful for the reduction of unsaturated carbonyl compounds to unsaturated alcohols.

Uses:

As mentioned above. It is used as reducing agent and in particular for reducing unsaturated carbonyl compounds.

Lithium Aluminium Hydride : ($LiAlH_4$)

Preparation :

1) By the direct synthesis from elements.

$$Li + Al + 2H_2 \longrightarrow LiAlH_4$$

2. By the direct combination of Lithium hydride and aluminium chloride in ether solution.

$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl_3$$

Properties:

i) It is a non-volatile colorless crystalline solid which is stable to air in the cold. It is soluble is either and other organic solvents.

ii) When heated, it gets decomposed.

iii) It is decomposed by water, liberating H_2 gas.

$$LiAlH_4 + 2H_2O \longrightarrow LiAlO_2 + 4H_2$$

iv) It is strong **reducing agent** and reduced certain halides.

$$4BF_3 + 3\,LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

$$AlCl_3 + 3\,LiAlH_4 \longrightarrow 3LiCl + 4AlH_3$$

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

v) **Aldehydes to alcohols:**

$$RCHO \xrightarrow{LiAlH_4} RCH_2OH$$

Uses:

i) It is used for reducing almost all the compounds containing a carbonyl group >C=O like ketones, carboxylic acids and their derivatives to alcohols.

ii) It is also used for the preparation of the hydrides of Si, B, Al etc. from their chlorides.

Carbonyls:

Carbonyls are the compounds in which the CO group is attached to a metallic element.

The metallic carbonyl may be classified into two types:

i) Mono nuclear carbonyls

ii) Polly nuclear carbonyls.

i) Mono nuclear carbonyls:

The mono nuclear carbonyls have the general formula $M(CO)x$. These contain only one atom of the metal per molecule of the carbonyl. Generally mono nuclear carbonyls are formed by metals which posses even atomic number.

Since mono –nuclear carbonyls are formed by metals with even atomic number, they have no unpaired electrons in their structure. So they are diamagnetic.

ii) Poly nuclear carbonyls:

The poly nuclear carbonyls have the general formula $Mx(CO)y$. They contain more than one atom of the metal per molecule, they are called binuclear carbonyl and they have general formula $M_2(CO)y$.

Since, metals with odd atomic numbers form binuclear carbonyls which again have no unpaired electrons in their structure. This binuclear carbonyls are also diamagnetic. Thus is general carbonyls are diamagnetic.

$Cr(CO)_6$:

Preparation:

1. **Job’s method :**

Carbon monoxide at 50 atmosphere pressure and room temperature is treated with Grignard reagent in the presence of at anhydrous chromic chloride. We get chromium hexa carbonyl.

2. Chromium hexa carbonyl can be prepared by treating a solution of a chromic

Salt dissolved in either with triethyl aluminium, $Al(C_2H_5)_3$ and carbon monoxide at high temperature and pressure.

Properties:

i) Chromium hexa carbonyl is a colourless solid which exists as rhombic crystals.

ii) It reacts with an alkali metal in liquid ammonia.

$$Cr(CO)_6 + 2Na \longrightarrow Na_2[Cr(sCO)_5] + CO$$

iii) It reacts with pyridine at temperature above 140oc

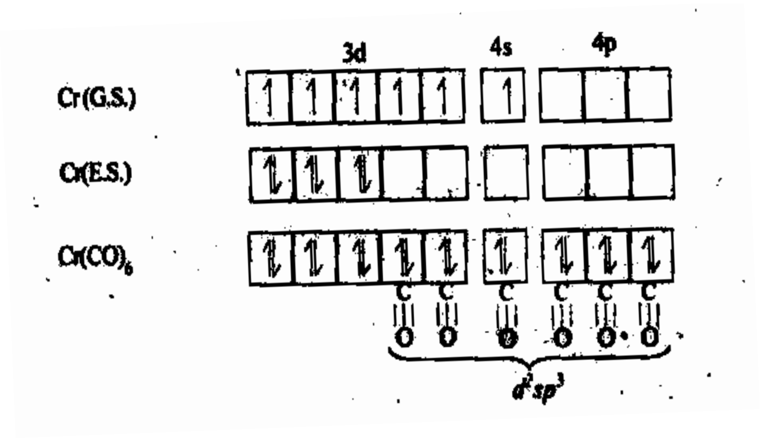
$$Cr(CO)_6 \longrightarrow Cr(CO)_2Py_2 \longrightarrow Cr_2(CO)_7Py_2 \longrightarrow Cr(CO)_3Py_2$$

iv) It reacts with potassium hydroxide in methyl alcohol at 100^0C to give a red solution.

$$Cr(CO)_6 + KOH + H_2O \longrightarrow K[Cr(CO)_2(H_2O)_2OH] + HCOOH$$

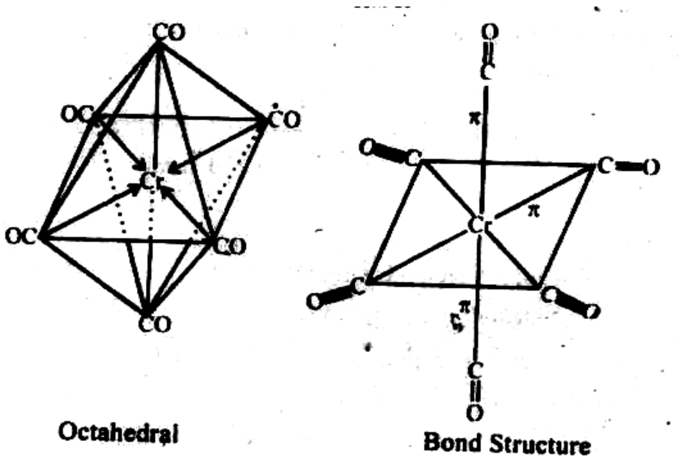
STRUCTURE :

1. The molecular formula is $Cr(CO)_6$. This makes us inter that to may possess octahedral configuration.
2. The octahedral configuration of $Cr(CO)_6$ is confirmed by the results of electron diffraction studies.
3. The electronic configuration of chromium is $Cr_{24} = 1s^2, 2s^2, 2p^6\, 3s^2, 3p^6, 3d^5\, 4s^1$. The configuration of the valance shell is shown below.



There are six vacant orbitals ($d^2 Sp^3$) in the exited state in the valiance shell. Thus is can accept six carbon monoxide molecules to form $Cr(CO)_6$. Hence it has octahedral configurations as shown in figure (1).

4. Recently it has been shown that the chromium atom has the following configuration Cr,4 = $Is^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. The bond structure of $Cr(CO)_6$ reveals two kinds of bonds between Cr and CO. Thus we have simple covalent bonds $Cr-C\equiv O^{+}$ and double bonds Cr - C = O as shown in figure.



Octahedral

Bond Structure

Figure

In the result resonance structure all Cr - C bonds are identical.

Uses:

It is used for the preparation of metal mirrors and plates.

$Fe(CO)_5$

Synthesis:

1. Iron penta carbonyl is the mono - nuclear carbonyl. It is prepared by the action monoxide on iron powder at 200atm and 100 - 200°C temperature.

$$Fe + 5CO \longrightarrow Fe(CO)_5$$

2. Recently it has been prepared by the action of carbon monoxide on ferrous iodide.

$$FeI_2 + 5CO \xrightarrow{2Cu} Fe(CO)_5 + Cu_2I_2$$

Reaction:

1. Action of Heat:

When it is heated above 1300^{0}C, it decomposes to give oron and carbon monoxide.

$$Fe(CO)_5 \longrightarrow Fe + 5CO$$

2. Action of Water: It is hydrolysed by water.

3. Action of acids: It is hydrolysed by sulphuric acids to give ferrous sulphate.

$$Fe(CO)_5 + H_2SO_4 \longrightarrow FeSO_4 + 5CO + H_2$$

4. Action of Base: It is also hydrolysed by weak bases.

$$Fe(CO)_5 \quad H_2O \quad NH_3 \longrightarrow H_2Fe(CO)_4 \quad NH_2COOH$$

5. Reducing action: It behaves as a reducing agent. The iron atom becomes divalent. Either CO or CO_2 is liberated. It gives the following reduction reactions.

$$Fe(CO)_5 + 2CCl_4 \longrightarrow C_5Cl_6 + FeCl_2 + 5CO$$

$$Fe(CO)_5 + SO_2Cl_2 \longrightarrow SO_2 + FeCl_2 + 5CO$$

$$Fe(CO)_5 + SnCl_4 \longrightarrow SnCl_2 + Fe(CO)_4Cl_3 + CO$$

$$Fe(CO)_5 + SbCl_2 \longrightarrow SbCl_5 + Fe(CO)_4Cl_2 + CO$$

6. When $Fe(CO)_5$ is irradiated by ultraviolet light $Fe_2(CO)_9$ is formed.

$$Fe(CO)_5 \longrightarrow Fe_2(CO)_9 \quad CO$$

7. When $Fe(CO)_5$ is heated with cyclo - pendadiene at 300°C it gives the π complex, ferrocene.

8. It reacts with halogens to give stable tetracarbonyl halide $Fe(CO)_4X_2$.

9. It reacts with nitric Oxide under pressure below 45°C to give $Fe(NO)_4$ which is a black crystalline solid.

It also forms Fe(CO)2(NO), with nitiric oxide.

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 +$$

10. With aqueous sodium hydroxide it uindergoes hydrolysis giving yellow carbonyl hydride.

$$Fe(CO)_5 + 3NaOH \longrightarrow Na[H_2Fe(CO)_4] + NaCO_3 + H_2O$$

11. With Ba(OH)$_2$, it hydrolyses.

$$Fe(CO)_5 + Ba(OH)_2 \longrightarrow [H_2Fe(CO)_4] + BaCO_3$$

12. With mercuric chloride or sulphate in acetone it gives the mercury derivative of iron carbonyl hydride.

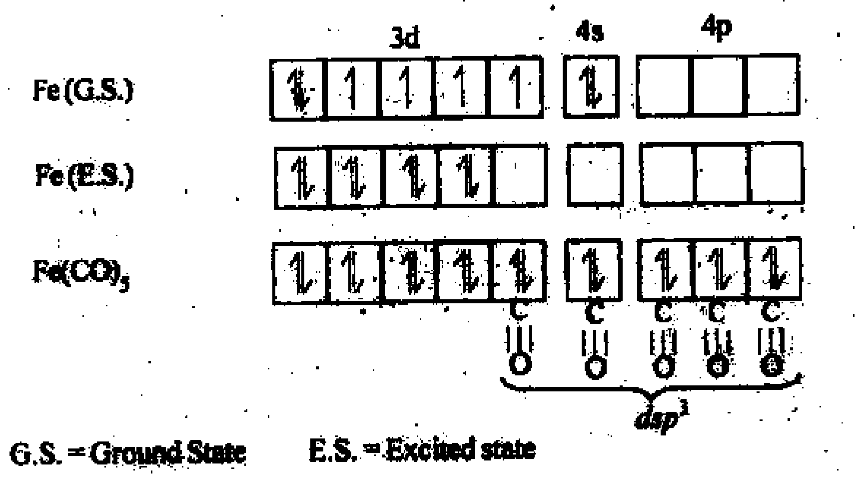
$$Fe(CO)_5 + 2HgCl_2 + H_2O \longrightarrow Fe(CO)_4Hg_2Cl_2 + 2HCl + CO_2$$

13. With pyridine it gives an ionic carbonyl complex.

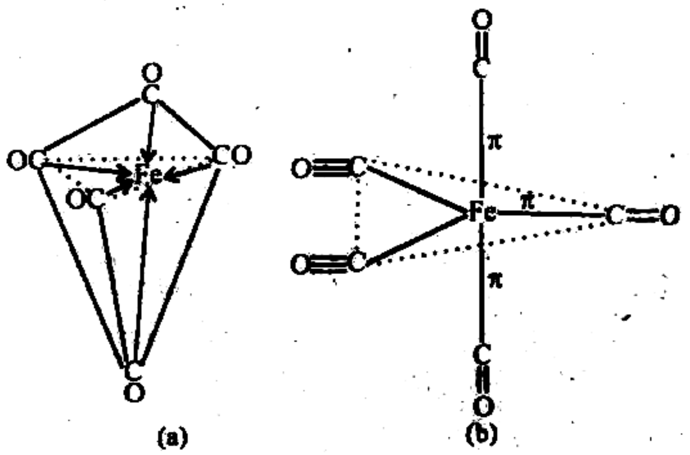
$$Fe(CO)_5 + NH_3 + H_2O \longrightarrow [C_6H_5NH]^+[HFe(CO)_4]^-$$

Structure

1. The vapour density and freezing points of benzene solution of iron penta - carbonyl show that its molecular formula is Fe (CO)$_5$
2. Electron diffraction and X - ray studies have revealed that Fe(CO)$_5$ posseses regular trigonal bi pyramid structure.
3. The molecule is diamagnetic and the distance Fe - C is 1.84A .
4. The electronic configuration of iron is $Fe_{26} = Is^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$. The configuration of the valency shell is given in Figure in the excited state of iron atom.
5.



There are five unoccupied orbitals (dsp^3) valency shell. Thus it can accept five CO molecules to from $Fe(CO)_5$ each CO group giving 2 electrons for the co - ordinate link. Hence it has bipyramid structure.



Trigonal π = pyramid structure of $Fe(CO)_5$

Figure B shows the bond structure of $Fe(CO)_5$

Uses:

1. Some times it is used as antiknock in petrol.
2. It is useful for the preparation of metal powders containing spherical particles.

$Ni(CO)_4$

Synthesis:

1. Nickel forms only more nuclear carbonyl $Ni(CO)_4$. Nickel carbonyl can be obtained by passing carbon monoxide over nickel at a temperature ofabout60°C.

$$Ni + 4CO \rightarrow Ni(CO)_4$$

2. When nickel iodide is headed with carbon monoxide in the presence of halogen acceptor, nickel carbonyl is obtained.

$$NiI_2 + 4CO \rightarrow Ni(CO)_4 + I_2$$

3. Carbon monoxide reacts with alkaline suspension of nickel sulphide or nickel cyanide to given nickel carbonyl.

$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + (CN)_2$$

$$Ni(CO)_4 + Ba(OH)_2 \longrightarrow H_2Ni(CO)_3 + BaCO_3$$

Reactions:

1.Action of heal : Nickel carbonyl is decomposed when heated to 180-200°C.

$$Ni(CO)_4 \longrightarrow Ni + 4CO\uparrow$$

2. Action of acids : Hydrochloric acid and hydrobromic acid have no action, sulphuric acid reacts to evoive carbon monoxide.

$$Ni(CO)_4 + H_2SO_4 \longrightarrow NiSO_4 + H_2 + 4CO\uparrow$$

4. Action of halogens: It reacts with gaseous chlorine to form nickel halide. Similarly, it reacts with bromine. In organic solvents, halogens react to form nickel halide and carbon monoxide.

$$Ni(CO)_4 + Cl_2 \longrightarrow NiCl_2 + 4CO\uparrow$$

$$Ni(CO)_4 + Br_2 \longrightarrow NiBr_2 + 4CO\uparrow.$$

5. Displacement reaction : The CO group can be displace of by other groups such as PCl_3, PF_3, NO_2 etc.

$$Ni\ (CO)_4 + 2PCl_3 \rightarrow Ni(CO)_2\ (PCl_3)_2 + 2CO\uparrow$$

$$Ni\ (CO)_4 + 2NO_2 \rightarrow Ni(CO_2)_2\ (PCl_3)_2 + 4CO\uparrow$$

6. **With HI :** It reacts rapidly with dry hydriodic acid.

$$2HI + Ni\ (CO)_4 \rightarrow NiI_2 + H_2 + 4CO\uparrow$$

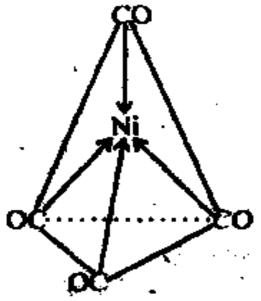
7. **Action of nitric oxide :** It reacts with most nitric oxide to give a compound of intense blue colour Ni(NO)(OH).

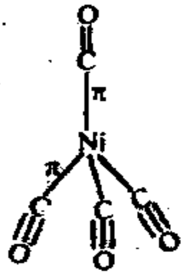
8. It is extremely toxic, colourless liquid, on heating suddenly it may explode mildly. It is miscible with benzene and is almost insoluble in water. Concentrated H_2SO_4 reacts with detonation.

Structures

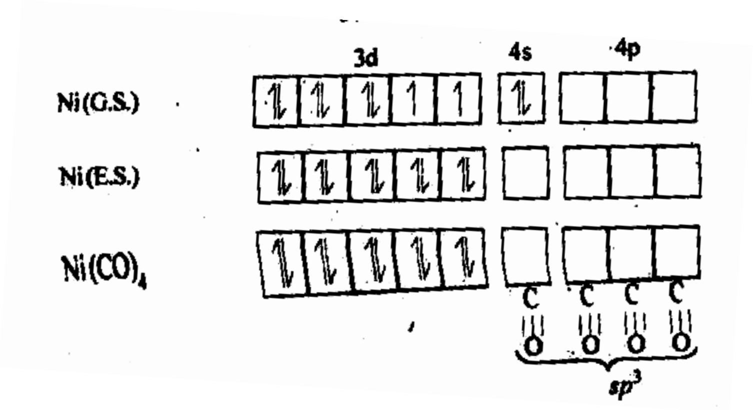
1. The vapour density of nickel carbonyl and the freezing point of its solution in benzene indicate the molecular formula to be $Ni(CO)_4$.
2. The electron diffraction studies on nickel carbonyl show that the configuration is tetrahedral and the Ni - C - O group is linear.
3. Raman spectral studies have revealed that the oxygen atom is triply bonded to carbon atom in the CO group.

4. It assumed that nickel atom has the configuration $Is^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2 4p^0$





Since the energy of the 3d and 4s electrons is not very much different, the 4s electrons easily go to fill the 3d orbitals, there by vacating 4s orbitals. Thus four orbitals (one 4s and three 4p) are now available for chemical bounding with four CO molecules to give $Ni(CO)_4$ Complex. Since all the four bounds are proved to be exactly identical it is clear that sp^3 hybridisation has taken place.



G.S. = Ground State

E.S = Excited State

The molecule has therefore a tetrahedral structure (Figure). Since in the arrangement has no unpaired electrons it is diamagnetic.

Recently it has been shows that it has structure as shown in Figure. (Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^1 4p^3$).

The complex follows EAN Rule. Number of electrons in Ni0 = 28 Electrons gained form 4CO molecules = 4 x 2 = 8.

Total = 36 = Number of electrons in Kr.

Uses:

1. Formation of nickel carbonyl is useful in the extraction of nickel by Mond’s process. Nickel sulphide is roasted. We get nickel Oxide. The

impure oxide is treated with water gas a 520 – 620 K. At this temperature the hydrogen in water gas reduces nickel oxide and copper oxide to metal but not reduce the oxide of iron. CO is passed over the product at 330K. Nickel forms nickel carbonyl which is volatile. Copper does not react. The nickel carbonyl is volatile. Copper does not react. The nickel carbonyl vapours are lead away and passed over nickel balls at 420 – 450 K. They decompose and nickel is set free and gets deposited on the nickel ball. The ball are removed and cast into ingots.

2. The formation of nickel carbonyl is utilized in the purification of nickel.
3. It is used for the preparation of metal mirrors and plates.

Uses :

1. The formation of nickel carbonyl is utilized in the purification of nickel.
2. It is used in glass plating
3. It is used as a catalyst.

COORDINATION CHEMISTRY

Definition Of Some Terms:

1) Simple Salts:

When an acid reacts with an alkali, neutralization takes place and a simple salt is produced.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

When dissolved in water these salts ionize and produce ions in solution. 2) **2) Molecular or Addition compounds:**

When solutions containing two or more salts in stoichiometric (i.e. simple molecular) proportions are allowed to evaporate, we get crystals of compounds known as molecular or addition compounds.

These are of two types depending on their behavior in aqueous solution.

i) Double Salts or Lattice compounds:

The addition compounds having the following characteristics are called double salts.

a) They exist us such in crystalline state.

(b) When dissolved in water, there dissociate into ions in the same way in which the individual compounds of the double salts do.

$$FeSO_4(NH_4)_2SO_4\ 6H_2O \longrightarrow Fe^{2+}{}_{(aq)}+2NH_4{}^{+}{}_{(aq)}+ 2SO_4{}^{2-}{}_{(aq)}+6H_2O$$

ii) Coordination (or) complex compounds:

It has been observe that when solutions of $Fe(CN)_2$ and KCN are mixed together and evaporated, Potassium Ferro cyanide, $Fe(CN)_2 . 4 KCN$ is obtained which in aqueous solution does not give test for the Fe^{2+} and CN^- ions . But gives the test for K^+ ion and Ferrocyanide ion, $Fe(CN)_6^{4-}$.

$$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2 . 4KCN \rightleftarrows 4K^+ + Fe(CN)_6^{4-}$$

Thus we see that in the molecular compound like $Fe(CN)_2$ 4KCN, the individual compounds lose their identify. Such molecular compounds are called coordination (or) complex compounds.

3) Ligands:

The neural molecules or ions (usually anions) which are attached with the central metal ion are called Ligands.

Eg. In the complex ion,$[Fe(CN)_6]^{3-}$ the six CN- ions are the ligands.

4) Coordination Number (C.N) or Ligancy:

It is the total number of the atoms of the ligands that can coordinate to the central metal ion.

Eg. $[Fe^{III}(CN)_6]^{3-}$ - Coordination number of Fe^{3+} is six.

5) Coordination sphere:

The central metal ion and the ligands that are directly attached to it are enclosed in a square bracket which Werner has called coordination sphere or first sphere of attraction.

Classification of ligands:

1) Unidentate or monodentate Ligands:

Ligands which donate only one pair of electrons and can thus coordinate to the central ion through only one atom are known as unidentate or monodentate ligands.

These ligands may be neutral molecules, negatively charged ions or positively charged ions.

Examples:

Neutral molecules : H_2O(aquo), NH_3(ammine), CO(Carbonyl) etc.

Negative ligands : $CH3COO^-$ (acetate), F^- (Fluoro), Cl^- (Chloro), Br^- (Bromo), I^- (Iodo), CN^- (Cyano) etc.

Positive ligands : NO^+(nitrosylium) and $NH^2NH_3^+$(hydrazium)

2)Bidentate ligands :

The ligands having two, three, four five or six donor atoms are called di, tri, tetra, penta and hexa dentate ligands respectively.

Nomenclature:

The following rules are recommended by IUPAC, are applied for naming the coordination compounds.

1. In ionic complexes, the cation is named first and then the anion. Non-ionic or molecular complexes are given a one word name.
2. Co-ordinated groups are listed in the following order: Negative ligands, neutral ligands and then positive ligands.
3. If the name of the ligand ends in ‘ide’ it is changed into O.

   Examples: Chloride - Chloro
   Cyanide - Cyano
   Oxide - Oxo
   Hydroxide - Hydroxo

   If the name ends in ‘ate’ or ‘ite’ then ‘e’ changed into ‘o’

   Examples: Cyanate - Cyanato
   Sulphate - Suphato
   Sulphite - Sulphito
   Acetate - Acetato
   Carbanate – Carbonato
   Oxalate - Oxalato
4. Neutral ligands are named as the molecule. But water is named as aquo and ammonia as ammine or amino.
5. Positive ligands end in ‘ium’.

   Example: Hydrazinium $H_2N\text{-}NH_3^+$
6. If the complex ion is a cation, the central atom is referred to by its usual name. If it is an anion the name of the central ion ends in ate. Neutral complexes have no special ending.
7. The ligands so named are followed by the name of central atom and oxidation state of the central ion is indicated by a Roman numeral in brackets following its name.
8. If ligands have simple names such as chloro, bromo, nitro, oxalate etc., their number is indicated by prefixes such as di, tri, tetra, penta etc., If the ligands have complex names their number is indicated by prefixes such as bis, tris, tetyrakis etc.

9. If the complex contains more than one negative ligand they are named in the increasing order of increasing order of electronegativity and also in the order of increasing complexity. When the two ligands have the same numbher of atoms, the order is that decreasing atomic number of the central atomic species in the ligand.

   Example: CrO_4^{2-} first and SO_4^{2-} next.

   Neutral ligands are named in the order H2O (aquo), NH3 (ammine).

   Neutral organic ligands are named in alphabetical order.

Examples:

$[Pt(NH_3)_3Cl_3]$ Cl - Tri ammine trichloro platinum (VI) Chloride

$[Ag(NH_3)_2]Cl$ - Di ammine silver (I) Chloride

$[Co(NH_3)_6]Cl_3$ - Hexammine cobalt (III) Chloride

$[Cu(NH_3)_4]SO_4$ - Tetrammine copper (II) Sulphate

$[Pt(NH_3)_2]Cl_2$ - Diammine di chloro platinum (II)

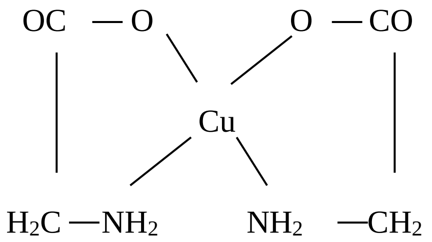
$K_2[Ni(CN)_4]$ - Potassium tetracyano nickelate(II)

$K_4[Ni(CN)_6]$ - Potassium hexacyano ferrate (II)

Chelation and Chelate effect:

Polydentate ligands whose structure permits the attachment of their two or more donor atoms to the same metal ion simultaneously and thus produce one or more rings are called Chelate or Chelating ligands.

Example:



The formation of such ring is termed as Chelation and the resulting ring structure is called Chelate rings or Chelates. This process of cyclisation is called Chelation.

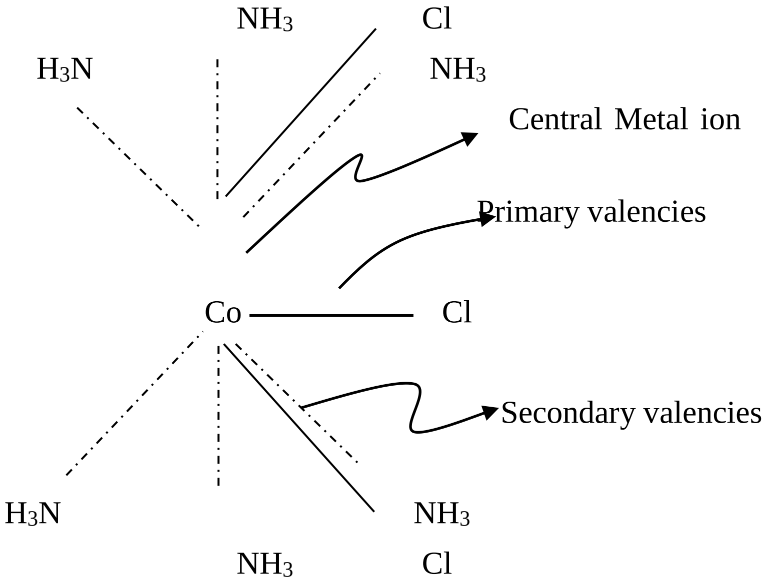
Ordinarily such chelate rings as mentioned above are most stable, because of reduced strain, when they have 5 or 6 members including metal ion. The enhanced stability of complexes containing chelated ligands is known as the **Chelate effect**.

Werner's theory:

In 1893 werner proposed a theory to explain the structure of coordination compounds . He proposed that there are two types of valency in a coordination compound.

1. Primary valency, and
2. Secondary valency.

For example , in the complex [CO(NH$_3$)$_6$] Cl$_3$, the three Cl groups are linked to the metal Co by primary valencies. The primary valency (oxidation state of the metal) corresponds to the normal valency of the metal and these valencies constitute ionic bonds. The six NH$_3$ groups are linked to the metal by secondary Valencies.The secondary Valencies are called the coordination number of the metal. The NH$_3$ molecules are said to be coordinated to the central metal ion. Such groups are called ligands. Thus [CO (NH$_3$)$_6$] Cl$_3$ is represented by the structure.



Werner thus divided the combining power of an atom into two spheres of attraction, the inner of coordinate sphere and the outer or ionization sphere. To distinguish between these two spheres of attraction, Werner used the square brackets [ ]. The atoms or groups making up the coordination complex and not ionized are enclosed with in the square brackets along with the metal ion.

Consider the complex [Pt (NH$_3$)$_6$] Cl$_4$. The four chloride groups in this complex, satisfying the primary valency of platinum are ionic. These can be precipitated by silver ions. On the other hand, in K$_2$ [Pt Cl $_6$], the six Chlorine atoms are bonded by non-ionized linkages (Secondary Valencies) and therefore cannot be precipitated with silver ions.

Werner realized that the arrangement of ligands around the central metal ion produced a symmetrical grouping. The coordination numbers which permit such spatial symmetry are 2,3,4,5 and 8. Among these, coordination numbers 4 and 6 are common.

Sidgwick's Theory:

i) Complexes are formed by donation of an electron pair from the ligand to the metal or metal ion.

ii) The metal ion will continue to accept electrons till the total number of electrons in the metal or metal ion and those donated by ligands is equal to the atomic number of the inert gas which follows the central metal in the periodic table.

Explanation :

In the formation of complexes, saturated molecules or ions take part. This suggests the operation of dative or coordinate covalency. In the formation of the ammonium radical, a proton accepts and shares a pair of electrons from the nitrogen atom of a saturated ammonia molecule.

$$\mathbf{H^+ + :NH_3 \longrightarrow [H : NH_3] \text{ or } [NH_4]^+}$$

Similarly, a cobaltic ion plays the role of an acceptor which receives and shares 6 pairs of electrons from 6 NH_3 molecules.

A fresh shell of electrons is thus formed around the cobaltic ion. This shell now consists of 12 electrons. This is also a stable grouping.

The cobaltic ion (2, 8, 14) accepts these 12 electrons. So it attains a structure 2,8,14 and 12. All the electrons in the last shell are shared. The total number of electrons now belonging to cobalt is 36. This is the number for the inert gas krypton.

The NH_3 molecules in the $[Co(NH_3)_6]^{3+}$ may be replaced by H_2O molecules one by one till a hexa hydrate, $[Co(H_2O)_6]^{3+}$ is formed. Similarly the NH_3 molecules in $[Co(NH_3)_6]^{3+}$ may be replaced partly by Cl^- ions. Eg. $[Co(NH_3)_4Cl_2]$.

The central metal atom may be Fe^{2+} instead of Co^{3+}. The coordinating groups may be 6 CN^- ions. We get the complex ferro cyanide and ferricyanide ions respectively.

$$\mathbf{Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]}$$

$$\mathbf{Fe(CN)_3 + 3KCN \longrightarrow K_3[Fe(CN)_6]}$$

The original Fe^{2+} and Fe^{3+} ions with 2 and 3 positive charges respectively, after coordinating with 6 negatively charged CN^- ions are converted into complex ferrocyanide and ferricyanide ions with 4 and 3 negative charges respectively.

Fluoride ions may coordinate with a boron atom of BF_3 or a silicon atom of SiF_4 giving a borofluoride comple ion BF_4^- or a silico fluoride complex ion SiF_5^-.

$$\mathbf{BF_3 + F^- \longrightarrow [BF_4]^-}$$

Borofluoride ion

$$\mathbf{SiF_4 + F^- \longrightarrow [SiF_5]^-}$$

Silicofluoride ion

In the case of salts containing several molecules of water of crystallization, eg., $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$ etc., both the cations and anions may be regarded as being coordinated with water molecules.

Effective atomic Number:

Sidgwick suggested that metal ions will tend to accept electron pairs from donors until they have obtained a sufficient number of electrons such that the metal in the resulting complex ions has an effective atomic number of the next inert gas.

Definition :

$$\left.\begin{array}{l}\text{The effective atomic}\\ \text{number (EAN) of a}\\ \text{metal in a complex}\end{array}\right\} = \left\{\begin{array}{l}\text{Atomic number of the metal - Electrons}\\ \text{lost in ion formation + number of}\\ \text{electrons gained by co-ordination.}\end{array}\right.$$

In many cases the EAN of the metal in complex corresponds to the next heavier inert gas element.

Effective Atomic Number concept (EAN concept)

Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through bonding the total number of electrons on the central atom, including those gained from ligands in the bonding is called the effective atomic number (EAN) of the central metal ion and in many cases this total number of electrons(i.e EAN) surrounding the coordinated metal ions is equal to the atomic number of the inert gas.

Example :

EAN of CO(III) in $[CO(NH_3)_6]^{3+}$ cam be calculated as follows.

Electrons in CO^0 atom = atomic number = 27 e^-s

Electrons in CO^{3+} ion = 27-3 = 24 e^-s

Electrons donated by $6(NH_3)$ = 2x6 = 12 e^-s

EAN of CO(III) in $[CO(NH_3)_6]^{3+}$ =24+12 = 36 e^-s

EAN (= 36) of CO(III) is evidently equal to the atomic number of Kr.

Pauling's Theory or Valence bond Theory :

1. The central metal atom or ion provides a number of empty s,p nd d atomic orbitals equal to its CN. These orbitals can accommodate electrons donated by the ligands.
2. The vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridizing together. These are vacant, equivalent in energy an have definite geometry.
3. The metal oritals and ligland orbitals overlap to form strong bonds.(Coordinate bonds)
4. The d-orbitals involved in the hybridization may be inner (n-1) d orbitals (d_2sp_3) or outer (n d orbitals (sp_3d_2). The complexes formed using these orbitals are transferred to as low spin or inner orbital complexes and high spin or outer orbital complexes respectively.
5. Each ligand donates a pair of electrons to the central metal ions.
6. The non-bonding metal electrons present in the inner orbitals do not take part in chemical bonding.
7. If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain unpaired electrons it is diamagnetic.
8. Under the influence of a strong ligand, the electrons can be forced to pair up against Hund's rule of maximum multiplicity.

Explanation by Valence bond theory:

According to Pauling strong bonds are not formed by pure s, p or d orbitals. Strong bonds are generally formed by hybridized orbitals. Thus they postulated that hybridization takes place in the central atom. There are several types of hybridizations. Each hybridization leads to a definite geometry various hybridizations and the related geometries are given as before.

Magnetic properties of complex compounds:

The complexes having paired electrons do not exhibit magnetic moment and they are said to be diamagnetic. The complexes having one or more unpaired electrons how definite value of magnetic moment and are called paramagnetic complexes. Te greater the number of unpaired electrons in a substance the greater is the magnetic moment of the substance. The magnetic moment of a substance can be calculated using the formula.

$$\mu = \sqrt{n(n+1)} \text{ B.M}$$

μ = Magnetic moment

n = Number of unpaired electrons

B.M = Bohr Magneton.

When $n = 1$, $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ B.M.

Using this formula the number of unpaired electrons in an ion can be calculated. The magnetic studies will reveal whether a co-ordination compound has unpaired electrons in it or not.

Explanation by V.B. Theory :

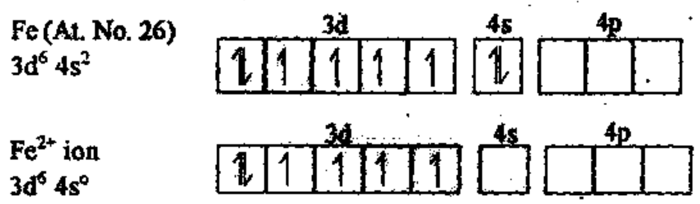
The magnetic properties of co - ordination compounds can be interpreted successfully by Pauling's V.B. Theory.

I. Octahedral complexes:

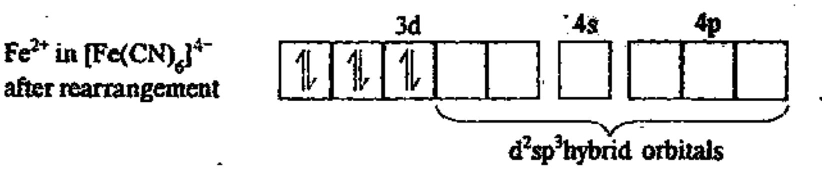
Octahedral complexes result from either d^2sp^2 or sp^3d^2 hybridisation.

E.g.l: $K_4[Fe(CN)_6]$

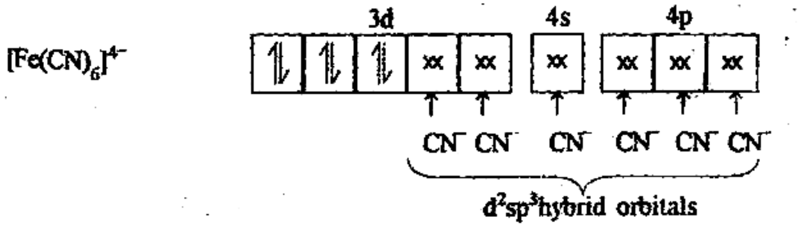
Fe^{2+} is the central metal ion and $[Fe(CN)_6]^{4-}$ is the complex ion Electronic structure of



In the presence of CN^- ligands the electron in the 3d orbitals are forced to pair up against Hund'sRule of maximum multiplicity to make room for the electrons donated by the ligands.



In order to give the same properties and strength to all the metal ligand bonds, all the six orbitals (two'3d, one 4s and three 4p orbitals) hybridise to give six equivalent d2sp3 hybrid orbitals. These six hybrid orbitals which are vacant accept six electron pairs donated by six CN^- ligands and thus form $[Fe(CN)_6]^{4-}$ ion.

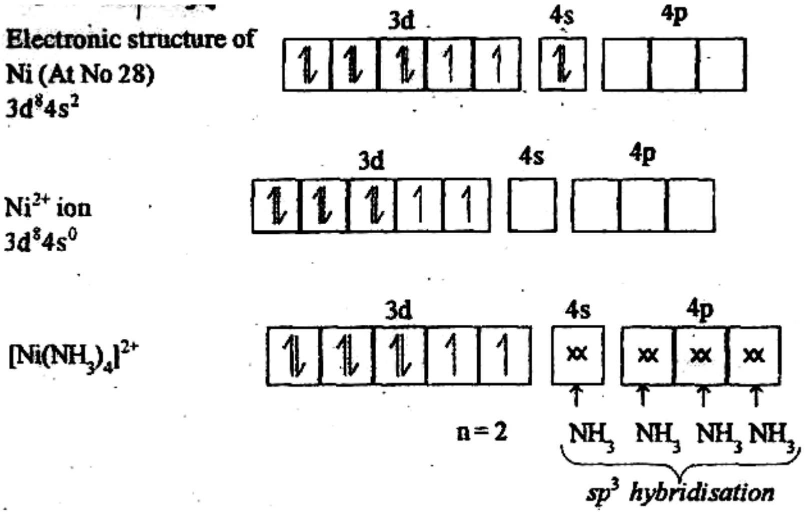


Since the complex results from d'sp3 hybridisation, it has octahedral shape. Since there are no unpaired electrons in the complex the complex is diamagnetic. In the above complex the d orbitals used are from a lower shell (3d) than the s and p-orbitals (4s and 4P). Complexes using the inner d - orbitals (3d orbitals) are called inner complexes. They are also known as covalent complexes or spin paired or low spin complexes.

Other Examples: i) $[Co(NH_3)_6]^{3+}$ ii) $[Co(CN)_6]^{3-}$

Tetrahedral Complexes:

Eg. $[Ni(NH_3)_4]^{2+}$

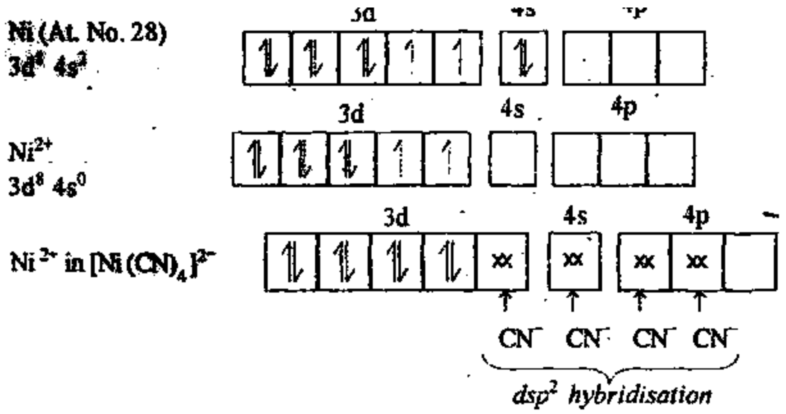


Since sp3 hybridisation is involved, the complex has a tetrahedral structure. There are two unpaired electrons and the ion is therefore paramagnetic.

Square planar complexes:

These are formed by dsp2 hybridisation;

Example: $[Ni(CN)_4]^{2-}$



Ni $(CN)_4]^{2-}$ is diamagnetic. Hence it must involve dsp2 hybridisation resulting in square planar structure. The two unpaired 3delectrons are coupled making one d - orbital empty and available for hybridisation so that dsp2 hybrid orbitals can be formed. These vacant orbitals accept four electron pairs donated by four CN^- ligands, to form a square planer ion.

Other examples:

i) $[Pt(NH_3)_4]^{2+}$; ii) $[Pt(Cl_4)]^{2-}$

Merits of Valence Bond Theory:

1. It provides a satisfactory pictorial representation of the complex.
2. It is a good model for qualitative prediction of the magnetic behaviour and reactivity of complexes. Thus V.B. theory is an improvement on Werner's theory.

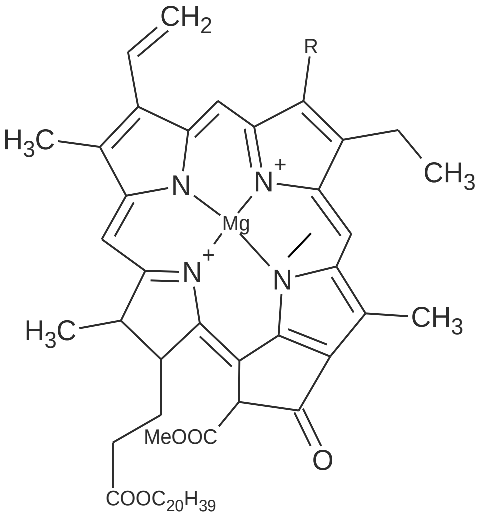
Limitations of Valence Bond theory :(Pauling Theory)

1. It is limited to qualitative explanation; quantitative interpretation of the stability of the complexes is not possible.
2. It does not offer any explanation to the absorption spectra of reactivities.
3. The colour and magnetic moments of transition metal complexes are due to their possessing d-orbital electrons. So, there should be a quantitative connection between spectra and magnetic moment. But this connection is not revealed by Pauling's theory.
4. VBT does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.

5. Sometimes the same metal assumes different geometries when formation of complex takes place. This theory does not explain as to why at one time the electrons must be rearranged against Hund's rule while at other times the electronic configuration is not disturbed.

Biological role of chlorophyll:

Chlorophyll the green pigment of plant contains two closely related coloured substances. Both of these are magnesium chelates cotaining four pyrole nuclei united by methylene groups to form the porphyrin ring in figure.



R = CH ; Chlorophyll-a

R – CHO ; Chlorophyll-b

Chlorophyll plays a vital role in photosynthesis in plants. Photosynthesis is a complex sequence of changes in which absorption of sunlight is the first step. Then several redox reactions occurs leading to the overall endothermic process of combining water and Carbon dioxide to give glucose. In this process molecular oxygen is released.

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

In photosynthesis, chlorophyll molecules present in the chloroplast absorb protons in the red region (near 700nm) of the visible spectrum. Chlorophyll then passes on this energy to other molecules in the reaction chain. The conjugated polyene structure of the phorphine ring unit gives chlorophyll the ability to absorb visible light. The magneisim present in chlorophyll has two functions.

1) It makes the chloropyll molecule a rigid and stable chelate structure so that the absorbed energy is not easily lost thermally.

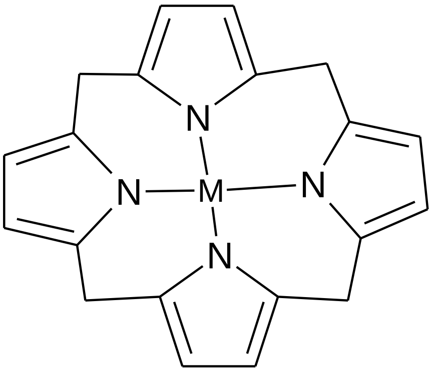
2) It helps the chlorophyll molecule in the transfer of its energy into the redox chain through the formation of a triplet state. Chlorophyll aids the conversion of light energy into chemical energy, Which is crucial to the existence of all photo synthetic plant life on earth.

Biological role of Haemoglobin:

It is a conjucated protein, the protein part being globin and the prosthetic group being heme. It is present in the red cells of blood.

Sturucture:

Each molecule of haemoglobin contains four heme groups.



Porphyrin Complex

Porphyrin Complex (M = Fe^{2+})

Heme is an iron(II) complex of protophyrin which has a basic porphyrin nucleus with certain substituents on the peripheri of the ring. In haemoglobin the hemes are bound via the imidazole rings of histidine molecules (present in the protein). Three histidines are involved to give 7 coordinate Fe^{2+}

Biological importance:

It forms the main constituent of blood.

Application of coordination compounds in Qualitative and quantitative analysis:

1) Separation of copper and cadmium ions:

When KCN is added to a solution containing Cu(II) and Cd(II) ions, both form soluble complexes. Viz, K_3 [Cu $(CN)_4$] and K_3 [Cd$(CN)_4$] . The Cu(II) complex is more stable than the Cd complex. Therefore when H_2S is passed through the solution, Cd (II) ion gets precipitated as CdS and Cu(II) remains in solution.

2) Idetification of copper.

The confirmatory test for Cu (II) involves formation of the reddish brown precipitate K_2 Cu[Fe(CN)$_6$] when K_4 Fe(CN)$_6$ is added to Cu(II) solution. Cu (II) forms a blue soluble complex $[Cu\ (NH_3)_4]^{2+}$ with excess of ammonia. This also indicates the presence of copper.

3) Identification of Fe.

Fe(III) can be detected by the formation of blood red complex ion $[Fe(CNS)_4]^-$ on the addition of NH_4 CNS to the solution containing Fe (III).

4) Identifiaction of Ni

In the fourth group, Ni (II) can be detected by the addition of dimethyl glyoxime reagent. Ni (II) forms a scarlet precipitate, which is a chelate complex.

Quantitative Estimation of Nickel:

Ni (II) gives a rosy-red precipitate with dimethyl glyoxime (DMG) reagent in ammoniacal solution. From the weight of Ni – DMG complex, the amount of Ni^{2+} can be calculated.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

UNIT – II

2.1. Covalent Bond-Orbital Overlap-Hybridisation – Geometry of Organic molecules-Methane, Ethylene, Acetylene and Benzene.

2.2. Electron displacement Effects: Inductive, Resonance, Hyper conjugative & steric effects. Their effect on the properties of compounds.

2.3. Stereoisomerism: Symmetry-elements of symmetry- cause of optical activity, Tartaric acid. Racemisation.Resolution. Geometrical isomerism of Maleic and Fumaric acids-Keto-enol tautomerism of Acetoacetic ester-conformers of n-butane with brief explanation

2.4. Aromatic compounds-Aromaticity-Huckel's rule

2.5 Electrophilic substitution in Benzene-Mechanism of Nitration, Halogenation-Alkylation, Acylation.

2.6. Isolation, preparation,properties and structure of Naphthalene Haworth's synthesis.

2.6. Heterocyclic compounds:- Preparation, properties and uses of Furan, Thiophene, Pyrrole and Pyridine.

Orbital Overlap:

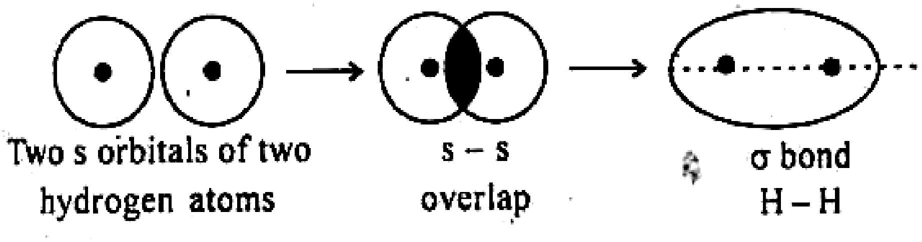
Organic compounds contain covalent bonds. A covalent bond is formed by the sharing of a pair of electrons between two atoms. For this purpose the two atoms must be so located that on orbital of one of the combining atoms overlaps with the orbital of the other atom ; each combining orbital containing one electron. The strength of the chemical bond is proportional to the extent overlapping of the orbitals.

Types of orbital overlapping :

i s-s Overlapping:

If one s - orbital of an atom overlaps with one s - orbital of another atom to form a covalent bond, it is called s-s overlapping

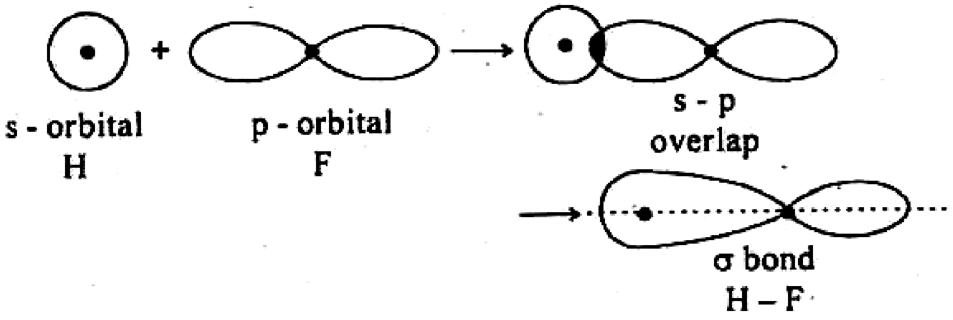
Eg., A molecule of hydrogen is formed by the overlapping of one 1s orbital of a hydrogen atom with one Is orbital of another hydrogen atom.



ii. s-p Overlapping:

If one s - orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond, it is called s - p overlapping.

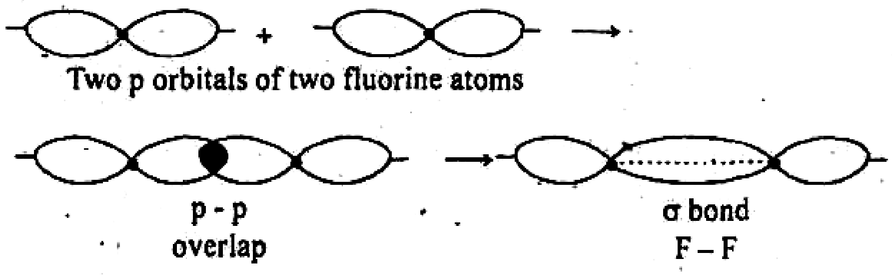
Eg., A molecule of hydrogen fluoride is formed by the overlapping of one s - orbital of a hydrogen atom with one p -orbital of fluorine atom.



iii. p - p Overlapping:

If one p -orbital of an atom overlaps with one p - orbital of another atom to form a covalent bond then it is called p - p overlapping.

Eg., A molecule of fluorine is formed by the overlapping of one 2p orbital of a fluorine atom with one 2p orbital of another fluorine atom.

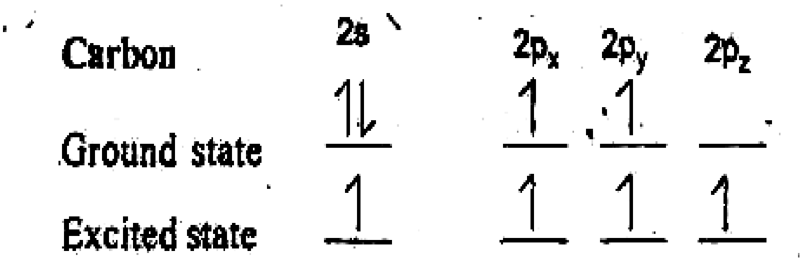


HYBRIDISATION

We have also seen the shapes of orbitals and formation of various types of bonds, but these concepts are not enough to explain the observed shapes of various molecules. So, to account for the shapes of various molecules the concept of hybridization was introduced.

The tetra valency of carbon is explained as follows:

It is assumed that, at the time of bond formation the carbon atom attains an excited state. In the excited state, the two 2s electrons are unpaired and one of them is promoted to the vacant 2p, orbital.



Now the tetra-valency of carbon has been accounted for, by proposing an excited state structure for carbon atom with four unpaired electrons. The four unpaired electrons are not identical. There is one s - electron and three p - electrons. To explain the equivalent nature of the four bonds of carbon in its saturated compounds a new concept called hybridization has been proposed.

According to this concept, the atomic orbitals of an atom which lie close to one another in energy tend to merge or mix and then re-distribute their energy and shape to produce an equivalent number of new orbitals which are identical in all respects called hybridised orbitals.

Definition:

Hybridisation is the concept of mixing or merger of orbitals of an atom having nearly equal energies, to produce entirely new orbitals, which are equal in number to the mixing orbitals. The hybridised new orbitals will have equal energies; identical shapes and are symmetrically placed in space.

Conditions for hybridisation of atomic orbitals:

1. The orbitals of an-isolated, single atom only could undergo hybridisation.
2. The hybridising orbitals must differ only slightly in their energy content.

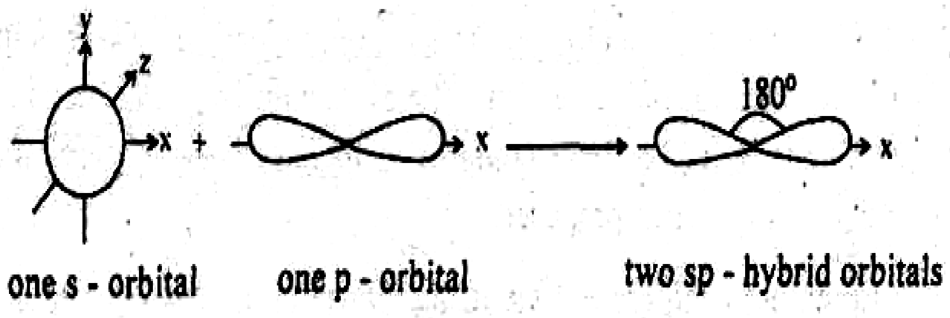
Characteristics of hybrid orbitals:

1. The number of hybridised orbitals is equal to the number of pure atomic orbitals which mix up.
2. A hybrid orbital can have only two electrons as the pure atomic orbitals. The two electrons must have opposite spins.
3. The electron waves in hybrid orbitals repel each other. So they tend to be as far away as possible.
4. The hybrid orbitals distribute themselves in such a way that they assume the direction o the dominating orbitals.

Modes of hybridisation and shapes of hybrid orbitals:

1. sp - hybridisation :

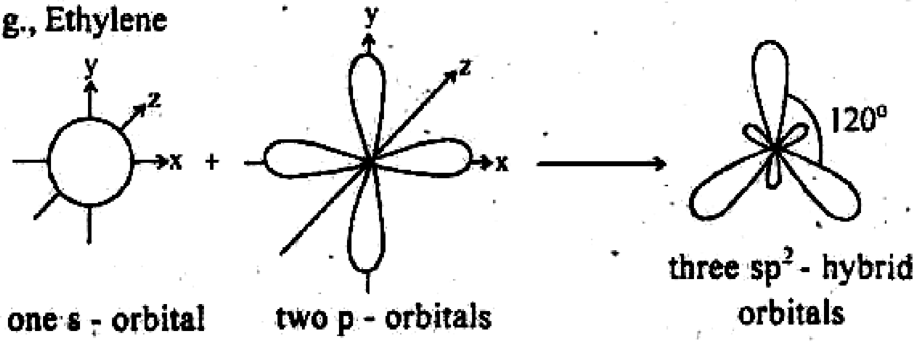
One s and one p orbitals mix and give two identical hybrid orbitals. This is known as sp hybridisation. These hybrid orbitals are co-linear. The bond angle is 180°. E.g., $BeCl_2$,.



2. sp^2 - hybridisation :

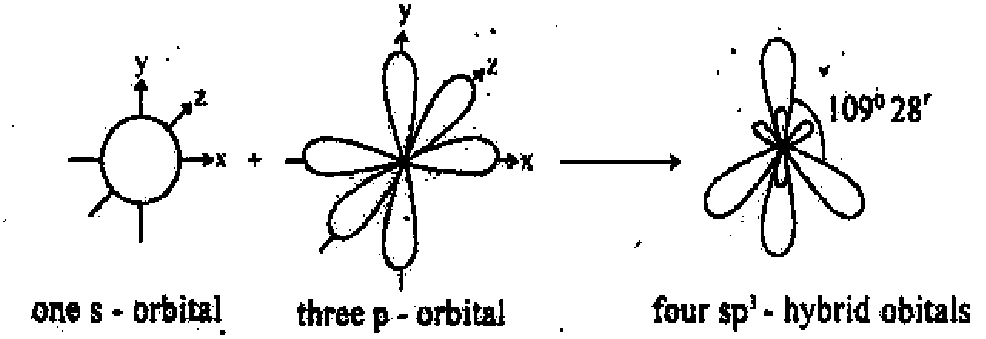
One s orbital and two p orbitals mix and give three identical hybrid orbitals. This is known as sp^2 hybridisation. These hybrid orbitals lie in the same plane. The shape is plane tri angular. The bond angle is 120°.

E.g., Ethylene



3. sp^3 - hybridisation :

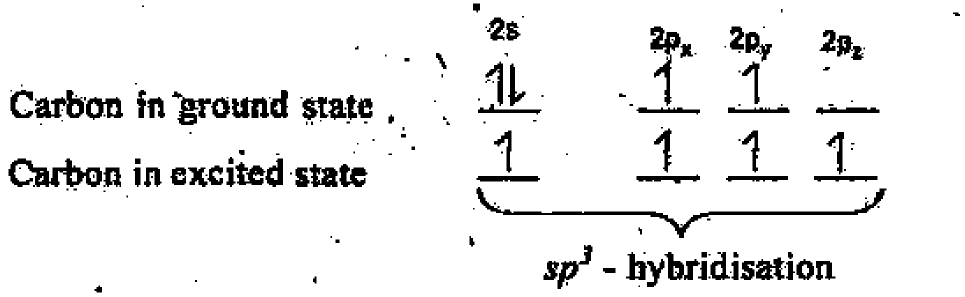
One s orbital and three p orbitals mix and give four indentical orbitals. This is known as sp^3 hybridisation. The four hybrid orbitals are oriented towards the four corners of a regular tetrahedron. The bond angle is 109° 28′. E.g.,: Methane

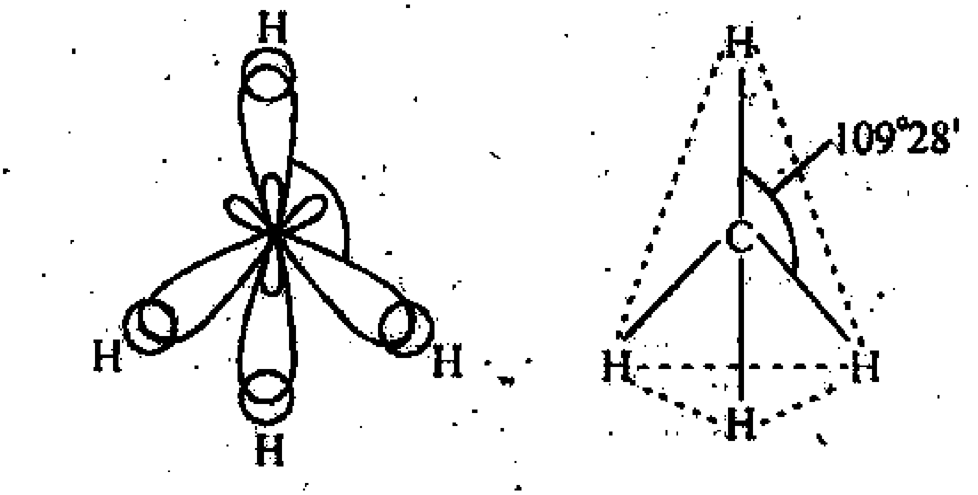


Geometry of molecules

1. Methane

In methane the carbon atom is in a state of sp^3 hybridisation. One 2s orbital and three 2p orbitals of carbon hybridise and give four sp^3 hybridised orbitals. There are four electrons in the valency shell of carbon. Each occupies one sp^3 hybridised orbital. Thus there are four single unpaired electrons in each of the four sp^3 hybrid orbitals.



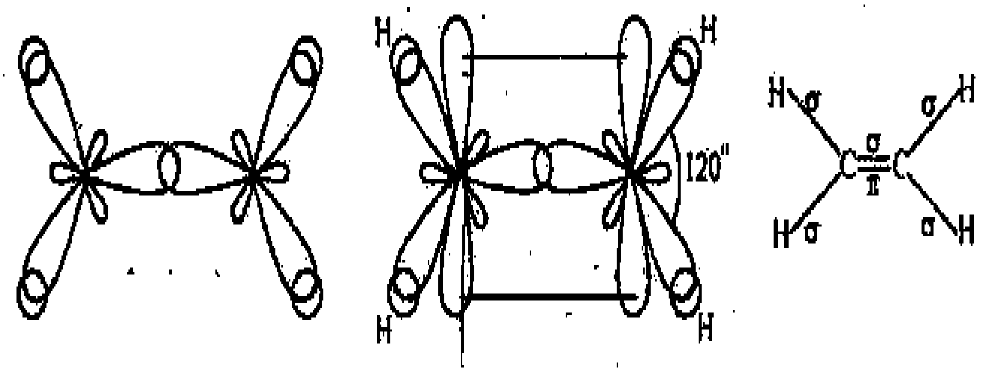


Is orbitals of four hydrogen atoms overlap with four sp^2 hybrid orbitals of carbon and give four sigma bonds, i.e., there are four bonded pairs of electrons around carbon in methane. As per VSEPR theory, only if they are-arranged tetrahedrally the bonded pairs will be as far apart as possible. That is why the methane molecules assume a tretrahedral shape H-C bond angle is 109° 28′.

2. Ethylene:

In ethylene both the carbon atoms are in a state of sp^2-hybridisation. These sp^2-hybrid orbitals lie in the same plane. The bond angles are 120°. Each carbon atom has three sp^2-hybrid orbitals and one pure p - orbital. One sp^2-bybrid orbital of one carbon atom overlaps with one sp^2- hybrid orbital of the second carbon and forms a sigma bond. Each of the two carbon atoms now has two sp^2-hybrid orbitals and one pure p - orbital left. The two sp^2- hybrid orbitals on each of the two carbon atoms overlap with the 1 s orbital orbitals on each carbon atom overlap in a side wise fashion and form an- bond. The electron cloud of the n - bond lies above and below the C-C sigma bond. Thus in ethylene the following bonds are present.

Type of bond	**Name of bond**	**Number of bond**
C-C	σ	1
C-H	σ	4
C-C	π	1



Ethylene has a double bond in it. The double bond in ethylene contains one σ - bond one π - bond. The shape of the molecule is trigonal planar.

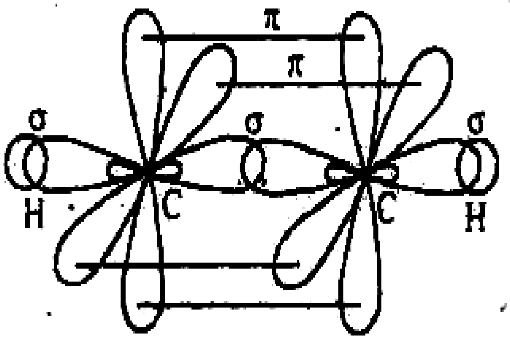
3. Acetylene

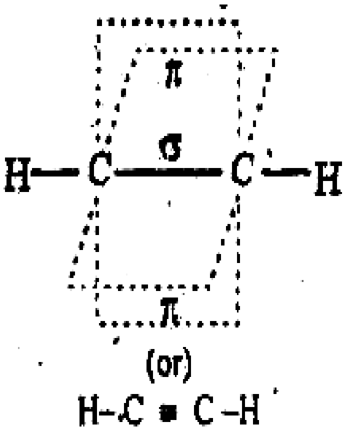
In acetylene both the carbon atoms are in a state of sp - hybridisation. These sp - hybrid orbitals are co-linear. The bond angle is 180°. Each carbon atom has two sp - hybrid orbitals and two pure p - orbitals. One sp - hybrid orbital of one carbon atom overlaps with one sp - hybrid orbital of the second carbon atom and forms a σ - bond. Each of the two carbon atoms now have one sp - hybrid orbital and two pure p - orbitafs left. The hybrid sp - orbital on each of the two carbon atoms overlaps with 1s orbital of the hydrogen atom and forms s- sp sigma bond. The two pure p - orbitals on each carbon atom overlap in a sidewise fashion and form two π - bonds. The electron clouds of the π - bonds lie above and below the C - C sigma bond. These two π - bonds are in two planes which are perpendicular, to each other. Each of the n - bonds is perpendicular the following bonds are as well.

Thus in acetylene the following bonds are present :

Type of bond	Name of bond	Number of bond
C-C	σ	1
C-H	σ	2
C-C	π	2

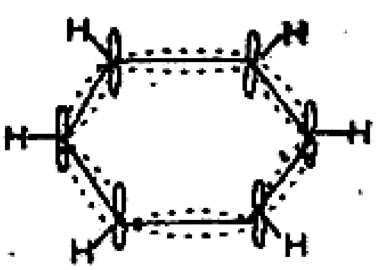
We say acetylene has a triple bond in it. The triple bond in acetylene contains one σ - bond and 2π - bonds. The shape of the molecule is linear.



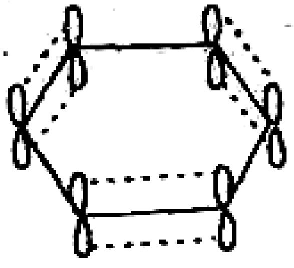


4. Benzene

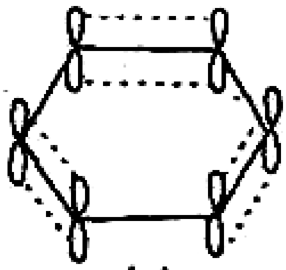
In benzene molecule the carbon atoms are in a state of sp^2 - hybridisation.



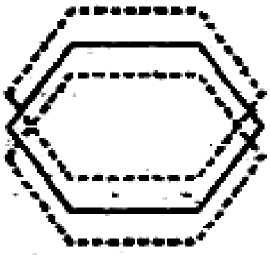
(a)



(b)



(c).



(d)

The three hybridised orbitals of each carbon are involved in the formation of three o - bonds. (Two bonds are formed with adjacent carbon atoms and one with hydrogen).

Thus all the six carbon and the six hydrogen atoms lie in the same plane. The unhybridised p -orbitals are perpendicular to the plane of the carbon hexagon (fig.a). Side overlap of these orbitals takes place. They can give three localised n - bonds (fig. b or c). But there is no reason why the overlap should be limited in this way. Thus the mutual overlapping of all the unhybridised p - orbitals give a delocalised molecular orbital. The net result is that there are two continuous ring-like electron clouds, one lying above and the other below the plane of atoms as show in fig. d.

Electron displacement effects:

1. Inductive effect:

When a hydrogen atom is attached to a carbon atom (C-H) by a covalent bond, the shared pair of electron is symmetrically placed between them. If instead of hydrogen atom we have a substituent X having higher electronegativity, then the shared pair of electrons in the

C-X bond will move towards X. On the other hand, if a substituent Y having lower electronegativity is attached to carbon as C-Y, then the shared pair of electrons in the C-Y bond will move towards C.

Thus, if the electronegativity values of the atoms forming a bond are different, the bond is said to be polarized.

Let us consider a chain of carbon atoms with a chlorine atom linked to the end carbon atom such as $–C_4\text{-}C_3\text{-}C_2\text{-}C_1\text{-}Cl$. Due to greater electronegativity of chlorine, the electron pair shared between C_1 and Cl is displaced towards the chlorine atom. As a result of this, chlorine acquires a small negative charge, which C1 becomes slightly positively charged as show below.

$$–C_4\text{-}C_3\text{-}C_2\text{-}\overset{\delta^+}{C_1}\text{-}\overset{\delta^-}{Cl}$$

The positively charged C_1 attracts the electron pair shared between C_1 and C_2. The shared pair of electron moves slightly towards C_2. Thus, C_2 gets a slight positive charge. But the charge on C_2 is smaller than that on C_1. The positive charge on C_2 in turn attracts the electron pair between C_2 and C_3. This effect falls rapidly as we move away from C_1.

This process of electron shift along a chain of atoms due to the presence of a polar bond in the molecule is called inductive effect. It is represented as

$$C_4 \rightarrow C_3 \rightarrow C_2 \rightarrow C_1 \rightarrow C$$

The inductive effect is a permanent effect. When the substituent X attached to the carbon atom is electron, attracting it develops a negative charge on X and the effect is called negative inductive effect or –I effect. The following groups cause –I effect. They are given in the order of their decreasing effect.

$$NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$$

If the substituent Y attached to the carbon atom is electron repelling, it develops a positive charge on Y and the effect is called positive inductive effect or +I effect. The following groups cause +I effect. They are given in the order of their decreasing effect.

$$(CH_3)_3C- > (CH_3)_2CH- > CH_3\text{-}CH_2- > CH_3-$$

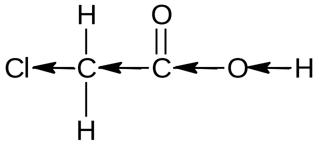
Inductive effect and properties of organic compounds:

1. Why monochloro acetic acid is more acidic than acetic acid?

We know that acetic acid is a weak mono basic acid. It ionizes as follows.

$$H_3C—COOH \rightleftharpoons H_3C—COO^- + H^+$$

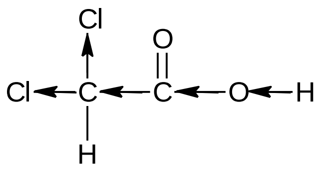
The strength of the acid is measure of the ease with which H^+ ion leaves from COOH. If one of the hydrogen atoms of methyl group is replaced by a chlorine atom, the following situation arises. The chlorine atom is electron withdrawing group. The electron pair between carbon and chlorine moves towards chlorine. In turn the electron pair between C and CO moves towards carbon and so on. Thus, the –I effect prevails in the chloro acetic acid molecule as shown below,

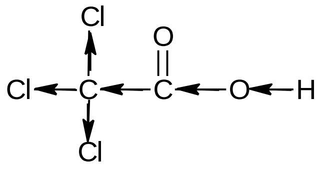


$$\mathrm{Cl} \leftarrow \overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}} \leftarrow \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} \leftarrow \mathrm{O} \leftarrow \mathrm{H}$$

This makes the separation of hydrogen atom as ion easier. Thus, chloro acetic acid is stronger than acetic acid.

In a similar manner we can show that, dichloro acetic acid is stronger than chloro acetic acid and trichloro acetic acid is stronger than dichloro acetic acid.


Dichloroacetic acid


Trichloroacetic acid

In dichloro acetic acid there are two chloro groups with –I effect and in trichloro acetic acid there are three chloro groups with –I effect. Thus, the separation of hydrogen atom as ion becomes progressively easier as we move from mono to di to tri chloro acetic acids. Thus, their acid strengths increase in the order.

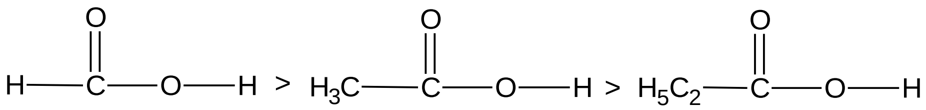
2. Why α-Chloro propionic acid is stronger than β-Chloro propionic acid?

$$H_3C—CHCl—COOH > ClH_2C—CH_2—COOH$$

This is because inductive effect decreases with distance. In β-Chloro propionic acid the chloro group with –I effect is two carbons away from the COOH group, while in α-Chloro propionic acid it is one carbon away. So the chloro group in β-Chloro propionic acid has only less electron withdrawing effect. So it is weaker.

3. Strength of aliphatic acids.

The strength of aliphatic acids decrease in the following order.



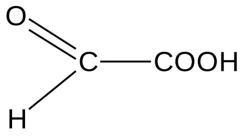
$$H—\overset{\overset{\displaystyle O}{\|}}{C}—O—H > H_3C—\overset{\overset{\displaystyle O}{\|}}{C}—O—H > H_5C_2—\overset{\overset{\displaystyle O}{\|}}{C}—O—H$$

Reason:

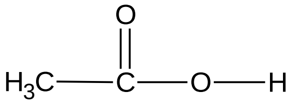
In formic acid, the COOH group is attached to H, while in acetic acid it is attached to $-CH_3$ group has +I effect. This pushes electrons towards H. This strengthens O-H bond. ie. Removal of H as H^+ becomes difficult. This effect is absent in formic acid.

Between acetic acid and propionic acid and propionic acid the stronger is acetic acid. It is because in acetic acid a $-CH_3$ group is attached to –COOH. In propionic acid a $-C_2H_5$ group is attached to –COOH. C_2H_5 is bulkier than CH_3. So it has more +I effect than CH_3. Thus it pushes electrons towards the O-H bond more forcibly than CH_3. So it becomes more difficult for H to leave as H^+ form propionic acid than from acetic acid.

4. Glyoxalic acid is stronger than acetic acid:



Glyoxalic acid



Acetic acid

This is because –CHO group is strong –I group. This facilitates H to leave as H^+. But, in acetic acid the $–CH_3$ group is a +I group. This pushes electrons towards the O-H bond making it difficult to part with H^+.

2. Steric Effect:

The presence of a bulky group or groups near a reaction site in a compound makes it behave in a peculiar way.

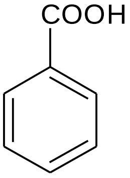
The effect of size of substituents and their spatial arrangement in compound are called steric effects.

Steric effects may affect the speed and mechanism of a reaction. When the steric effect slows down a reaction, it is called steric hindrance, when it speeds up a reaction, it is called steric acceleration.

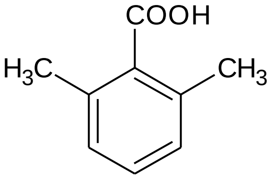
In aromatic compounds the properties of ortho substituted compounds differ considerably from those of meta or para isomers. In ortho substituted compounds, the attack of the reagent at the reaction centre is hindered by the bulky groups present in the ortho positions. These effects are also known as ortho effects or proximity effects.

Examples:

i) Benzoic acid(I) reacts with methanol and hydrogen chloride to form methyl benzoate, but 2,6 – dimethyl benzoic acid(II) does not form the corresponding product under the same conditions.

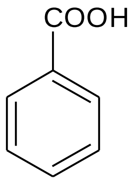


I

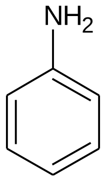


II

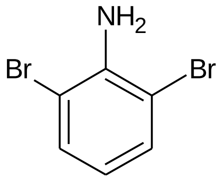
ii) Benzaldehyde reacts with aniline to form an anil, but not with 2,4,6 – tribromo aniline.



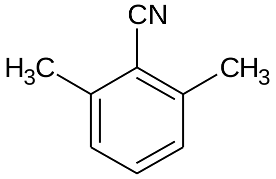
III



IV



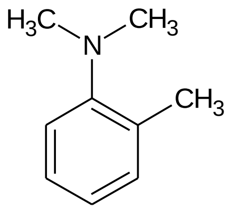
V



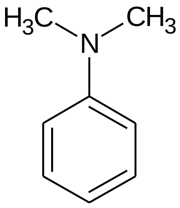
VI

iii) Phenyl cyanide undergoes hydrolysis, where as 2,6 – dimethyl phenyl cyanide does not.

iv) N,N – dimethyl o-toluidine is more basic than N,N – dimethyl aniline.



VII



VIII

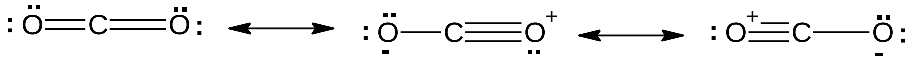
Reason:

The extra stabilization due to resonance is less in (I) than in (II), because of steric hindrance the lone pair of electrons on the nitrogen is more readily available in compound (I). So, it is more basic.

3. Mesomeric Effect or Resonance Effect:

A molecule containing multiple bond may be represented by several electronic formula.

For example, Carbon dioxide has the following electronic arrangements.



But the actual condition of the molecule is in between these three structures. This type of effect is known as mesomeric effect (or) resonance effect. It is represented by the symbol M or R respectively.

If a molecule can be assigned two or more structural formula, each of which can explain most but not all the properties of the compound, the actual structure lies in between the various possible structures. This phenomenon is called mesomerism or Resonance.

The effects arising out of the presence of the presence of mesomerism or resonance is called mesomeric or resonance effect respectively.

The various possible structures are called canonical structures. The actual structure is called resonance hybrid. The canonical structures are represented by putting double headed arrow (↔) in between them. The resonance hybrid is not a mixture of various structures. It is an entirely new and individual structure, which is in between the several canonical structures.

The mesomeric effect, like the inductive effect, may be + or - and is denoted by +M or –M.

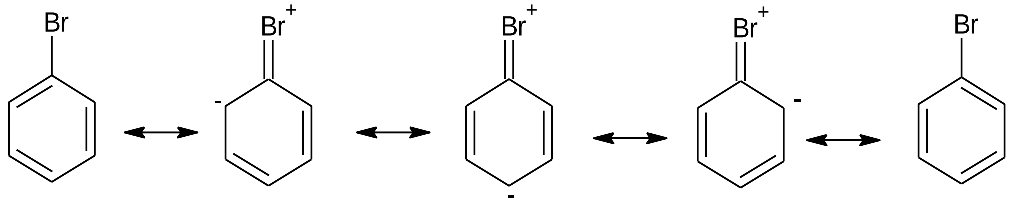
A group of atoms is said to have +M effect, when the direction of electron displacement is away from it. Such groups have lone pairs of electrons.

-OH, -OR, $-NH_2$ and –SR groups have +M effect.

A group of atoms is said to have –M effect, when the direction of electron displacement is towards it.

>C=O, $-NO_2$, -CN, and $–SO_3H$ groups have –M effect.

The +M effect of halogen atom brings a double bond character between the halogen and the carbon atom attached to the halogen. Because of the double bond character, the halogen is held firmly. Thus, the halogen atom in vinyl halides and aryl halides are less reactive than alkyl halides.



The halogen in alkyl halide cannot have resonance and hence it cannot have double bond character. So it can be easily hydrolysed.

Difference between inductive and mesomeric effects:

	Inductive Effect	Mesomeric effect
1. Nature of electron displacement.	σ - electrons along a single bond transmitted through the chain – decreases as the distance.	Π - electrons – negative charge flows towards on side of the molecule – effect is uniform.
2. Charge	Respective atoms attain partial negative and positive charges.	Charge separation is complete.
3. Reaction with stability of the molecule.	None.	Stabilises the molecule.
4. Effect on bond	None.	Affected.

length.		
5. Effect on colour.	Nil	Causes perceptible colour.

Conditions for mesomerism or Resonance:

1. The contributing structures must be reasonably stable.
2. The number of electrons in each contributing structure must be the same.
3. All the contributing structures should have the same or nearly the same amount of energy.
4. When the contributing structures differ in energy contents. ie. Relative stabilities, the more stable structure makes greater contribution towards the resonance hybrid.
5. The various contributing structures should differ from each other only in the positions of electrons. The relative arrangement of atoms must be the same.

Resonance Energy:

The energy of a resonance hybrid is always less than any one of the contributing structures. The difference between the energy of the most stable contributing structure and that of the resonance hybrid is known as the resonance energy or delocalization energy.

A resonance hybrid, ie. the actual molecule is always more stable than any one of the contributing structures. Because of this fact we say that, the compound is stabilized by resonance.

Example:

The enthalpy of formation of benzene calculated from bond energy values is -5384.1 KJ/mole. The experimental value of enthalpy of formation of benzene is -5535.1 KJ/mole. This difference is called the resonance energy of benzene. We say benzene is stabilized by resonance to an extent of 151KJ/mole.

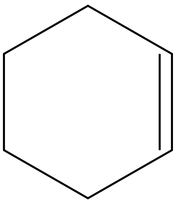
Effects of resonance:

1. Stability:

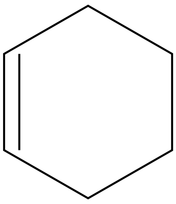
The compounds which exhibit resonance are more stable than their contributing structures.

Example:

Though there are three double bonds in the contributing structures of benzene (I) and (II), it behaves as a saturated compound. It does not undergo addition reactions instead undergoes only substitution reactions. The resonance energy is a measure of the stability caused by resonance.



(I)



(II)

2. Bond length:

The bond length in a resonance hybrid is different from those in the contributing structures.

Example:

The contributing structures of benzene suggest that, there are three C-C and three C=C bonds. Actually in benzene all the six carbon – carbon bond lengths are the same. Their lengths are in between those of C-C and C=C bonds.

3. Dipole moments:

The observed dipole moments are different from the values expected from the contributing structures.

4. Colour:

The colour of organic compounds is a consequence of resonance.

Example:

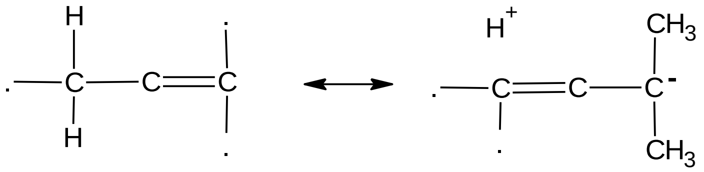
When the number of contributing structures increases, the intensity of the colour also increases.

5. Hyperconjucation:

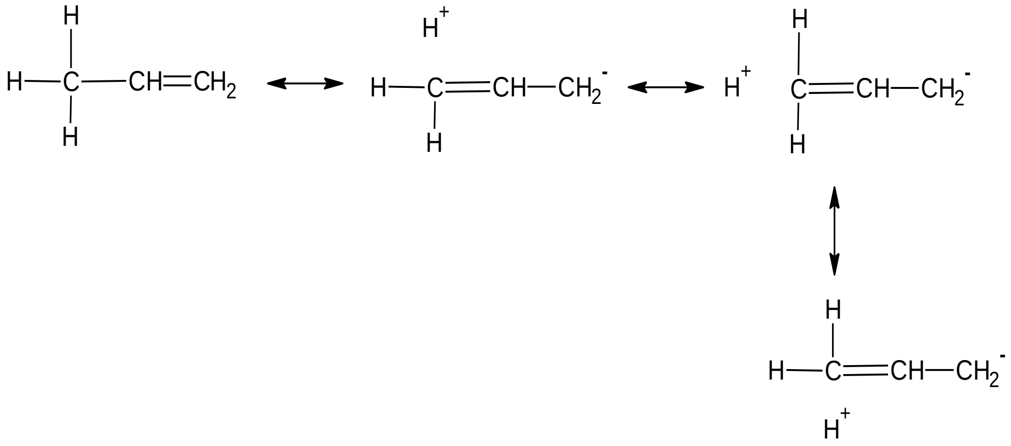
The resonance involving the delocalization of σ - electrons in conjugation with π – electrons of an adjacent double bond is called hyperconjucation.

Explanation:

The hyperconjucative effect operates in a system containing a C-H bond directly attached to a double bond. In other words, the hyperconjucative effect takes place through the interaction of σ - electrons of the carbon-hydrogen bond with π – electrons of the double bond. In hyperconjucation, the electron displacement takes place towards the double bond as shown below.



The three C-H bonds of methyl group in the propylene molecule contribute to this effect as follows.

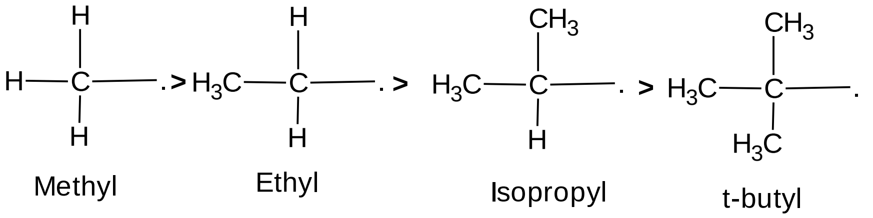


While discussing inductive effect, it was pointed out that the inductive effect of the alkyl group in the order.

$$3^0 > 2^0 > 1^0$$

This order is reversed when an unsaturated system (C=C) is attached with the alkyl group. As we have seen just now, the σ - electron from the C-H bonds at the α-carbon to the unsaturated system gives the no bond resonance. As the number of C-H bonds is greater, greater would be the hyperconjucative effect. Thus, methyl group (3 C-H bonds)

Has the maximum hyperconjucative effect. Ethyl group (2 C-H bonds) has lesser effect. Isopropyl group (1 C-H bond) has the least effect. Tertiary butyl group (0 C-H bonds) has no hyperconjucative effect at all.



Hyperconjucation is a temporary effect. In the canonical forms, there is no bond between carbon and hydrogen. The proton in such hyperconjucative form does not move any distance away than its normal bonding distance to carbon. This type of resonance is different from tautomerism, where the proton moves from one position to another. Hyperconjucation can also be regarded as an overlap of σ – orbital of the C-H bond with the π – orbital of the carbon-carbon double bond. This is analogous to the π – π orbital overlap in resonance. Hyperconjucation can also be regarded as a second order resonance.

Hyperconjucation is also called Baker – Nathan effect or No bond Resonance.

Stereo isomerism

Isomerism

The phenomenon in which two or more, different compounds have the same molecular formula is called isomerism.

E.g., i) Ethyl alcohol C_2H_5OH,

ii) Dimethyl ether CH_3OCH_3

These two are entirely different compounds. But they have the same molecular formula, viz., C_2H_6O

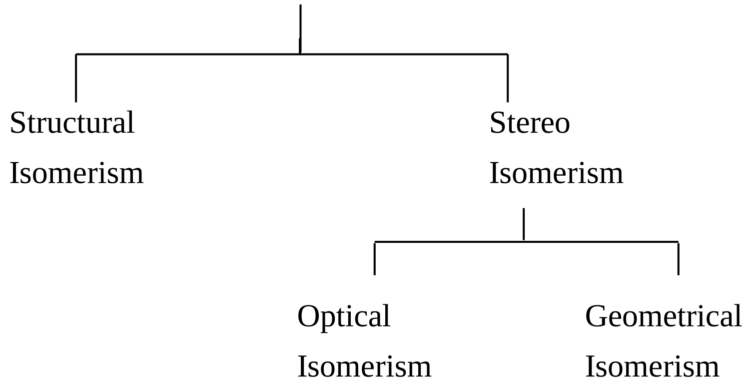
Isomerism is divided into two types:

i) Structural isomerism and

ii) Stereoisomerism.

You must have studied about structural isomerism in your earlier classes. We shall read about stereoisomerism here.

Isomerism



What is stereoisomerism?

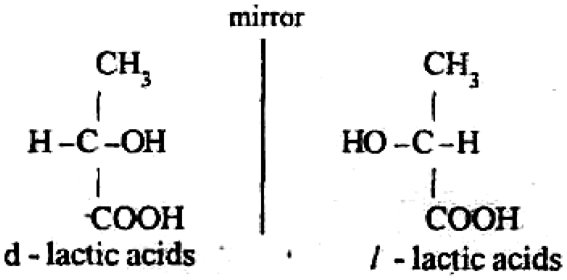
The phenomenon in which different compounds have the same molecular and structural formula but have different configuration, i,e., different arrangement of atoms and groups in space, is called stereoisomerism.

E.g., i) d-and l -lactic acids and

ii) maleic and fumaric acids.

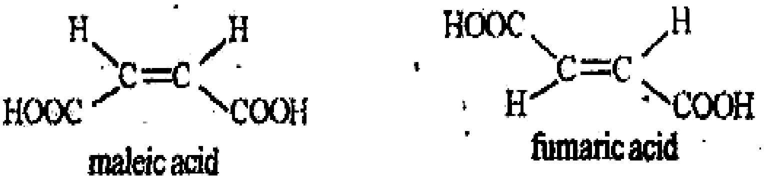
Explanation:

i d - and l - lactic acids are two different compounds. Both have the same molecular formula, viz., C,H_6O_3. Both have the same structural formula, viz., $CH_3CH(OH)$ COOH. But they have different configurations. "That is, the arrangement of various atoms and groups in space, of the two acids are different. The structure of one compound is the mirror image of the other.



Thus d-and l - lactic acids are a pair of stereoisomers.

ii) Maleic and fumaric acids are two different compounds. Both have the same molecular formula, viz.. $C_4H_4O_4$. Both have the same structural formula, viz., CH(COOH) = CH (COOH). But they have different configurations. That is, the arrangement of various atoms and groups in space, of the two acids, are different as shown.



Thus maleic and fumaric acids are another pair of stereo isomers. Stereoisomerism is divided into two types,

i) Optical isomerism and

ii) Geometrical isomerism.

OPTICAL ISOMERISM

Definition:

Optical isomerism is the phenomenon in which different compounds have same molecular formula, same structured formula but has different configurations, i.e., the arrangement of atoms and group in them are different. They rotate the plane of the plane polarised light in different directions.

The two compounds which have the same molecular and structural formulae and have different configurations and which rotate the plane of plane polarised light in different directions are called optical isomers. E.g., d - and l - lactic acids.

Optical activity:

Solutions of some organic compounds have an unique property of rotating the plane of the plane polarised light. This property is called **optical activity.** Such substances are galled **optically** active **substances.** If they rotate the plane of the plane polarised light towards the right (clock wise) they are called dextro-rotatory. If they rotate the plane polaresed light towards the left (anti-clock-wise) they are called laevo-rotatory.

Conditions for optical activity

The molecule must be chiral i.e., it must have two structures which are mirror images and which cannot be super imposed on one another.

Asymmetric centre

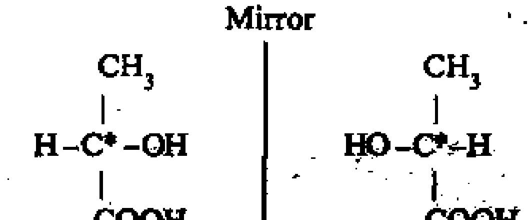
Any structural feature of a molecule which gives rise to optical activity may be called an **asymmetric center. In** many reactions a new asymmetric center is created, for example,

$$CH_3CH_2COOH \xrightarrow{Br_2} CH_3{}^*CHBrCOOH$$

Chiral and Achiral molecules

Chiral molecule and Chiral centre

According to Vant Hoff and Le Bel theory in a molecule like methane the carbon atom is at the centre of a regular tetrahedron and the four atoms or groups are present at the four corners. If the four groups attached to a central carbon atom of a molecule are different, then the molecule is not superimposable on its mirror image such a molecule is called chiral molecule and that carbon is called **chiral carbon** or **chiral centre** or **asymmetric carbon** or asymmetric centre. The phenomenon is called chirality. Chirality is the necessary condition for the existence of enantiomers. Eg. Lactic acid.

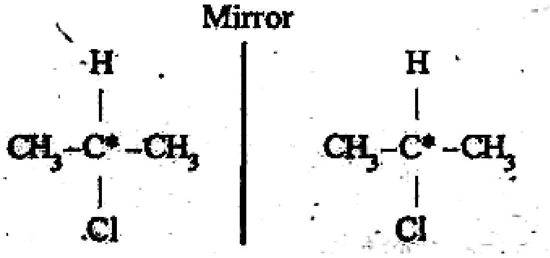


$$\begin{array}{c} CH_3 \\ | \\ H-C^*-OH \\ | \\ COOH \end{array} \quad \Bigg| \quad \begin{array}{c} CH_3 \\ | \\ HO-C^*-H \\ | \\ COOH \end{array}$$

Lactic acid - chiral (not superimposable)

Achiral molecule

Molecules that are superimposable on their mirror images are called achiral. Achiral molecules can not exist as enantiomers. Achiral molecules possess symmetry. Eg. Isopropyl chloride.



Isopropyl chloride - Achiral (superimposable)

Elements of Symmetry

Presence of asymmetric carbon atom is not sufficient to decide whether the molecule is optically active or not. The molecule as a whole must be asymmetric. A simple device to decide whether a molecule is symmetrical or not is to ascertain whether is contains the elements of symmetry. The following are the elements of symmetry.

1.Plane of symmetry

2.Centre of symmetry

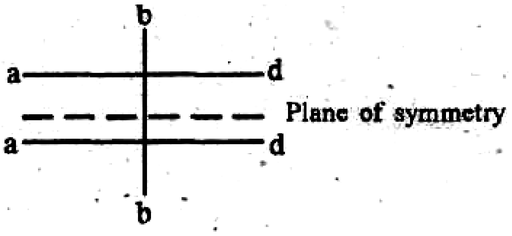
3.Alternating axis of symmetry and

4.Centre of symmetry

If any, one of the elements of symmetry is present in the molecule, then the molecule is symmetrical. That is, the molecule becomes superimposable on its mirror image. So it will not be optically active.

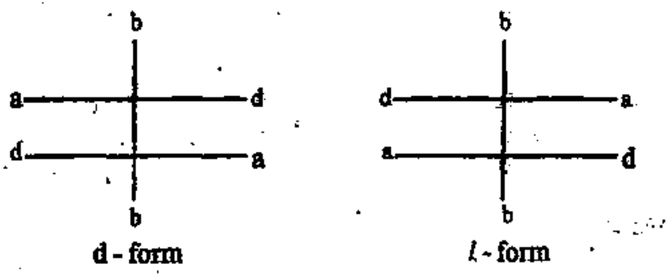
1. **Plane of Symmetry**

A plane which devides an object into two identical halves is called plane of symmetry. A ball can be devided by a plane into two identical halves. It is a non chiral object i.e., it possesses a plane of symmetry. A plane of symmetry divides a molecule in such a way that points (atoms or groups of atoms) on the one side of the plane form mirror images of those on the other side. The following molecule possesses a plane of symmetry. It is a mesoform.



E.g., meso tartaric acid

Whereas the d and l forms of the above compound do, not possess the plane of the symmetry.

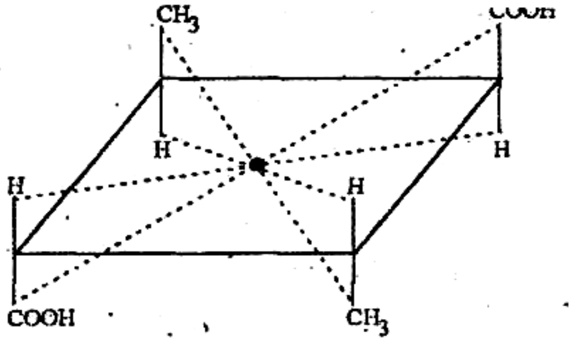


E.g., d and l tartaric acids.

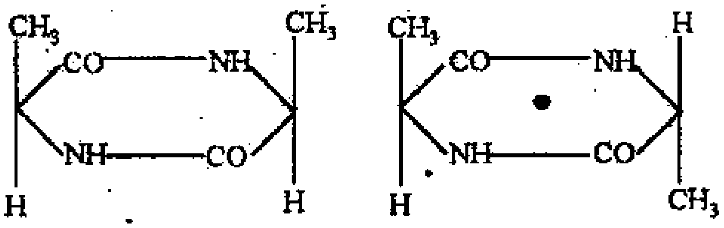
2. Centre of symmetry

A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.

This test is possible only to three dimensional formula, particularly those of ring systems. The following molecule possesses a centre of symmetry.



In the following example dimethyldiketopiperazine exists in two geometrical forms namely **cis** and trans forms.



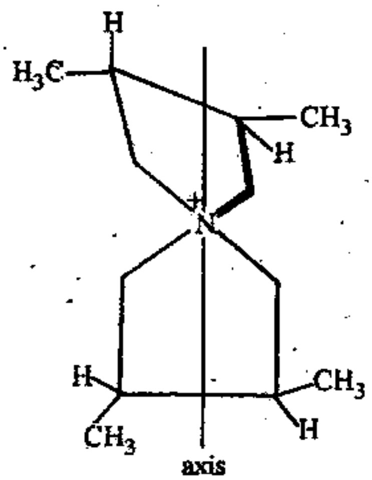
I
Cis

II
Trans

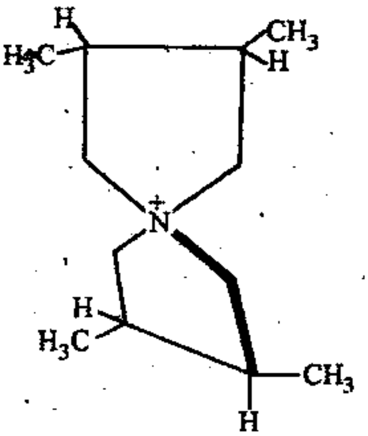
Structure I has neither a plane nor a centre of symmetry. So it is optically active. Structure II has a centre of symmetry. So it is not optically active.

3. Alternating axis of symmetry

A molecule possesses an **n** fold alternating axis of symmetry if when rotated through an angle of 360/n about this axis and then followed by reflection in a plane perpendicular to the axis, the molecule is the same as it was in the starting position. The following molecule possesses alternating axis of symmetry.



III

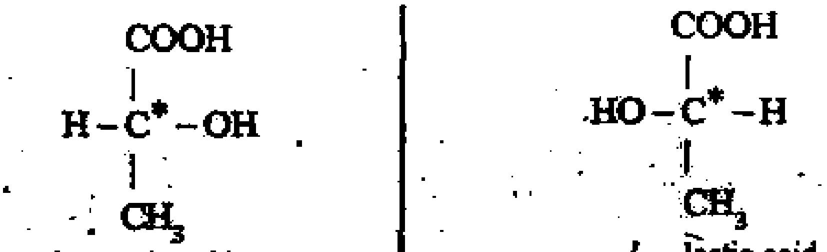


IV

ISOMERISM OF LACTIC AND TARTARIC ACIDS

Optical Isomerism of Lactic acid

Lactic acid CH_3*CHOH COOH, cotains an asymmetric carbon atom. So it exists in two forms. One of the isomers rotates plane polarised light towards the right. It is called dextro rotatory lactic acid or (+) lactic acid. The other isomer rotates the plane polarised light towards the left. It is called laevo rotatory lactic acid or (-) lactic acid.



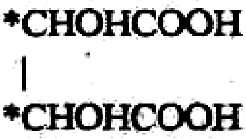
$$\begin{array}{c} COOH \\ | \\ H-C^{*}-OH \\ | \\ CH_3 \end{array} \qquad\qquad \begin{array}{c} COOH \\ | \\ HO-C^{*}-H \\ | \\ CH_3 \end{array}$$

d - lactic acid
(+) lactic acid

l - lactic acid
(–) lactic acid

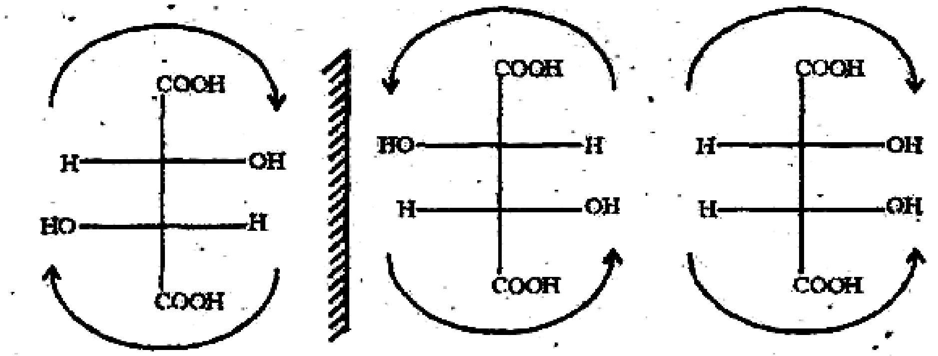
The (+) and (-) lactic acids have identical physical properties except in the sign of rotation. The lactic acid prepared by synthesis is always optically inactive. It is because it contains a mixture of equimolecular amounts of d-and /-lactic acids. Such a mixture is called **racemic mixture.**

Optical Isomerism of Tartaric Acid



$$\begin{array}{l} ^{*}CHOHCOOH \\ | \\ ^{*}CHOHCOOH \end{array}$$

Tartaric acid contains two similar asymmetric carbon atoms. Each carbon atom contains COOH, OH, H and CHOH COOH groups.



d (or) (+) tartaric acid
I

l (or) (—) tartaric acid
II

Meso tartaric acid
III

According to Vant Hoff-La-Bel theory it should exist in $2^2 = 4$ isomeric forms. Since the two asymmetric carbon atoms are similar it exists in 4-1=3 isomeric forms. They are (1) dextrorotatory or (+) tartaric acid I (2) laevorotatory or (—) tartaric aci'd II and (3) meso tataric acid III.

In structure I both the carbon atoms rotate the light towards the right. So the molecule as a whole is dextrorotatory. In structure II both the carbon atoms rotate the light towards the left. So the molecule as a whole is laevorotatory.

In structure III one of the carbon atoms rotate the light towards the right while the other rotates it towards the left. Hence **the net** effect is zero. Therefore meso tartaric acid is internally compensated. Further the molecule has a plane of symmetry. Because of these, it is optically inactive. When d-tartaric acid l-tartaric acid are mixed in equal proportion, again we get a form which does not rotate light. But this form is externally compensated and it is called racemic **mixture.** Thus tartaric acid exists as d-, l-, meso- and d/ (racemic) forms. The racemic form can be resolved into d-and l-forms while meso-form cannot be resolved.

The fact that meso tartaric acid, though it is having two aysmmetric carbon atoms, is optically inactive shows that a substance may be optically inactive though it may contain asymmetric carbons.

Racemization

Definition : Racemisation is the process of converting an optically active compound into the racemic modification.

Racemic modifications are also called racemic mixtures or racemates.

Methods to bring about Racemisation

i) Action of heat

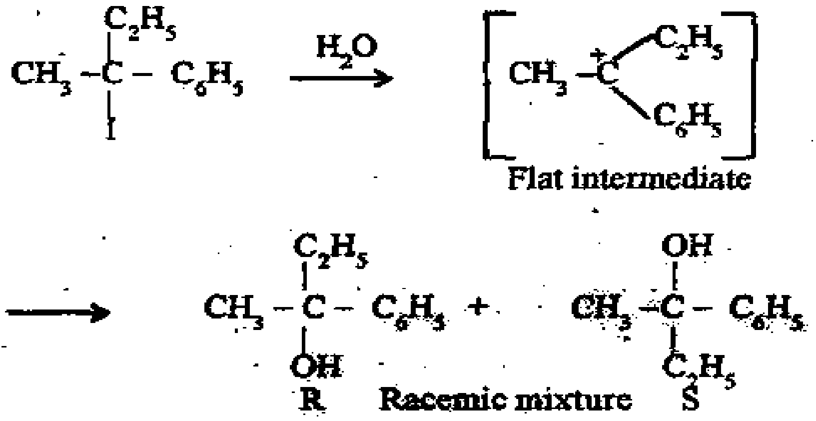
When d or 1 isomer is heated we get the 6.1 mixture.

ii) Treatment with chemical reagents

Many substances undergo racemisation when treated with chemical reagents. E.g.. mandelic acid ($C_6H_5CHOHCOOH$) forms (+) bromo-acid when treated with hydrobromic acid.

iii) Substitutions and rearrangements

Substitutions and rearrangement reactions which take place via S_N^1 type stepwise mechanism end up in recemised products. E.g.

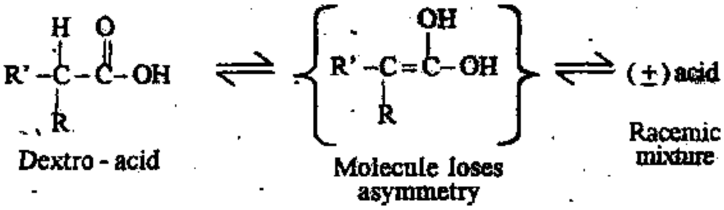


iv) Auto - racemisation

In some cases racemisation occurs spontaneously at room temperature, e.g., dimethyl bromo succinate undergoes racemisation on standing at room temperature. This type of racemisation is termed as **auto racemisation.**

Mechanism of racemisation

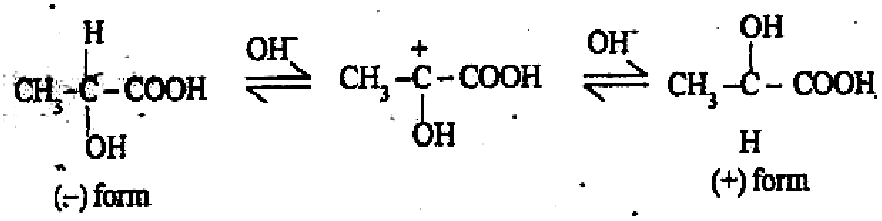
Compounds which racemise readily are found to. contain an asymmetric carbon atom joined to a hydrogen atom and a negative group. Such compounds readily undergo tautomeric change and racemisation occurs via enolisation. For example.



The intermediate enol form is not asymmetric. When it reverts to the stable form, there are equal chances to produce the dextro and laevo forms. So it gives a racemic mixture.

In the case of a compound which can not undergo tautomeric change, mechanism of racemisation is uncertain. However the racemisation is said to take place via the formation of a planar intermediate which when reverts to the stable form, there are equal changes to produce the dextro and laevo forms. So it gives a racemic mixture.

This can be illustrated by taking the base catalysed racemisation of (—) lactic' acid.



Resolution :

Definition: "The separation of a racemic mixture into its enantiomers (dextro-and laevo-components) is termed as resolution".

Explanation: Any attempt to prepare an optically active form of a compound ends up in a racemic mixture only. So they have to be separated into d and l forms. The process of such separation is called **resolution.**

Methods used for resolving racemic compounds

i) Mechanical separation:

When the enantiomers [(+) and (-) forms] of the optically active compound or their salts form well-defined crystals, showing hemihedral faces, they can be separated by simple hand-picking. Pasteur separated in this manner crystals of sodium ammonium racemate, $NaNH_4C_4H_4O_6.2H_2O$.

ii) Bio - chemical separation:

Certain bacteria or fungi when allowed to grow in a solution of the racemic compounds destroy one of the optical isomers at much quicker rate than the other due to selective assimilation. For example, when penicllium glaucum is allowed to grow in a solution of ammonium racemate, it destroys the d-tartrate by assimilation leaving behind the l-tartrate practically unaffected.

However, the separation is not always complete and one component is always lost. Some other side-products may also be formed and the sample may be difficult to purify.

iii) By means of salt formation:

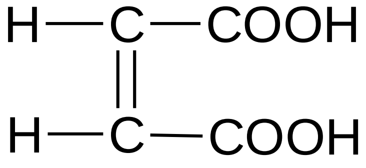
This method is the best of all methods of resolution. In this method the active constituents of a racemic mixture are converted into diastereoisomers [salts] with another active base or acid.

$$[d_{acid} + l_{acid}] \quad + \quad 2d_{base} \longrightarrow [\, d_{acid}\, d_{base}\,] + [l_{acid}\, d_{base}]$$

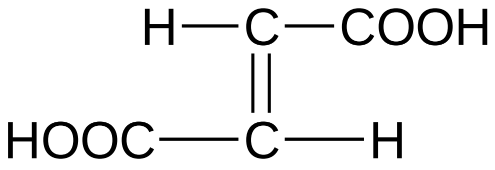
Racemic mixture	Active	Optically active salts
[acid]	base	[Diastereo - isomers]

The two salts thus obtained often differ in their solubilities and can be separated by fractional crystallization. The salts can be hydrolysed with inorganic acids or alkalis to get the original active compounds. For example, racemic tartaric acid is separated by this method. The optically active bases used for this purpose are mainly alkaloids like quinine, brucine, cinchonine, and morphine. Similarly racemic bases can be separated by using optically active acids like tartaric acids, camphor sulphonic acid, etc. .

Geometical isomerisms in maleic and fumaric acids:



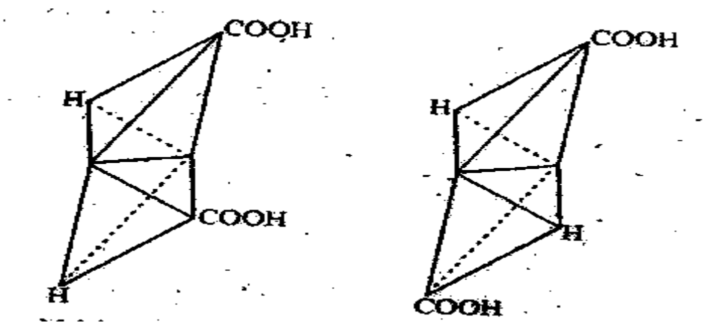
$$\begin{array}{c} \mathrm{H{-}C{-}COOH} \\ \| \\ \mathrm{H{-}C{-}COOH} \end{array}$$



$$\begin{array}{c} \mathrm{H{-}C{-}COOH} \\ \| \\ \mathrm{HOOC{-}C{-}H} \end{array}$$

Maleic acid (cis) Fumaric acid (trans)

The maleic acid and fumaric acid can be represented in ***tetrahedral forms*** as shown below.



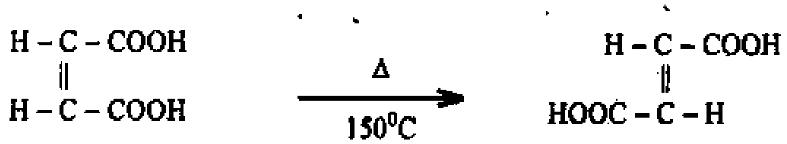
Maleic acid Fumaric acid

Tetrahedral models of maleic acid and furmaric acid

However, the two carbon atoms are united by a double bond, the two tetrahedral representing them must necessarily be in contact at two corners. In such a case all free rotation of the tetrahedral cases and the groups attached to the two carbon atoms are fixed relative to each other. Thus, different spatial arrangements of the groups about the double bonded carbon atoms now become possible. For example, the two tetrahedral models representing maleic acid and fumaric acid as shown before.

It is clearly noted that maleic acid and fumaric acid have quite different arrangements of groups about the double bond. While in one case similar groups are on the same side, in the other they lie on opposite sides. This type of isomerism due to the different geometrical arrangements of the groups about the doubly bonded carbon atoms is known as geometrical isomerism. When similar groups lie on the same side i.e.. two carboxyl group and two hydrogen are at same side is called ***maleic acid***, if they are opposite to each other is called ***fumaric acid***. Consequently this type of isomerism is often spoken of as cis-trans isomerism.

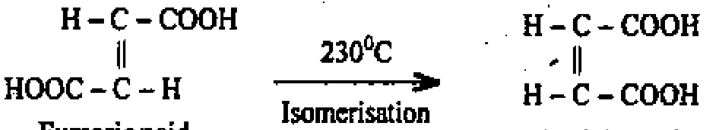
When on prolonged heating at 150°C maleic acid isomerises to fumaric acid.



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \xrightarrow[150^{0}C]{\Delta} \begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

Maleic acid (cis) **Fumaric acid (trans)**

When fumaric acid is heated about 230°C it undergoes isomerisation to give maleic acid.

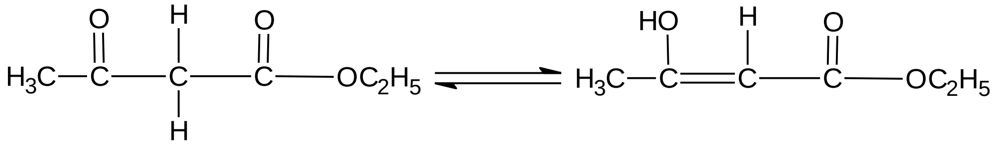


$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array} \xrightarrow[\text{Isomerisation}]{230^{0}C} \begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

Fumaric acid **Maleic acid**

Keto – Enol Tautomerism:

When 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.



$$H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons H_3C-\overset{\overset{HO}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

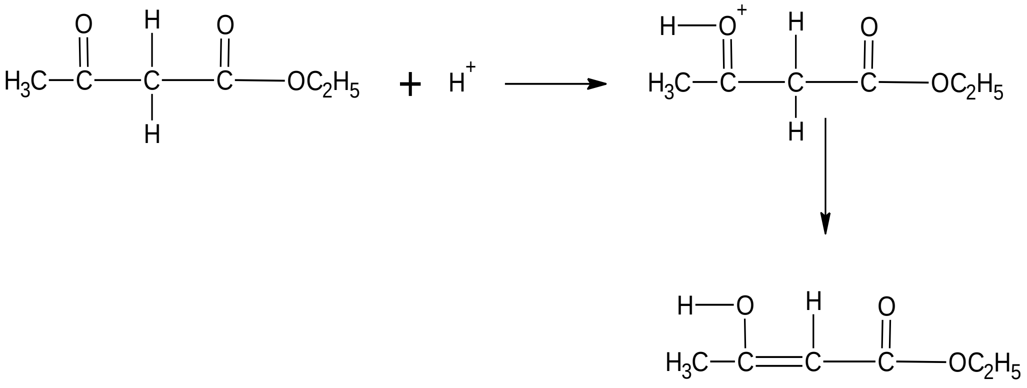
Keto – enol tautomerism of acetoacetic esters:

Acetoacetic ester behaves as an enol and also a ketone in its reactions. We say this is due to tautomerism. Thus, if a compound 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.

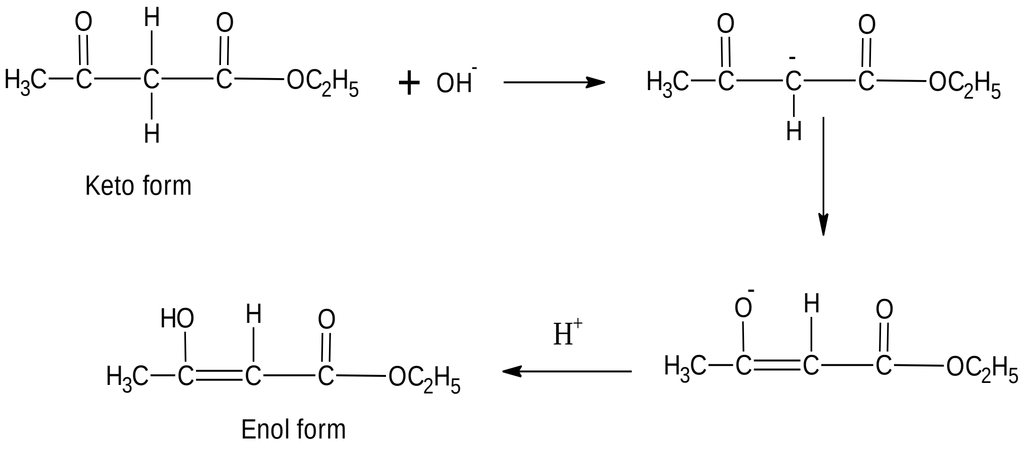
Acid and base catalysed mechanism:

The keto – enol tautomerism of acetoacetic ester is catalysed both by acids and bases.

1. Acid catalyzed mechanism:



2. Base catalysted mechanism:



CONFORMATIONAL ANALYSIS

Definition:

The different arrangements of a molecule that can be obtained by rotation around c-c single bonds are called **Conformational isomers or conformations**. The study of different conformations is called **conformational Analysis.**

Configuration

It means the arrangement in space of atoms or groups around the dissymmetric or rigid part of a molecule.

Conformations

The infinite number of momentary arrangements of the atoms in space that result from rotation about bond is called conformations.

Conformers

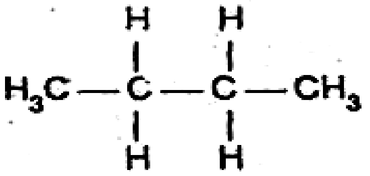
Conformations of minimum energy are called “conformational isomers” or “Conformers”.

Torsional strain:

Conformations are the result of free rotation about the carbon - carbon single bond. The1 barrier to rotate about C-C bond is called torsional strain.

Conformations of n-Butane.

n-Butane can be regarded-as derived from ethane by replacing one hydrogen atom on each carbon by methyl group.

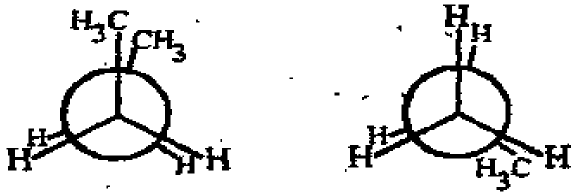


$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3$$

n - Butane

This molecule has three C-C bonds (ie, one central and two terminals) around which rotation can take place. However, if we consider the rotation around the control C-C bond only, (ie, C_2-C_3) the situation becomes similar to that of Ethane. The difference is that n-butane has more than one staggered conformation and more than one eclipsed conformation.

Eclipsed conformations of n-Butane



Eclipsed
(more repulsion)
(a)

Eclipsed
(less repulsion)
(b)

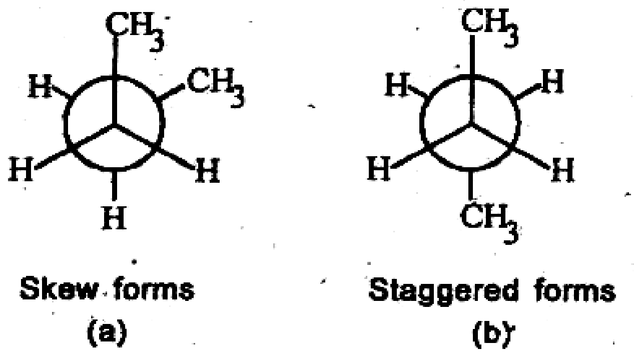
The conformation (b) is more stable than (a)

Explanation:

In these two eclipsed conformations, the one having larger methyl groups eclipsing (a) experiences more repulsive forces than the one where a methyl group is faced with a hydrogen atom (b).

Thus, the conformation (b) is more stable than (a)

Staggered conformations of n-Butane



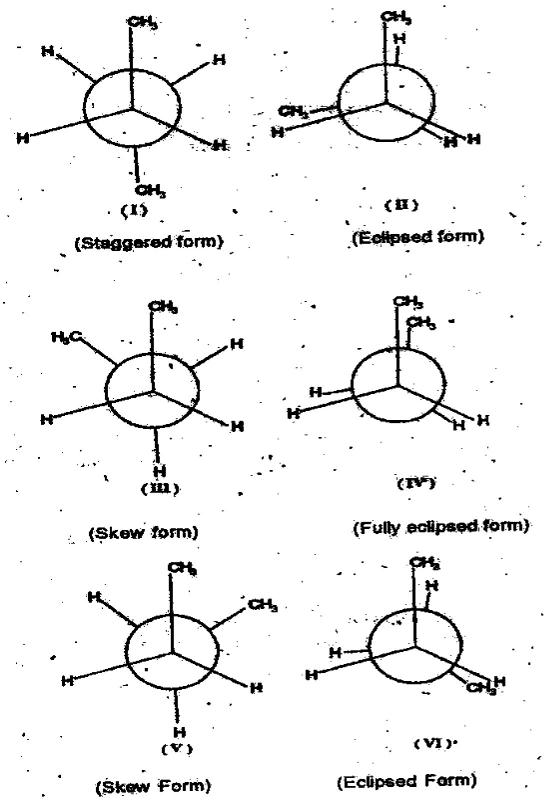
The staggered conformation (b) is more stable than Skew conformation (a)

Explanation:

In (a), the bulky methyl groups are at an angle of 60° to each other. But in staggered conformation (b), the bulky methyl groups are at an angle of 120° to each other.

Thus, the repulsive forces in (a) is greater than in (b) due to proximity of methyl groups in the former. Thus (b) is more stable than (a).

Various conformation of n - Butane



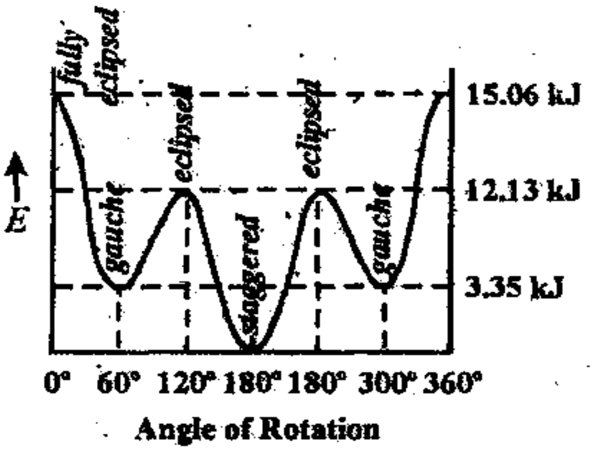


Figure : Energy changes in n-Butane during rotation around C_2-C_3 by 60^0 each time

Aromaticity:

Definition:

A compound is aromatic if it has a planar, cyclic structure, has (4n+2)π electrons has unusual stability due to π electron delocalisation and which has unexpected chemical properties, particularly substitution rather than addition.

Huckel's rule for aromaticity:

Rule: If the compound contain $(4n+2)\pi$ electrons, then it will be aromatic.

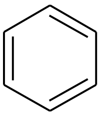
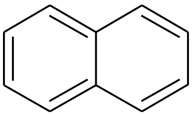
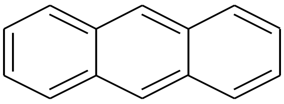
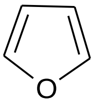
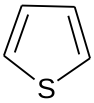
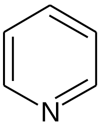
Here, $n = 0, 1, 2, 3...$

Explanation:

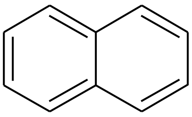
Huckrl through M.O. calculations connected aromatic character (stability due to high delocalisation energy or high resonance energy) with the presence of $(4n+2)\pi$ electrons in a closed shell. Here 'n' is an integer.

Examples of aromatic compounds:

The following compounds are aromatic, which obey Huckel's rule.

Name	No. of π electrons	n
1. Benzene	6	1
		
2. Naphthalene	10	2
		
3. Anthracene	14	3
		
4. Furan	6	1
		
5. Thiophene	6	1
		
6. Pyridine	6	1
		

Naphthalene:



Isolation:

It is present to extent of 6 – 10% in coal tar and is isolated from middle oil fraction.

i) The middle oil fraction of coal tar distillation is cooled. A major portion of naphthalene crystallises out. It is separated by centrifugation or by pressing out the oil in a hydrolic press. The crystals are washed with hot water and with aqueous sodium and phenols. It is then washed with a little concentrated sulphuric acid to remove basic impurities. We get crude naphthalene. It is purified by sublimation.

ii) It is also made, now a day, synthetically from petroleum by passing petroleum fractions over heated copper catalyst at 950 K at atmospheric pressure. A mixture of naphthalene and methyl naphthalene is obtained. The methyl naphthalene is heated with hydrogen under pressure in the presence of metal oxide catalyst. It is converted into naphthalene. This process is known as hydrodealkylation.

Properties:

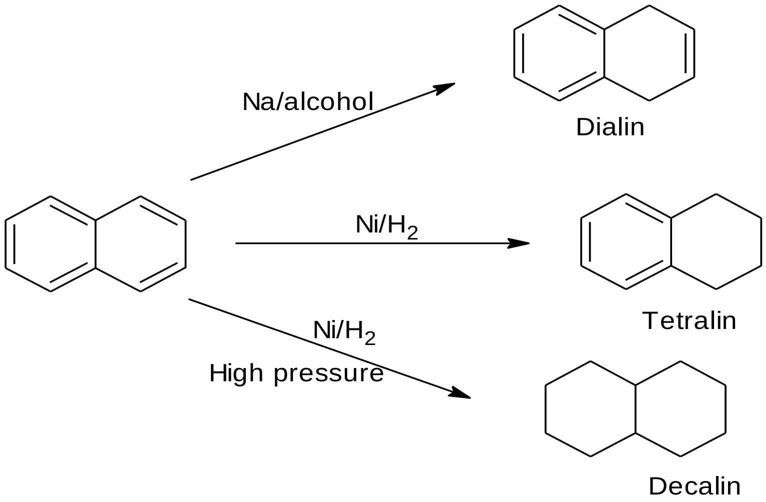
- Naphthalene forms colourless crystalline plates.
- m.p. 80^0c and b.p. 218^0c with characteristic smell.
- It is insoluble in water, but readily soluble in hot alcohol, ether and other solvents.

Chemical Properties:

- Naphthalene is aromatic. It contains 10π electrons obeying Huckel's $(4n+2)\pi$ electrons rule.
- Chemically, naphthalene resembles benzene, but it is more active.

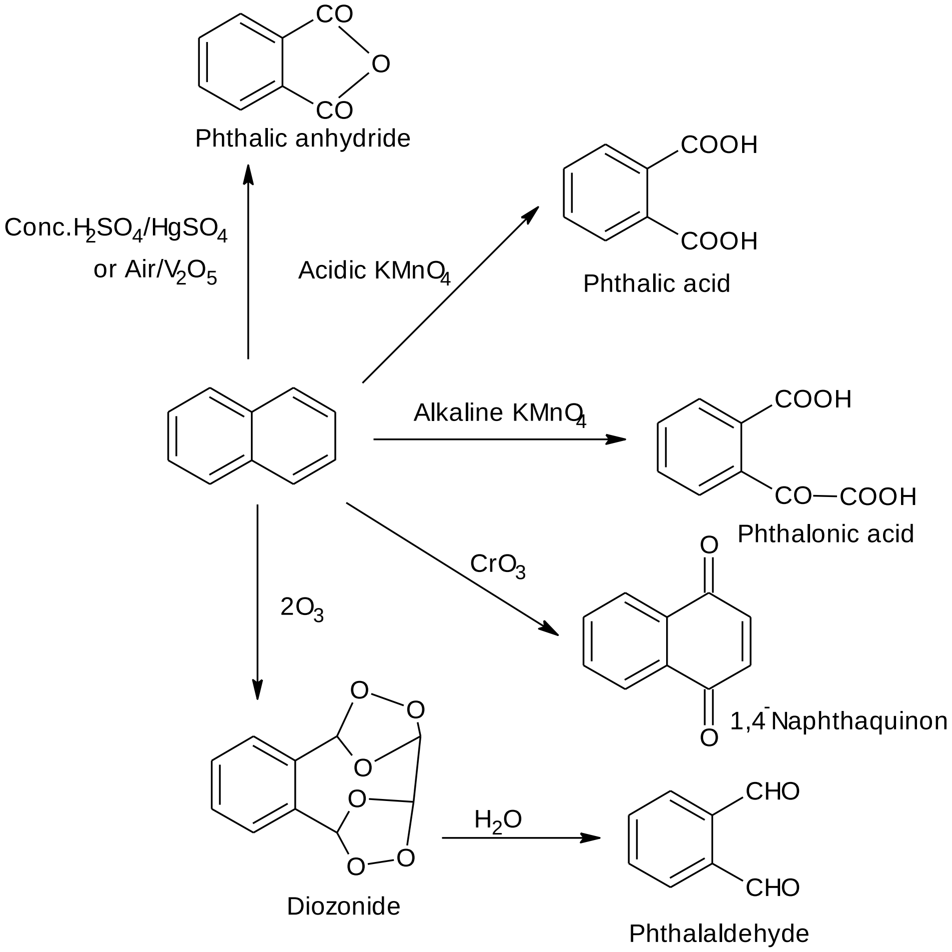
1. Hydrogenation:

Naphthalene reduced with different reducing agent gives different products.



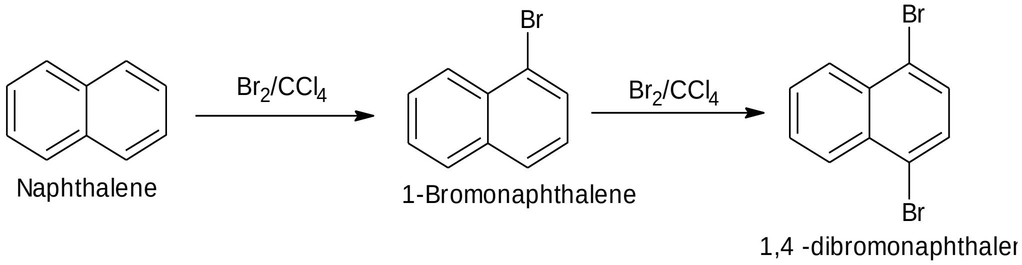
2. Oxidation:

Naphthalene oxidised with different oxidising agent gives different products.

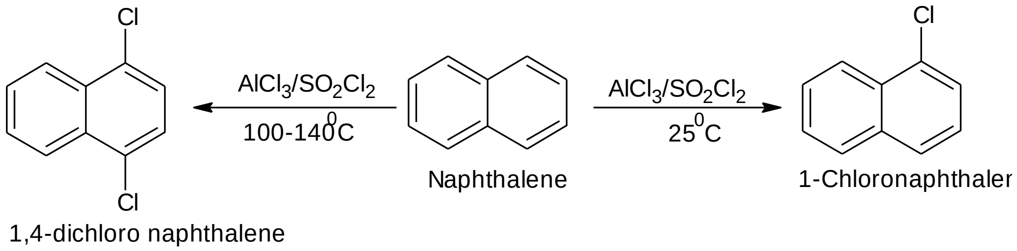


3. Halogenation:

Naphthalene on bromination with Bromine and boiling carbon tetrachloride solution gives 1,4-dibromonaphthalene, further bromination it gives 1,4-dibromonaphthalene

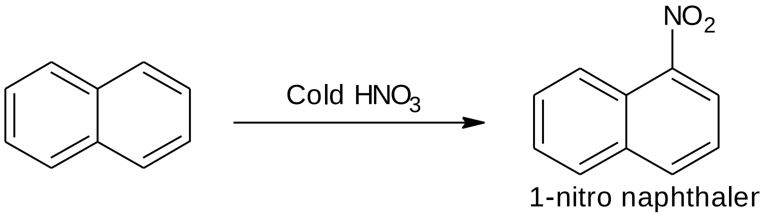


Chlorination can be carried out with sulphuryl chloride in the presence of aluminium chloride.

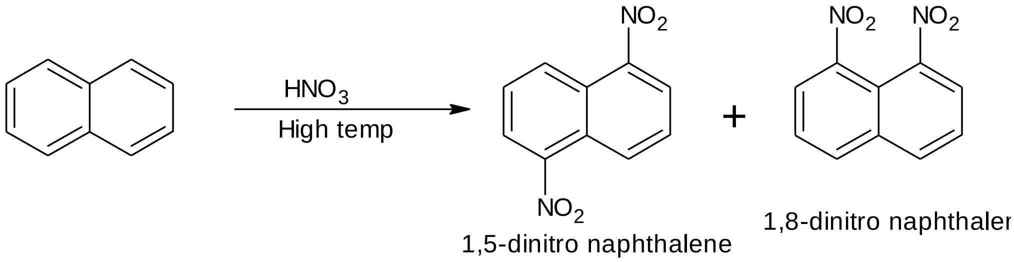


4. Nitration:

Nitration of naphthalene with nitration mixture (Conc. H_2SO_4 + Conc. HNO_3) or cold nitric acid gives 1-nitronaphthalene.

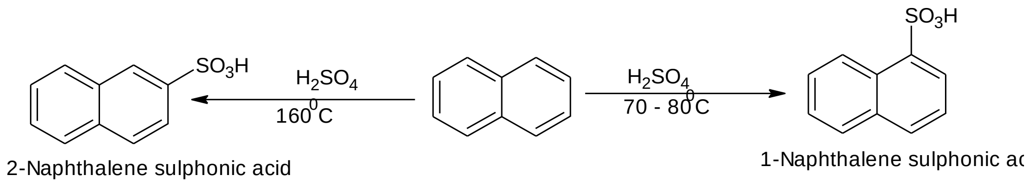


At high temperature a mixture of 1,5- and 1,8-dinitro naphthalenes are obtained.



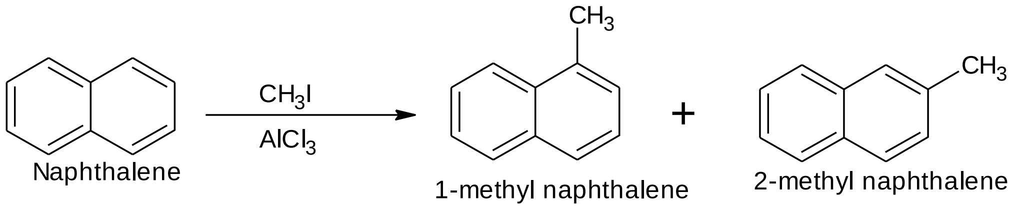
5. Sulphonation:

When naphthalene is treated with Conc. H_2SO_4 at 70 – 80^{0}c, 1-naphthalene sulphonic acid is the main product. If the temperature is raised to 1600c the 2-naphthalene sulphonic acid is the main product.



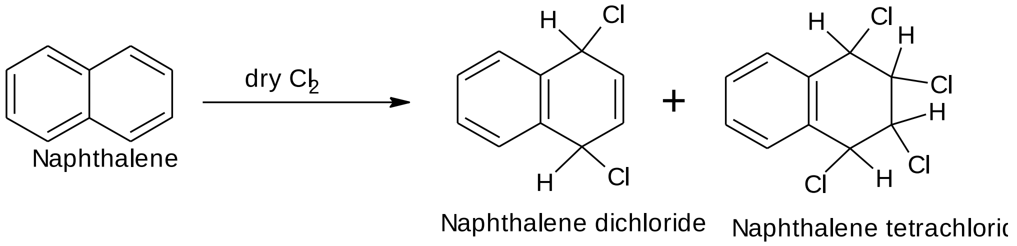
6. Friedel – Craft reaction:

Methyl iodide reacts with naphthalene in presence of $AlCl_3$ to give 1- and 2-methyl naphthalenes.



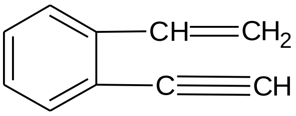
7. Addition to Halogens:

Naphthalene reacts with dry chlorine gives naphthalene dichloride and tetrachloride.



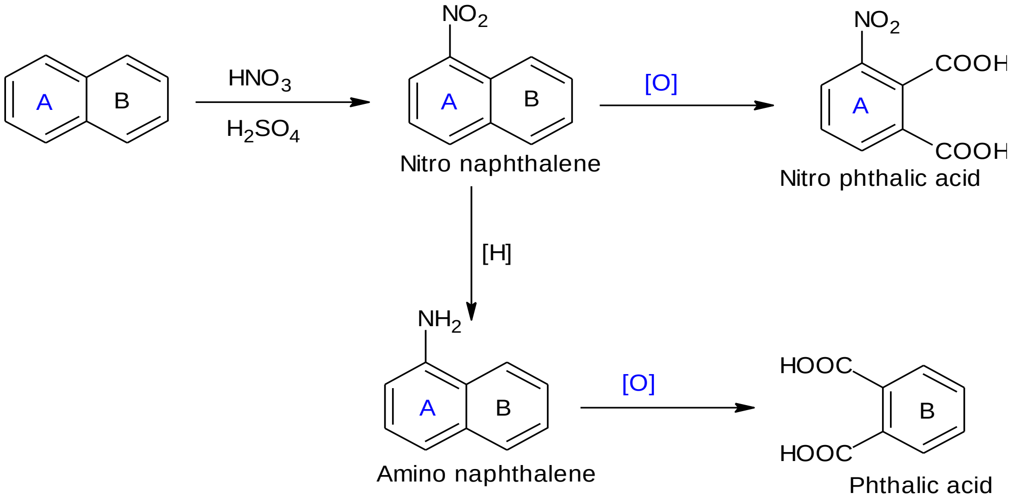
Structure:

1. The molecular formula of naphthalene is found to be $C_{10}H_8$.
2. Naphthalene resembles benzene in its chemical reactions. It can be nitrated, sulphonated and halogenated like benzene. Naphthalene is very stable. All these suggest a ring structure as for benzene.
3. Oxidation of naphthalene gives phthalic acid. There fore naphthalene molecule must contain one benzene ring with two ortho side chains or a closed chain linked to ortho position.
4. Therefore the possible structure for naphthalene with the side chain is,



This structure having two unsaturated side chains but, naphthalene could not explain this property in its reactions.

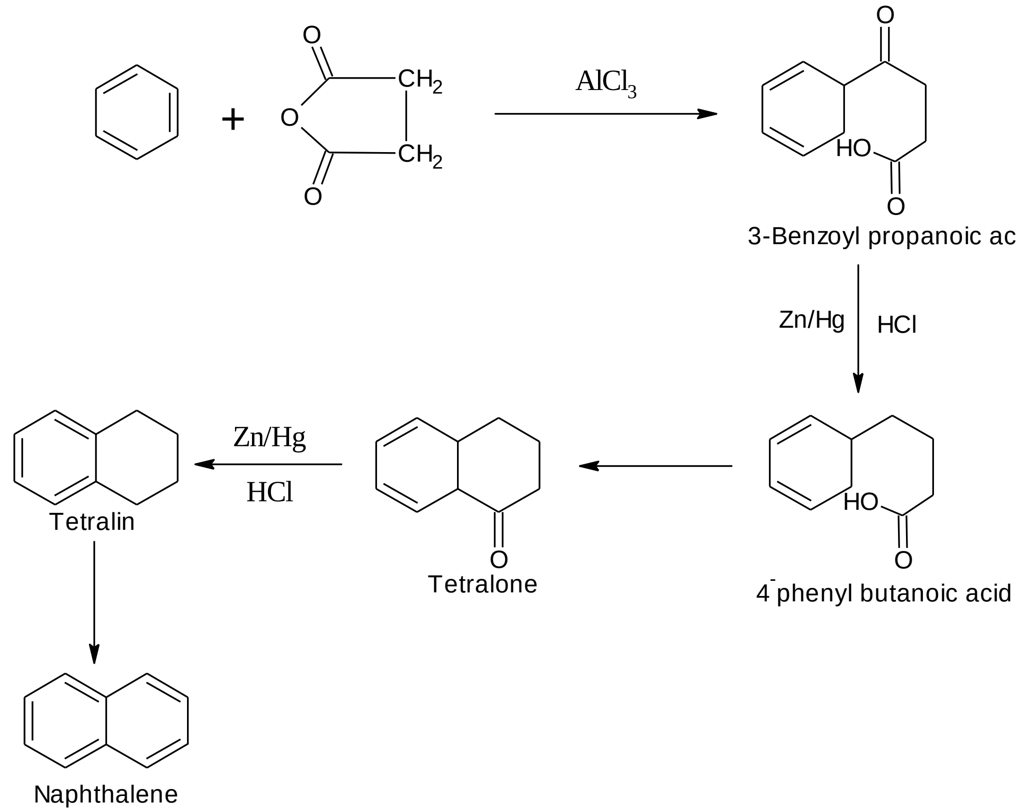
5. Naphthalene on nitration gives nitro naphthalene, which on oxidation gives nitro phthalic acid. This shows that the benzene ring A containing the nitro group remains unaffected during oxidation. If nitro naphthalene is reduced to amino naphthalene and if the amino naphthalene is oxidized, the product is phthalic acid. This shows that the benzene ring A to which amino group is attached is destroyed during oxidation. Therefore nitro naphthalene contains another benzene ring B apart from the on carrying the nitro group. These reactions may be represented as follows.



These reactions prove that there are two fused benzene rings in naphthalene.

6. Further the structure of naphthalene is confirmed by its synthesis.

Haworth Synthesis:

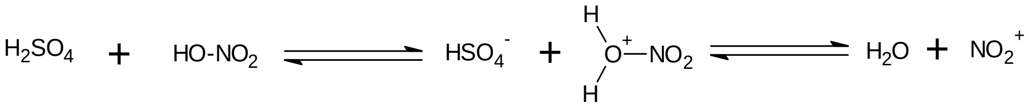


Electrophilic substitution in benzene:

Nitration:

In nitration, the attacking electrophile is nitronium ion NO_2^+, which is produced under the reaction, conditions usually a mixture of HNO_3 and H_2SO_4 is used.

HNO_3 acts as a base. If accepted a proton from the strong acid H_2SO_4, the protonated Nitric acid biassociate into nitronium ion.



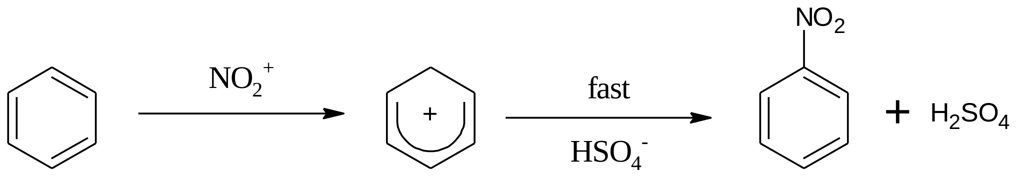
$$H_2SO_4 + HO\text{-}NO_2 \rightleftharpoons HSO_4^- + H_2\overset{+}{O}\text{—}NO_2 \rightleftharpoons H_2O + NO_2^+$$

$$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+$$

Overall reaction:

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

The electrophile nitronium ion attack the π-clouds of arene ring perform arenium ion in the slow step. The arenium ion, the proton is abstracted by the base HSO_4^- gives the product.



Halogenation:

Activated benzene rings can be halogenated lewis acid catalyst ALCL$_3$, FeBr$_3$, and ZnCl$_2$ are used. The function of the catalyst is the polasrised partially or completely the X—X bond.

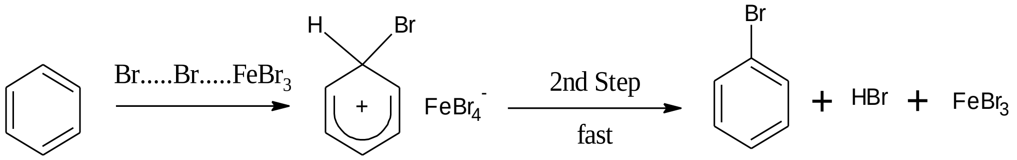
Let us consider,

$$Cl\text{--}Cl + AlCl_3 \rightleftharpoons Cl.......Cl......AlCl_3$$

$$Cl\text{--}Cl + AlCl_3 \rightleftharpoons Cl.......Cl......AlCl_3$$

$$Br\text{--}Br + FeBr_3 \rightleftharpoons Br.......Br......AlBr_3$$

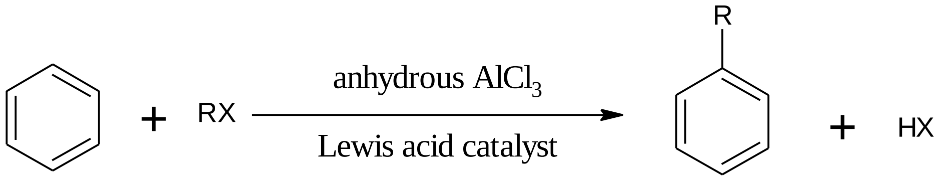
This polarised complex attacks the benzenering to form a σ - complex. Being this a slow step, this is rate determining step. In the second step proton is reoved and the product is formed.



Fridel Craft alkylation and acylation:

An alkyl or acyl group is introduced into an aromatic ring in the presence of lewis acid catalyst. It is called Friedel Craft reaction.

Alkylation:



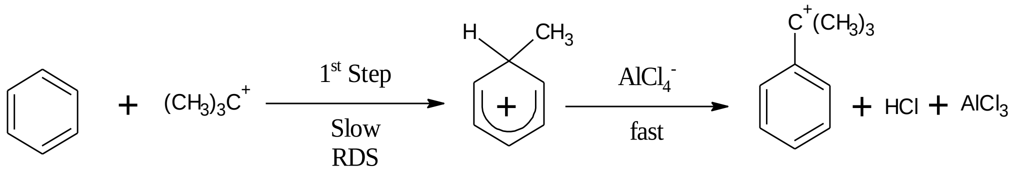
Two mechanisms are possible. In one mechanism free carbocation will be; the electrophile. In other mechanism polarised complex will be the electrophile. Nature of the electrophile is decided by the nature of the alkyl halide.

In tertiary alkyl halide, free carbonium ion will be the electrophile.

Example:

Reaction between benzene and tertiary butyl chloride in the presence of the catalyst AlCl$_3$.

$$(CH_3)_3C\text{-}Cl + AlCl_3 \longrightarrow (CH_3)_3C^+ + AlCl_4^-$$



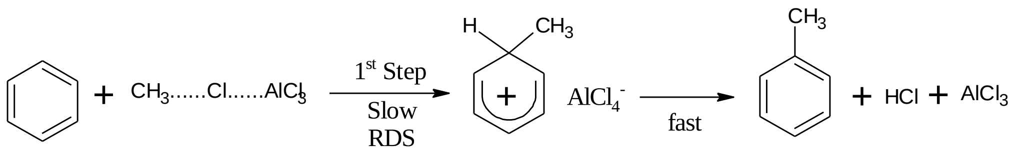
If primary alkyl halide is used, polarised complex will be the eelctrophile.

Example:

Reaction between CH_3Cl and benzene using the catalyst $AlCl_3$.

$$CH_3Cl + AlCl_3 \longrightarrow CH_3......Cl......AlCl_3$$

Polarised comple



For secondary alkyll halide, the electrophile may be the polarised complex or free carbocation.

Acylation:

In acylation, two electrophiles are to be considered as in alkylation. They are,

$R\text{-}CO^+ AlCl_4^-$ acylium ion

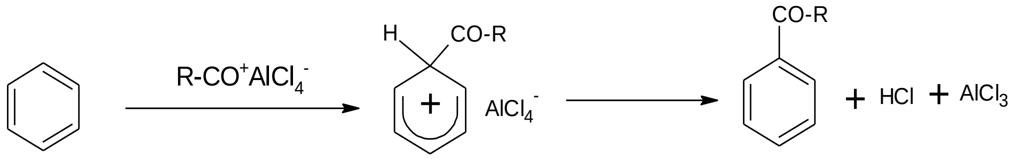
$R\text{-}CO......Cl.......AlCl_3$ Polarised Comple

Acylium ion is detected in solid complexes, in polar solvents like Nitromethane and also when 'R' group is bulky.

In less polar solvents acylium ion is not detected and in such cases, the electrophile is polarised complex.

Mechanism:

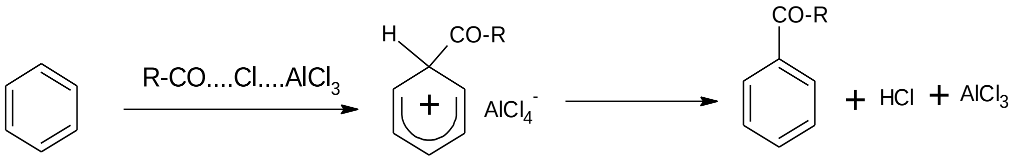
a) With acylium ion:



It does not show any primary kinetic isotopic effect. So σ - complex forming the first step is the RDS. In spectra analysis confirms the presence of the acylium ion.

b) With Polarised complex:

$$R\text{-}CO\text{-}Cl + AlCl_3 \longrightarrow \underset{\text{Polarised Complex}}{R\text{-}CO......Cl.......AlCl_3}$$



Generally, the polarised complex is formed in non-polar solvent. Here the acylium ion is not detected. Here also there is no primary kinetic effect.

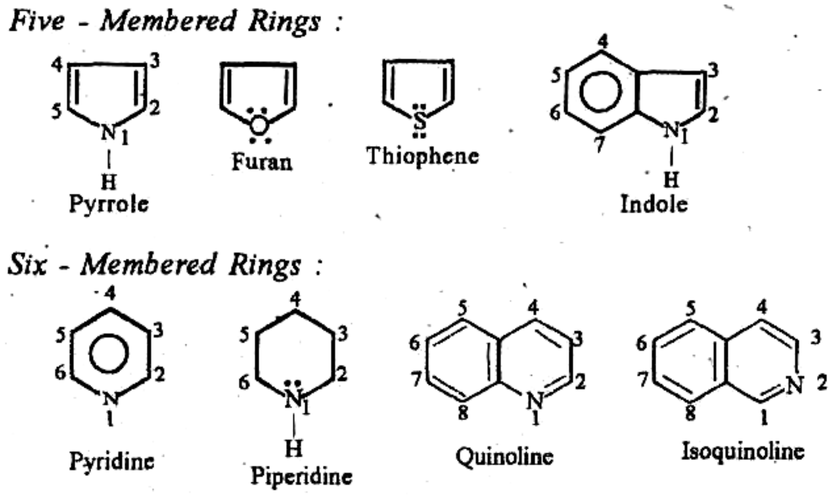
Heterocyclic Compounds

Cyclic compounds, in which the ring includes only one type of atoms, are called **homocyclic compounds**. E.g. Benzene. Cyclic compounds in which the ring includes only carbon atoms are called **carbocyclic compounds**. E.g. Benzene, naphthalene, etc. Cyclic compounds in which the ring includes, in addition to carbon atoms, one or more poly valent atoms such as O, N and S are called **heterocyclic compounds**. E.g.,Furan, thiophene, pyrrole, pyridine etc.

A variety of such heterocyclic compounds of different ring sizes are known. In this chapter we will restrict our study to the most important ones which are made of five and six membered rings.

Structure:

The common names of some of the most important five and six membered heterocyclic ring compounds are given below.



Noticed that the rings containing nitrogen usually end with - ole if five membered and with – ine if six membered. The hetero atom is always numbered as 1 (isoquinoline is an exception), and in such a way as to keep the substituent numbers as low as possible.

Aromatic characteristics of heterocyclic compounds

The heterocyclic compounds are much more stable and possess aromatic properties. Most of the heterocyclic compounds obeys Huckel's rule and show aromatic character.

According to Huckel's rule "If a system containing $(4n+2)\pi$ electrons will be aromatic in nature." Where n = 0, 1, 2,……….

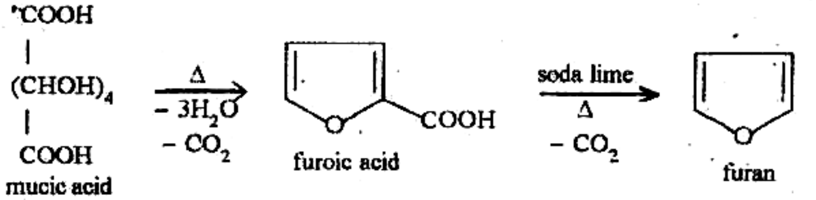
CHEMISTRY OF FURAN, (C_4H_4O)

Molecular formula : C_4H_4O.

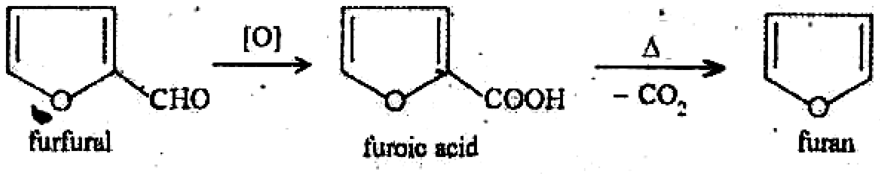
It contains one oxygen atom in its ring. The positions of side - chains or substituents are indicated by numbers or Greek letters. Number 1 is given to the oxygen atom. (In all the heterocyclic compounds containing one hetero - atom, number 1 is always given to the hetero - atom).

Preparation :

1. Mucic acid is heated. We get furoic acid. It is distilled with soda lime, we get furan.



2. When furfural undergoes oxidation and followed by heating it gives Furan.

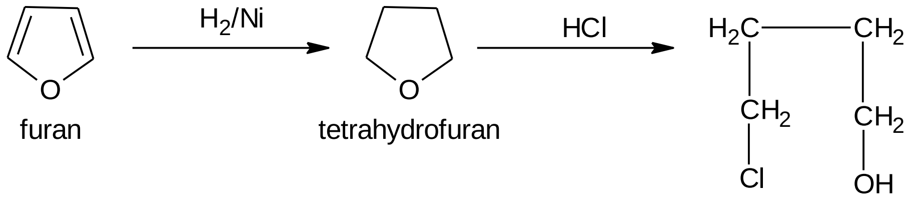


Properties

It is a colourless liquid. It is insoluble in water but soluble in alcohol and ether. It turns a pine splint moistened with hydrochloric acid green. (Test)

Reactions:

1. When furan is calalytically reduced with H_2, in the presence of Ni or Pd we get tetrahydrofuran (THF) which is used as a non aqueous solvent.

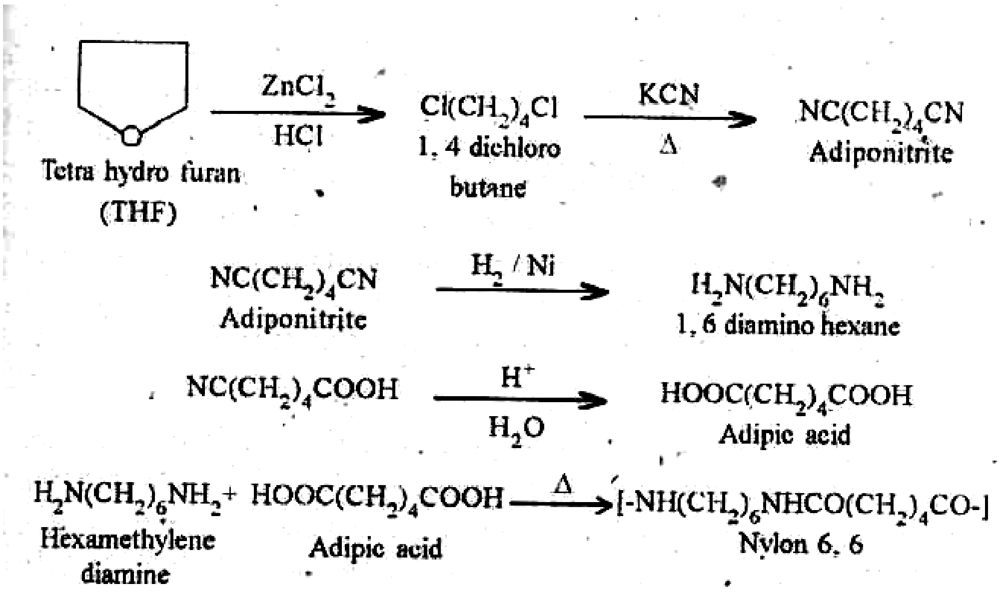


Tetra Hydro Furan (THF) is used

(i) as a solvent in the preparation of Grignard reagents and its reactions,

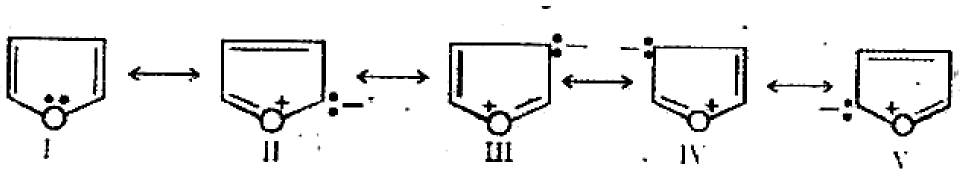
(ii) It is used in the manufacture of nylon 6, 6. It is used as a starting material for

this synthesis.



Electrophilic Substitution Reactions :

Furan is a resonance hybrid of the following five resonating structures (I to V).



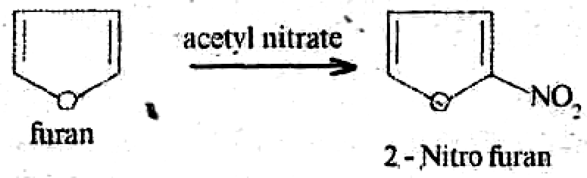
If obeys Huckel’s rule and contains (4n+2)n electron (here n = number of rings = 1). The molecule is planer. Therefore it is an aromatic compound. It is less aromatic than benzene. It has a larger electron density at position 2 or 5 than at 3 or

Therefore electrophilic substitution is expected to lake place in position 2 or 5 i.e., a - position. In practice 2 - substitution is favored. It is because attachment of the electrophilic reagent at position 2 results in the formation of a more stable carbonium ion which, is the resonance hybrid of three structures III. IV and V. On the other hand the attachment of the electrophilic reagent at position 3 results in the formation of a less stable carbonium ion which is the resonance hybrid of only two structures I &II.

Furan is more reactive than benzene i.e., less aromatic than benzene because the lone pair on the oxygen atom is involved in resonance. There by activating the ring. Thus furan undergoes substitution reactions more readily than does benzene. We get 2 or 5 substituted products. If both positions are occupied we get 3 - substituted products.

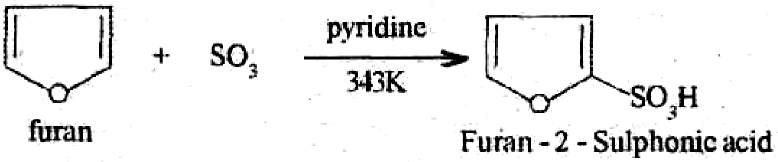
a) Nitration :

When furan is nitrated with acetyl nitrate or a hot solution of nitric acid and acetic anhydride, we get 2-nitrofuran.



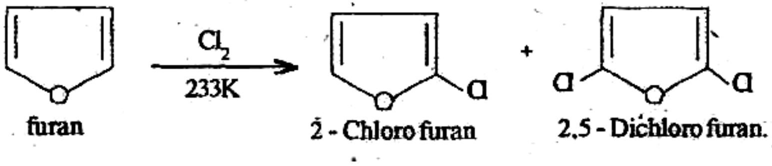
b) Sulphonation:

When furan is treated with pyridine and SO, mixture we get furan - 2 - sulphonic acid.



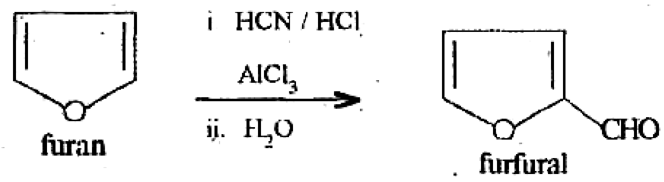
c) Halogenation :

When furan is treated with chlorine at 233 K we get 2-chlorofuran and 2,5-dichlorofuran.



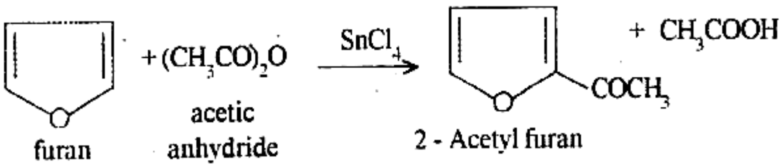
d) Gattermann reaction :

It undergoes Gattermann reaction to give furfural as the product.



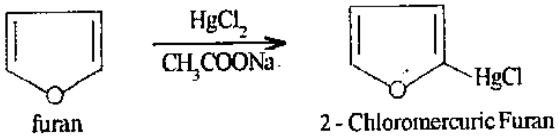
e) Friedel - Crafts Acylation :

Furan can be acylated with acetic anhydride in the presence of BF? or $SnCl_4$ at 273 K to yield 2 - acetyl furan.



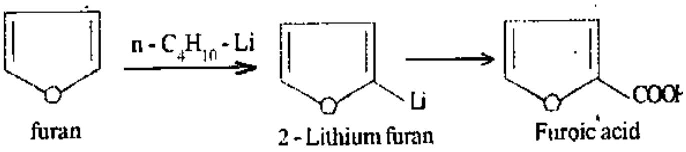
f) Mercuration :

It can be mercurylated to give 2 - chloromercuric furan.



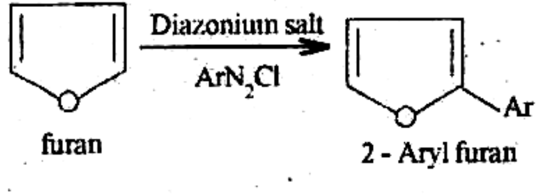
g) Reaction with n - butyl lithium :

It is used in synthesis of Furoic acid.



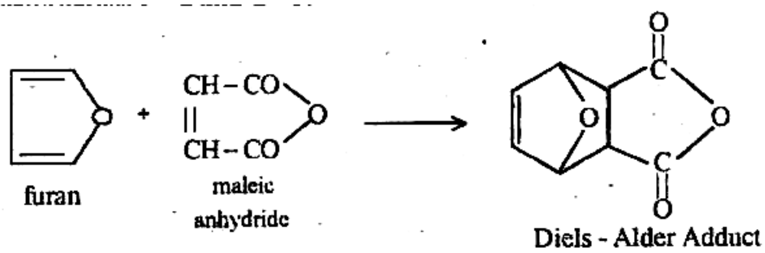
h) Gomberg reaction :

It is used in synthesis of 2 - Aryl furan.



3) Diels - Alder Reaction :

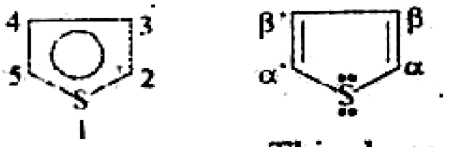
Furan is the only one of the five membered heterocyclic compounds to undergo the Diels - Alder reaction with maleic anhydride. The addition occurs across C - 2 and C – 5.



[Furan is less aromatic than thiophene and pyrrole. Thiophene and Pyrrole don’t give the adduct. In this reaction it reacts as a 1,3 diene].

CHEMISTRY OF THIOPHENE, (C_4H_4S) Molecular formula: C_4H_4S.

It contains one sulphur atom in its ring. The positions of side -chains or substituents are indicated by numbers or Greek letters. Number 1 is given to the sulphur atom. Benzene and thiophene resemble closely in their properties. Therefore the nomenclature of thiophene and its compound is also similar to that of benzene.



Thiophene

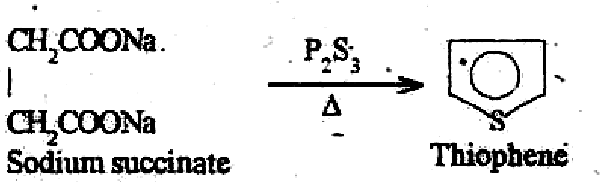
Isolation from coal tar :

Coal tar is fractionally distilled. The fraction collected upto 170°C is known as light oil. It is purified arid again distilled. Benzene is obtained at 80 - 82°C. This contains thiophene. Because of the marked similarity of the two compounds it is difficult to separate them by fractional distillation. Their boiling points are also very close to each other.

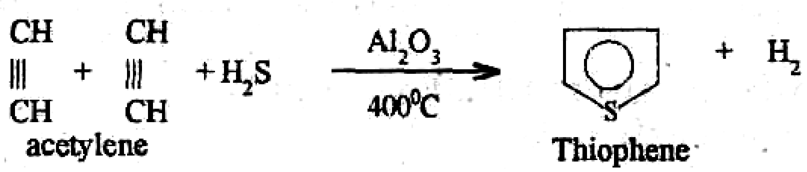
Thiophene is separated by refluxing the mixture with aqueous mercuric acetate. Thiophene is mercurated. Benzene remains unaffected. The mercurated derivative of thiophene is separated and distilled with hydrochloric acid and we get thiophene.

Preparation:

When sodium succinate is heated with phosphorus sulphide thiophene is formed.



2. When acetylene mixed with H,, S and passed through a tube containing A1,O3 at 400°C thiophene is obtained.



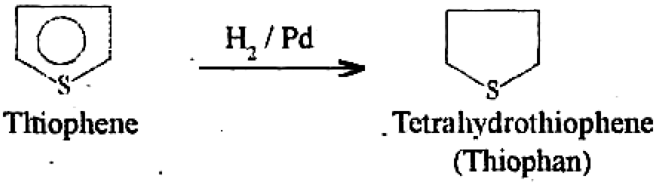
Properties :

It is a Colourless liquid smelling like benzene. It is insoluble in water but soluble in alcohol and ether.

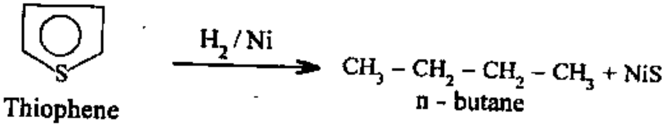
Reactions :

Thiophene resembles benzene very closely. It does not show basic properties. It is comparatively more stable than furan and pyrrole. i. **Reduction :**

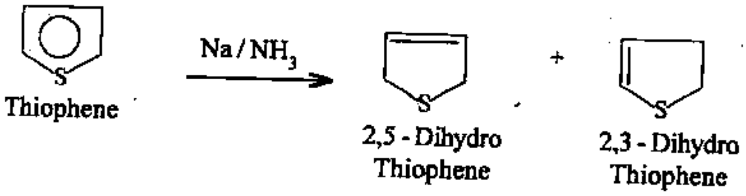
When reduced in presence of Pd with H., it gives tetrahydrothiophene.



ii. When reduced with Ni it forms n - butane.

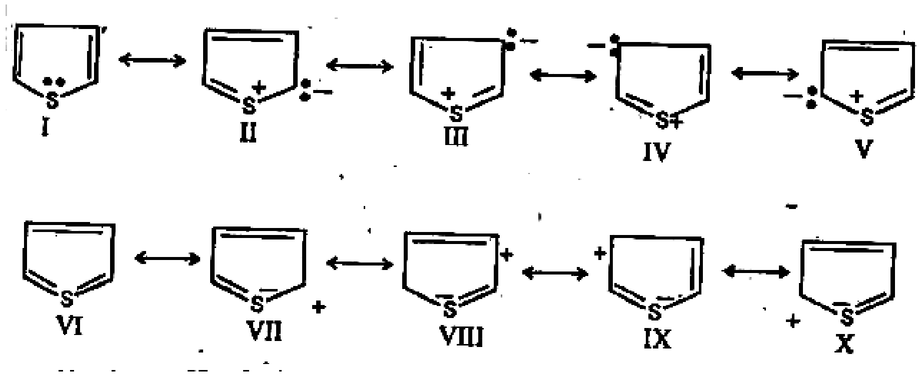


iii. When reduced with Na/NH_3 it give dihydro thiophenes.



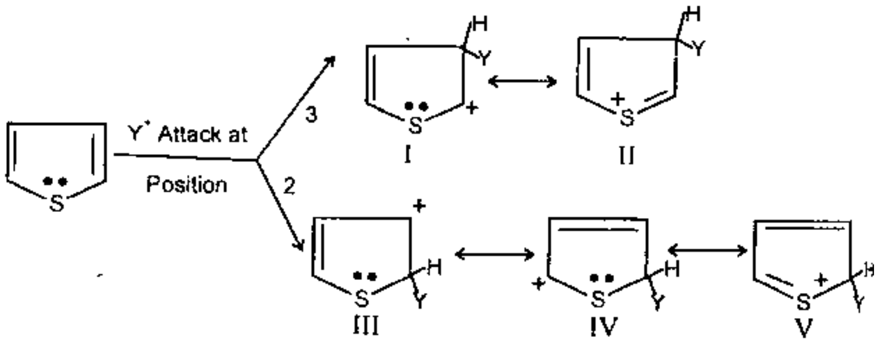
1. Electrophilic substitution:

Thiophene is a reasonance hybrid of the following ten resonating structures.



If obeys Huckel's rule and contains (4n+2)n electron (here n = number of rings = 1). The molecule is planar. Therefore it is an aromatic compound. Sulphur atom is less electronegative than oxygen or nitrogen atoms. Further it can use its vacant '3d' orbitals. Therefore there are 10 canonical forms (I to X) when compared to 5 canonical forms in furan or pyrrole. Therefore thiophene is comparatively more stable than furan or pyrrole. Structures I to V are got when sulphur use its p - orbitals. Structures VI to X result when sulphur uses its '3d' orbitals also.

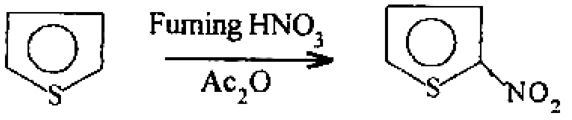
It has a larger electron density at position 2 or 5 than at 3 or 4. Therefore electrophilic substitution is expected to take place in position2 or 5. In practice 2 - substitution is favoured.



It is because attachment of the electrophilic reagent at position 2 results in the formation of a more stable carbonium ion, which is the resonance hybrid of the three structures III, IV and V. On the other hand, the attachment of the electrophilic reagent at, position 3 results in the formation of a less stable carbonium ion which is the resonance hybrid of only two structures I and II.

a) Nitration:

When thiophene is nitrated with fuming nitric acid in acetic anhydride it gives 2 – nitro thiophene.



Thiophene 2 - Nitrothiophene

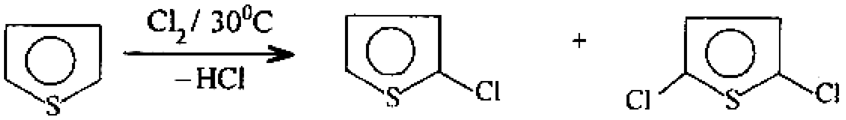
b) Sulphonation:

With cold concentrated sulphuric acid it gives thiophene - 2 - sulphonic acid.

Thiophene Thiophene 2 - Sulphonic acid

c) Halogenation:

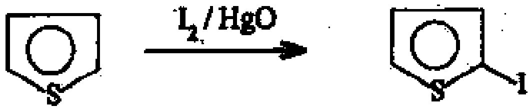
When thiophene is treated with chlorine at 373 K, we get 2- chlorothiophene.



2 - Chlorothiophene 2, 5 - Dichlorothiophene

With N-Bromosuccinimide (NBS) it gives 2 - bromothiophene.

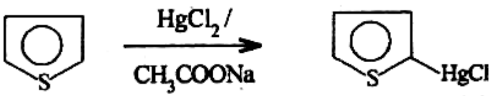
Thiophene **2 - Bromothiophene**



Thiophene **2 - Iodothiophene**

d) Mercuration:

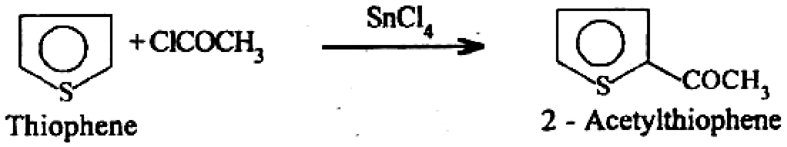
When thiophene is treated with HgCl2 in presence of sodium acetate, we get 2 - Chloromercuri thiophene.



Thiophene 2 - Chloromercuri thiophene

e) Friedel - Craft's reaction

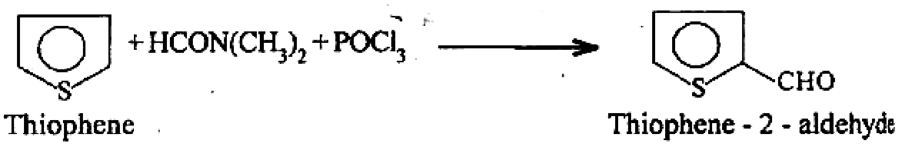
Thiophene may be acetylated with acetic anhydride in presence of phosphoric acid or with acetyl chloride in presence of stannic chloride to yield 2 - acetylthiophene.



f) Chloromethylation and formylation :

Thiophene reacts with formaldehyde and hydrochloric acid to give 2 - chloro methyl thiophene.

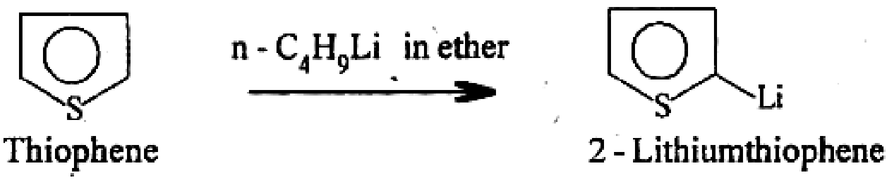
Thiophene reacts with dimethyl formamide and POC1$_3$ to give Thiophene - 2 - aldehyde.



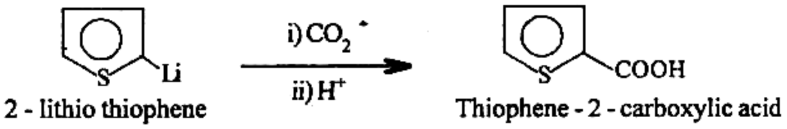
g) Thiophene - Not a thioether:

It does not behave as a thioether. That is, it does not give sulphonium salts. It cannot be oxidised to sulphoxide or sulphone (Tetrahydrothiophene can form). This shows that thiophene is aromatic.

h) Formationof lithium derivative :



This 2 - Lithiumthiophene is useful in the synthesis of various 2 - substituted thiophenes.

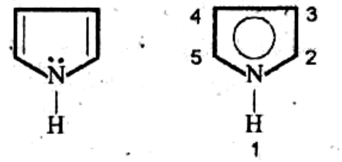


i) Indophenin reaction :

When thiophene is treated with isatin and sulphuric acid a blue colour is formed. This test is used to find out the presence of thiophene in benzene.

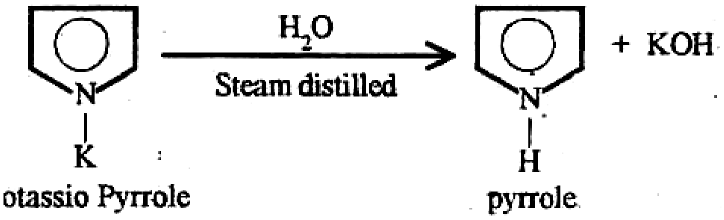
1. CHEMISTRY OF PYRROLE, (C_4H_5N)

Molecular formula : C4H5N. It is a five membered ring compound containing a nitrogen atom. The positions of side chains or substituents are indicated as follows.



Isolation from bone oil:

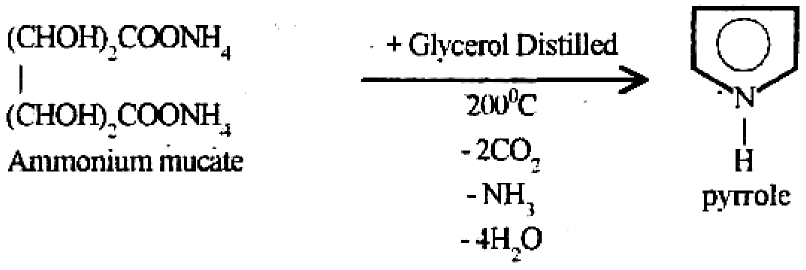
Bone oil is first washed with dilute alkali to remove acidic impurities and then with acid to remove basic impurities like pyridine. The liquid is then fractionated. Pyrrole distils over in the fraction boiling between 373K and 423K. This may be purified by fusing with potassium hydroxide. Solid potassio pyrrole is formed. This on steam distillation gives pure pyrrole.



Preparation :

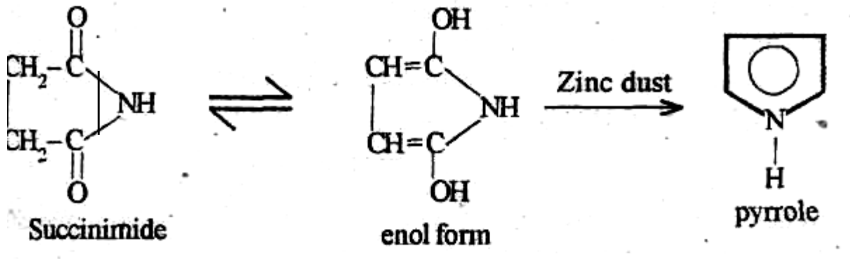
1. Manufacture from Pyrrole:

By distilling a mixture of ammonium mucate and glycerol at 470K.

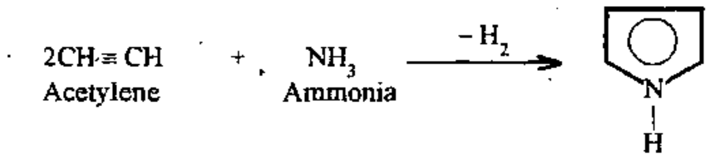


ii. Convenient preparation:

Succinimide undergoes Keto - Enol tautomerism and enol form undergoes reaction in presence of zinc dust to give pyrrole as the product.

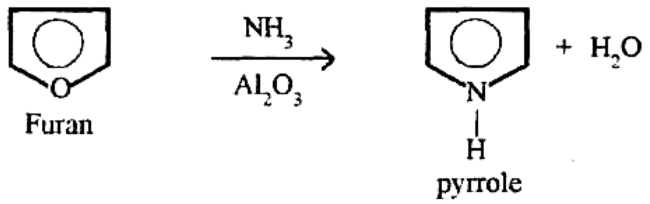


iii. Acetylene reacts with Ammonia to give pyrrole.



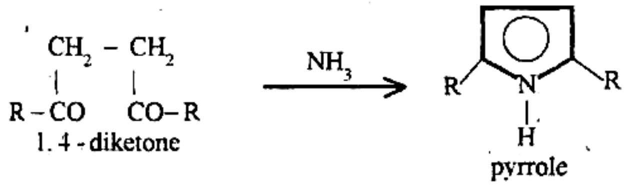
iv. Manufact

A mixture of furan ammonia and steam are passed over heated alumina catalyst. Pyrrole is got.



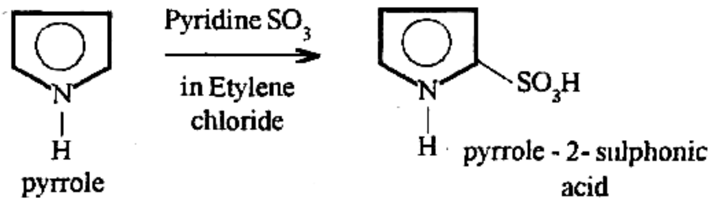
v. By Paal Knorr synthesis:

1,4- diketone is heated with ammonia. We get pyrrole



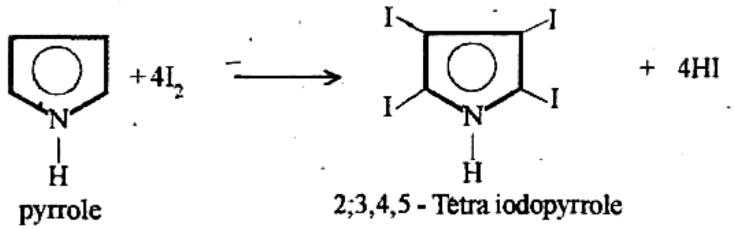
Properties :

1. It is a colourless liquid. It is sparingly soluble in water but readily soluble in alcohol and ether. Vapours of pyrrole turn a pine splint moistened with hydrocholoric acid red (Test - Distinction from Furan).



2. Halogenation :

On halogenation we get 2,3,4,5-tetra halogenopyrrole E.g., With iodine solution it gives 2,3,4,5-tetraiodopyrrole.

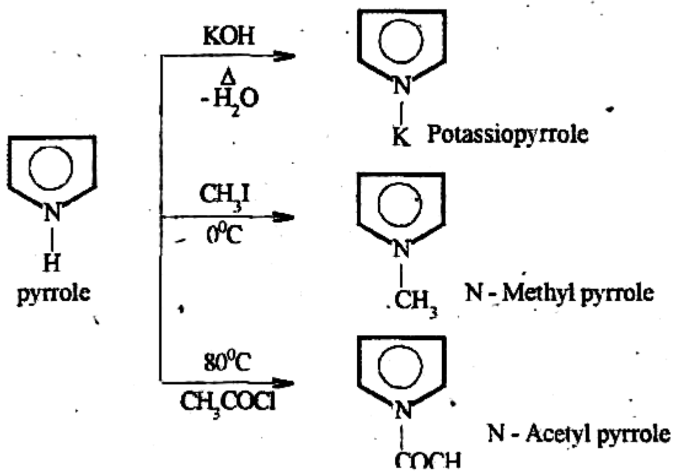


3. Basic nature :

Nitrogen atom in pyrrole contributes its lone pair of electrons to form aromatic sextet of electrons. Therefore the availability of the lone pair of electrons of the nitrogen atom for protonation is very much decreased. So it behaves as a weak base.

Because of above reason pyrrole is less basic than aniline. Also it is less basic than pyrrolidine. In this case also the lone pair on nitrogen in pyrrolidine is not involved in the formation of aromatic sextet of electrons in the molecule as pyrrole

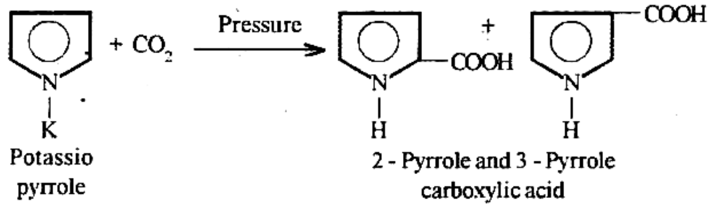
4. Displacement of Imino hydrogen



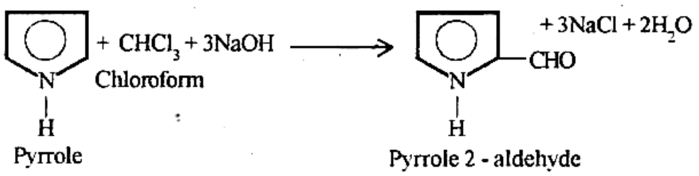
In these reactions it behaves as a weak acid because of the presence of a replaceable hydrogen.

[Methylation and acetylation at higher temperature give 2 or 3 substituted products instead of N - substituted compounds. This may be due to the rearrangement of the N - substituted compound which is formed first].

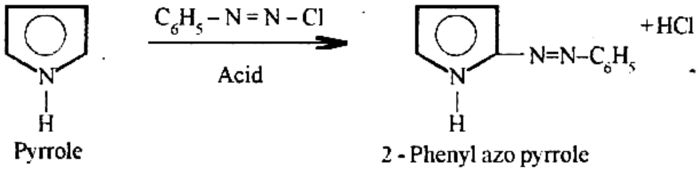
5. Reactions in which pyrrole resembles phenol a) Kolbe's reaction



b) Reimer-Tieman reaction

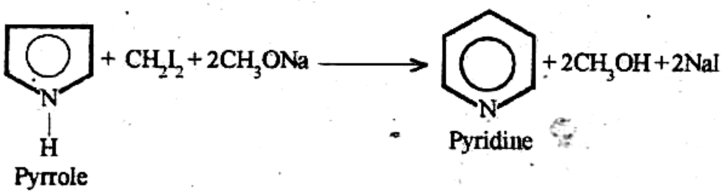


c) Coupling reaction:



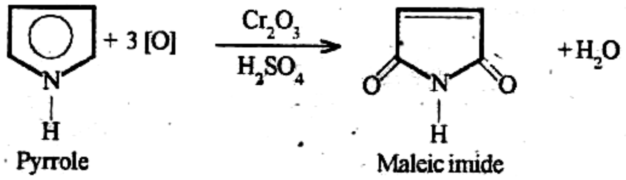
6. Ring expanding reaction:

When it is heated with methylene iodide in the presence of sodium methoxide, pyrrole ring (5-membered) expands giving pyridine (6 - membered).



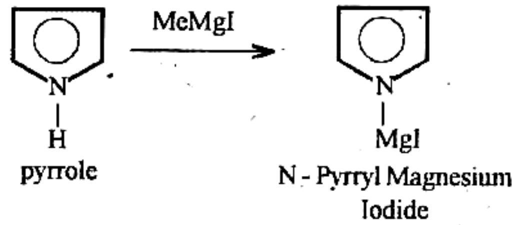
7. Oxidation :

Pyrrole is oxidised by chromic acid to give maleic imide.

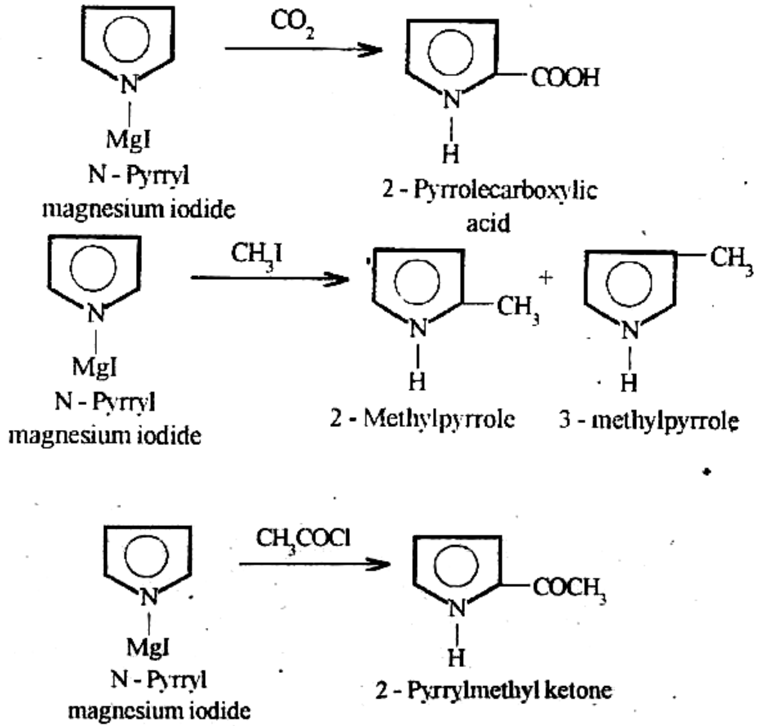


8. Reaction with Grignard reagent :

Pyrrole react with Grignard reagent to give N - Pyrryl Magnesium Iodide.

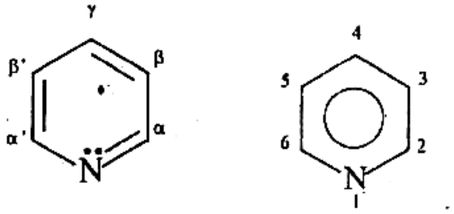


I behaves as if the MgI group is substituted in position 2 becasue it gives 2 substituted pyrroles.



CHEMISTRY OF PYRIDINE, (C_5H_5N)

Molecular formula : C5H5N. It is a six membered ring compound containing a nitrogen atom. The position of side chains or substituents are indicated as follows :



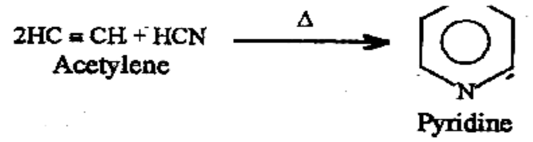
Isolation from coal tar:

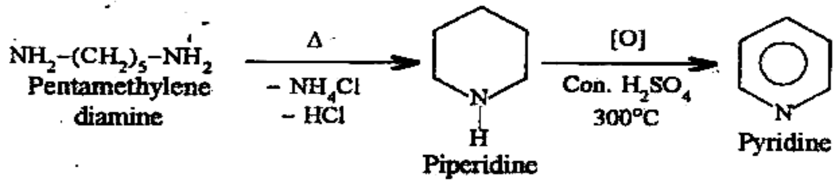
Coal-tar is fractionally distilled. The fraction collected up to 440K is called light oil fraction. It is treated with dilute H_2SO_4, pyridine and other basic compounds dissolve. The acid layer is separated and neutralised with NaOH. Pyridine and other bases are set free. From them, pyridine is separated by fractional distillation.

Preparation :

1. **From acetylene (Synthesis) :**

Acetylene and HCN are passed through a red hot tube, we get pyridine.





2. *Hantzsch synthesis :*

This is a method to prepare pyridine derivatives.

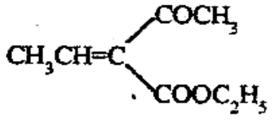
$$\text{2 molecules } \beta-\text{dicarbonyl compound + 1 molecule aldehyde + Ammonia} \xrightarrow{\text{condensation}} \text{Dihydro pyridine derivative} \xrightarrow[\text{[O]}]{HNO_3} \text{Pyridine derivative}$$

Examples

i. $CH_3COCH_2COOC_2H_5 \xrightarrow{NH_3} CH_3C(NH_2)=CHCOOC_2H_5$

Ethyl aceto acetate I

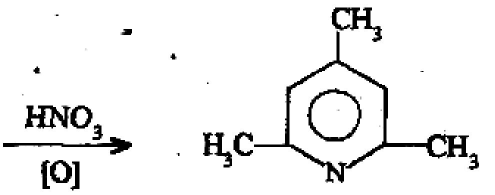
ii. $CH_3COCH_2COOC_2H_5 + CH_3CHO + NH_3 \longrightarrow$



$$CH_3CH=C\begin{matrix} COCH_3 \\ COOC_2H_5 \end{matrix}$$

II

iii. I + II ⟶ Dihydrophyridine derivative



2, 3, 5 - trimethyl pyridine

Properties :

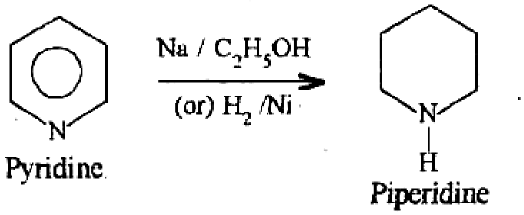
- i Pyridine is a colourless liquid.
- ii. The boiling point in 115°C
- iii. It possesses irritating smell.
- iv. It is miscible with water in all proportions and is hygroscopic.
- v. Pyridine is basic in nature.
- vi. Resembles benzene in many of its properties.

Reactions :

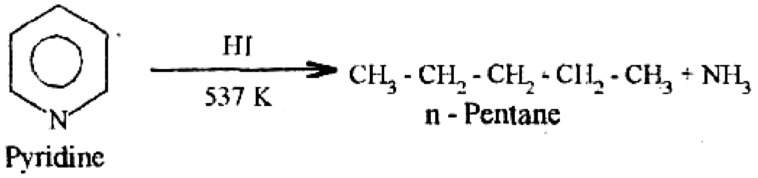
Pyridine shows the reactions of aromatic compounds. It is less reactive than benzene.

1. Reduction:

i Pyridine it is catalytically reduced with Ni and H2 or reduced with sodium and alcohol we get piperidine.

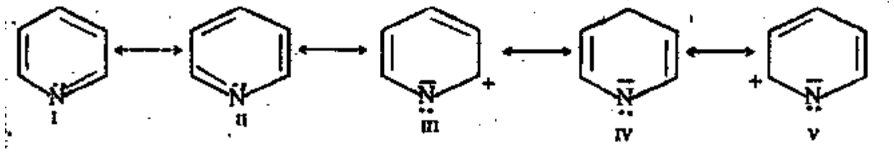


ii. Pyridine it is reduced with HI at 573 K the ring opening takes place. We get n - pentane and ammonia.



2. Electrophilic substitution :

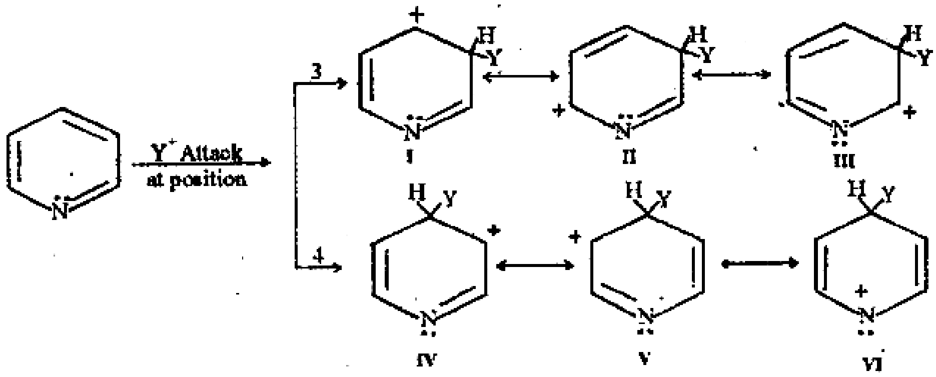
Pyridine is a reasonance hybrid of the following five resonating structures (1 to V)



In all these structures the lone pair on nitrogen atom is free to unite with a proton. Hence it is more basic than pyrrole.

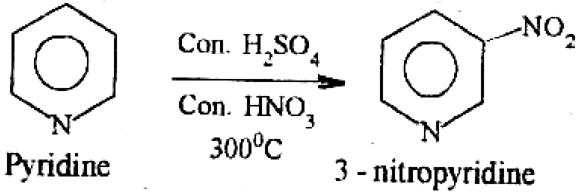
Pyridine obeys Huckel's rule and contains (4n+2)π electrons (here, n = number of rings =1). The molecule is planar. Therefore it is an aromatic compound. It is more aromatic than benzene.

It gives electrophilic substitution reaction. It resembles a highly deactivated benzene derivative. It undergoes nitration, sulphonation and halogenation only under very vigorous conditions and does not undergo Friedel - Crafts reaction. In practice substitution at 3 or (3 position is favoured. It is because an attack at position 3 yields a carbonium ion which is a resonance hybrid of structures I, II and III. On the other hand the attachment of the electrophilic reagent at position 4 yields carbonium ion which is a resonance hybrid of structures IV, V and VI. We find that an attack at position 3 yields a carbonium ion which is a resonance hybrid of three stable structures. Attack at position 4 yields a carbonium ion which is a resonance hybrid of only two stable structures since structure VI is unstable because in it, the electronegative nitrogen has only a sextet of electrons. Therefore substitution takes place at position - 3. Attack at position 2 resembles the attack at position 4.



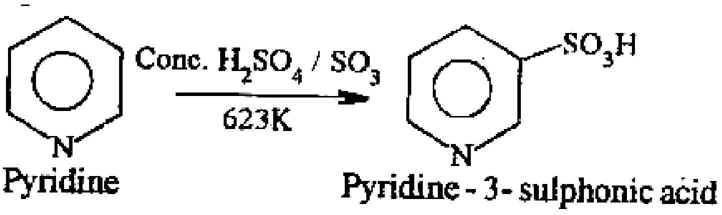
Structures I to VI are less stable than the corresponding ones for attack on benzene because of the electron withdrawing nature of the nitrogen atom, therefore substitution in pyridine is slower than in benzene. a) Nitration: ‘ <-

When pyridine is nitrated with fuming HNO3 we get 3 – nitro pyridine.



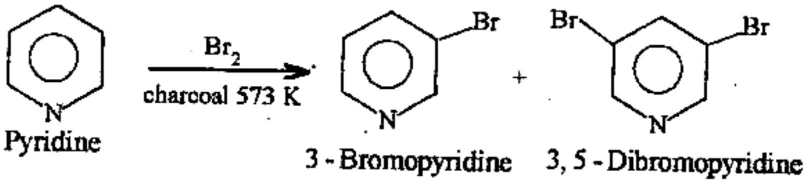
b) Sulphonation:

When pyridine is sulphonated with H2SO4 or SO3 at 623K we get pyridine-3-sulphonic acid.



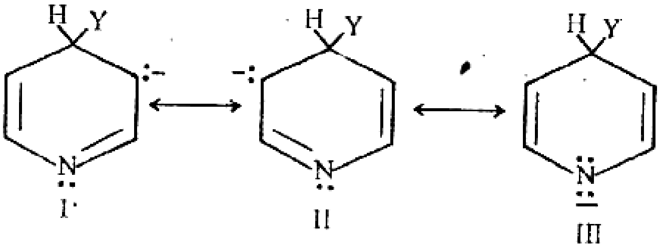
c) Halogenation:

Pyridine and bromine vapours are passed over charcoal catalyst at 573K. We get a mixture of 3-bromopyridine and 3,5-dibromopyridine.

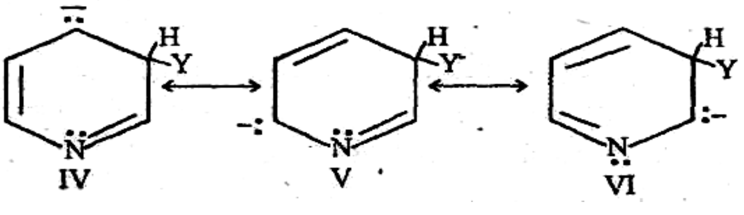


3. Nucleophilic substitution reactions:

Pyridine ring resembles a benzene ring containing strong electron withdrawing groups. So positions 2 and 4 become slightly electron deficient. Thus nucleophilic substitution takes place at 2 and 4 positions. Nucleophilic attack at position 4 yields a carbanion which is a resonance hybrid of structure I, II and III.



Attack at position 2 is similar to attack at position 4. On the other hand attack at position 3 yields a carbanion which is a resonance hybrid of structures IV, V and VI.



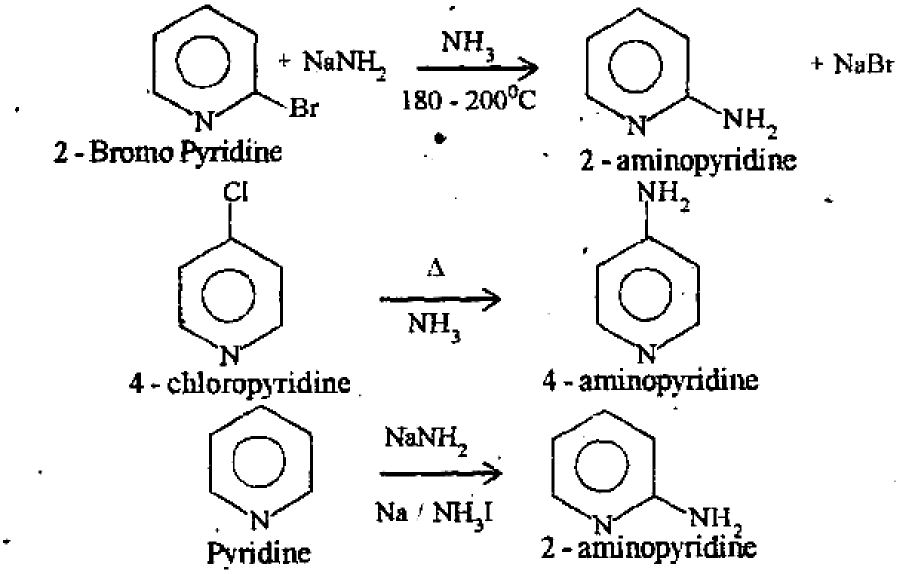
All the above structures are more stable than the corresponding benzene derivatives because of the electron withdrawing nature of nitrogen atom. Ill is especially stable because the negative charge is on nitrogen atom which is more electronegative than carbon atom. Therefore nucleophilic substitution occurs more rapidly at positions 2 and 4 than that at position 3.

The stability of these structures accounts for the nucleophilic substitution being more rapid in pyridine ring than in the benzene ring.

Thus the electron withdrawing nature of nitrogen makes pyridine unreactive towards electrophilic substitution and highly reactive towards nucleophilic substitution.

a. Animation (Chichibdin Reaction) :

Halogen substituted and unsubstituted pyridine when heated with ammonia gives the following products.



This reaction is known as **Chichibain reaction.**

4. Basic nature:

It is a strong base because it contains a tertiary nitrogen atom with a lone pair of electrons which can accept a proton. It forms salts with inorganic acids.

$$\underset{\text{Pyridine}}{C_5H_5N} + HCl \longrightarrow \underset{\text{Pyridinium chloride}}{[C_5H_5NH]^+Cl^-}$$

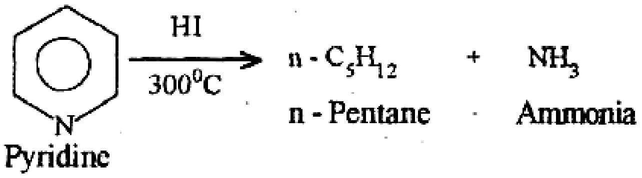
Pyridine is much stronger than pyrrole :

Reason :

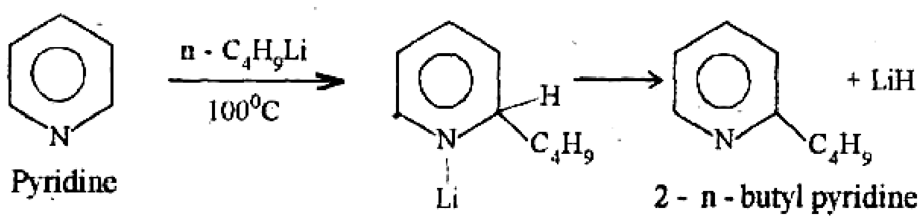
The lone pair of electrons on nitrogen in pyrrole is involved in the aromatic sextet. So it is not available for donation to a proton. In pyridine the lone pair of electrons on nitrogen are not involved in the aromatic sextet. So they are available for donation to a proton. Because of this pyridine is a stronger base than pyrrole.

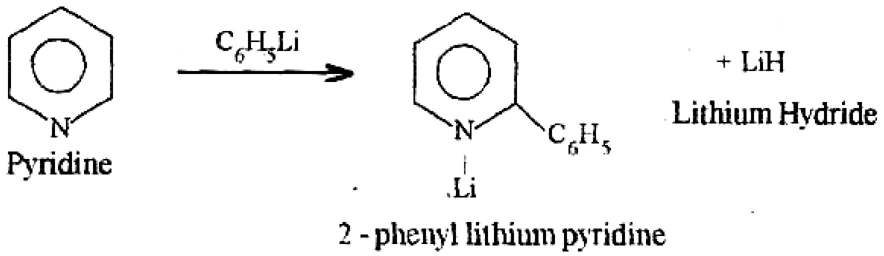
5. Ring cleavage

Pyridine when heated with HI gives n - pentane.



6. Reaction with n- butyl lithium





NOTES

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

UNIT - III

3.1 **Carbohydrates**: Classification, preparation and properties of Glucose and Fructose-discussion of open chain and ring structure of Glucose. Mutarotation. Preparation and properties of Sucrose. Structure (detailed discussion of structure not necessary) Properties of Starch, Cellulose and derivatives of Cellulose. Inter conversion of Glucose to Frutose and vice versa.

3.2. **Amino Acids**-classification, preparation and properties of Glycine. and Alanine. Preparation of peptides (Bergmann method only).

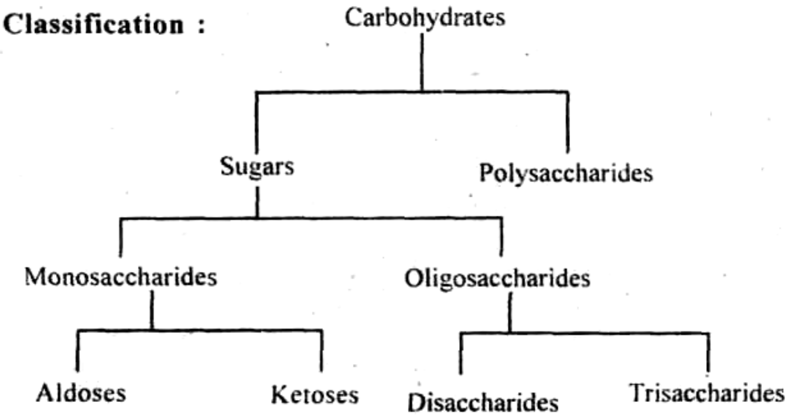
3.3. **Proteins:** classification according to composition, biological function and shape. Denaturation of proteins.

3.4. **Chemotherapy:** Preparation, uses and mode of action of sulpha drugs-prontosil, sulphadiazine and sulphafurazole. Uses of penicillin, chloramphenicol and streptomycin, Definition and one example each for-analgesics, antipyretics, tranquilizers, sedatives, hypnotics, local anaesthetics and general anaesthetics

Carbohydrates

All optically active polyhydroxyaldehydes, all polyhydroxy ketones and all compounds which give the above said two classes of compounds on hydrolysis are called carbohydrates. E.g., Glucose, fructose, maltose, cellobiose, starch, cellulose etc.

Classification :



Carbohydrates are divided into main classes, viz., sugars and polysaccharides. Sugars are crystalline substances. They have sweet taste. They are soluble in water. Polysaccharides are complex in nature. They have high molecular weights. Most of them are-non-crystalline. They are not sweet. They are insoluble in water or less soluble in water than sugars. Sugars are further subdivided into two groups namely mono saccharides and oligosaccharides.

i. **Monosaccharides**:

Sugars which can not be further hydrolysed into smaller molecules are called monosaccharides. Eg. Glucose and fructose.

ii. Oligosaccharides:

Sugars which yield 2 to 9 monosaccharide molecules on hydrolysis are called oligosaccharides. If sugar yields two monosaccharides on hydrolysis it is called a disaccharide. E.g. Sucrose, maltose, etc. If it yields three monosaccharides on hydrolysis it is known as a trisaccharide and so on.

iii. Polysaccharides:

Polysaccharides are carbohydrates which yield a large number of monosaccharide molecules on hydrolysis. E.g., Starch, Cellulose, etc.

Monosaccharides

Monosaccharides are further classified as aldoses and ketoses. If the monosaccharide is a polyhydroxy aldehyde, it is called an aldose. On the other hand, if the monosaccharide is a polyhydroxy ketone, it is called a ketose.

Monosaccharides may contain 4 to 10 carbon atoms Monosaccharides containing 4 carbon atoms are called tetroses. Those containing 5, 6 and 7 carbon atoms are called pentoses, hexoses and heptoses respectively Pentoses and hexoses are the most important.

Glucose (Dextrose)

Glucose is found along with fructose in sweet fruits like grapes, banana and also in honey, beetroot also contains glucose.

Preparation :

1. From cane sugar (Sucrose) (Laboratory method) :

An alcoholic solution of cane sugar is hydrolysed with a 4% solution of hydrochloric acid in alcohol. We get glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Glucoses is insoluable in alcohol. Therefore it crystallises on cooling Fructose is more soluble in alcohol. Therefore it remains in solution.

2. From starch (Manufacture):

Starch is hydrolysed with dilute minerals acid. We set pure glucose.

$$\underset{\text{Strach}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

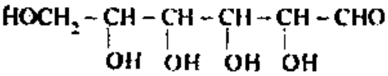
The starch material is mixed with three times its weight of water. Dilutesulphuric acid is added. The mixture is heated under pressure. When thereaction is complete the excess acid is neutralised with calcium carbonate.Calcium sulphate is precipitated. It is filtered off. The filtrate isdecolourised with animal charcoal. It is concentrated in vaacum pans. Glucose monohydrate crystallises out. It is filtered.

Properties :

It is a white crystalline solid. It is sweet. It is optically active. It is dextro rotatory. Therefore it is also called dextrose.

Reactions :

The structural formula of glucose is



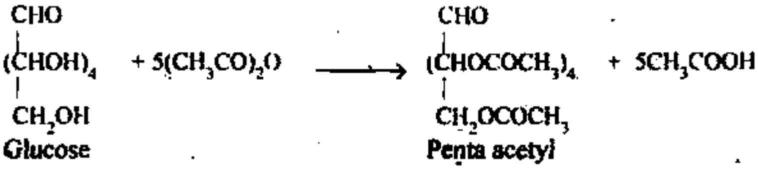
$$HOCH_2-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CHO$$

Therefore it behaves as an aldehyde, a primary alcohol and a secondary alcohol.

a. As an alcohol :

i. Acetylation :

It reacts with acetic anhydride giving a penta acetyl derivative of glucose.



$$\begin{matrix}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix} + 5(CH_3CO)_2O \longrightarrow \begin{matrix}CHO\\|\\(CHOCOCH_3)_4\\|\\CH_2OCOCH_3\end{matrix} + 5CH_3COOH$$

ii. Formation of glucosides:

With methanol in the presence of dry Hydrochloric acid gas it gives two methyl glucosides.

$$C_6H_{11}O_5OH + HOCH_3 \xrightarrow[- H_2O]{\text{dry HCl}} C_6H_{11}O_5OCH_3$$

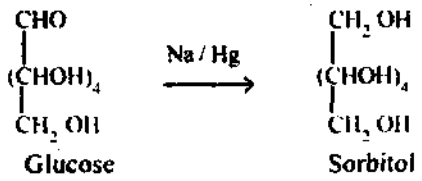
iii. Formation of glucosates :

Glucose reacts with metallic hydroxides giving glucosates. For example, with calcium hydroxide it gives calcium glucosate ($C_6H_{12}O_6CaO$).

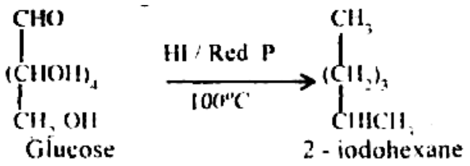
b. As an aldehyde :

i. Reduction :

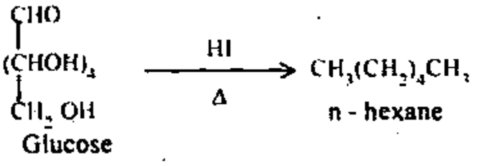
When glucose is reduced with sodium amalgam inaqueous solution, we get sorbitol.



When glucose is reduced with concentrated hydriodic acid and red phosphorous at 100°C we get 2 - iodohexane.

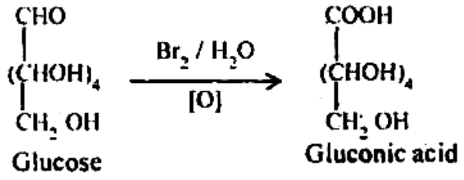


Prolonged heating with concentrated hydriodic acid gives n - hexane.

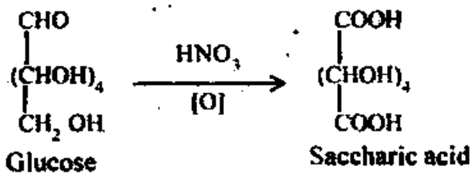


ii. Oxidation:

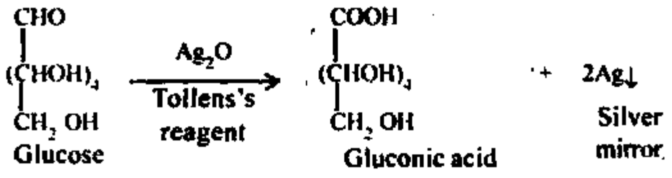
Glucose on treatment with bromine water (mild oxidising agent) is oxidised to gluconic acid. The bromine water is decolourised.



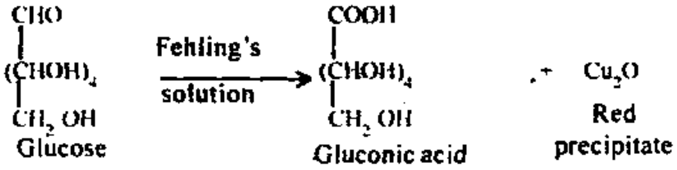
When glucose treated with nitric acid (strong oxidising agent) is oxidised to saccharic acid.



It reduces Tollens's reagent (ammoniacal silver nitrate solution) giving silver mirror. It is oxidised to gluconic acid

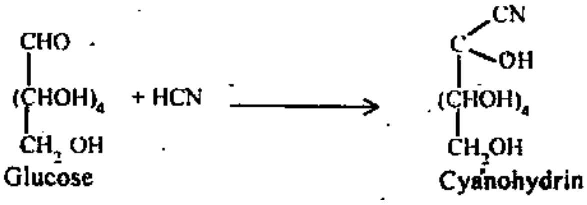


It reduces Fehling's solution giving a red precipitate. It is oxidised to gluconic acid.



iii. Addition reactions :

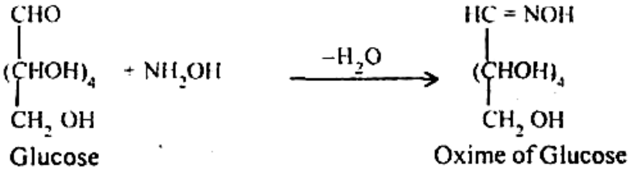
It adds HCN giving the cyanohydrin of the glucose.



It does not add sodium bisulphite and ammonia. This is. because giucose possesses a ring structure. HCN is able to open the ring and react with the aldehydic group whereas sodium bisulphite or ammonia could not open the ring structure and react with the aldehydic group.

iv. Condensation reactions :

It condenses with hydroxylamine giving the oxime of glucose.



Action with phenyl hydrazine :

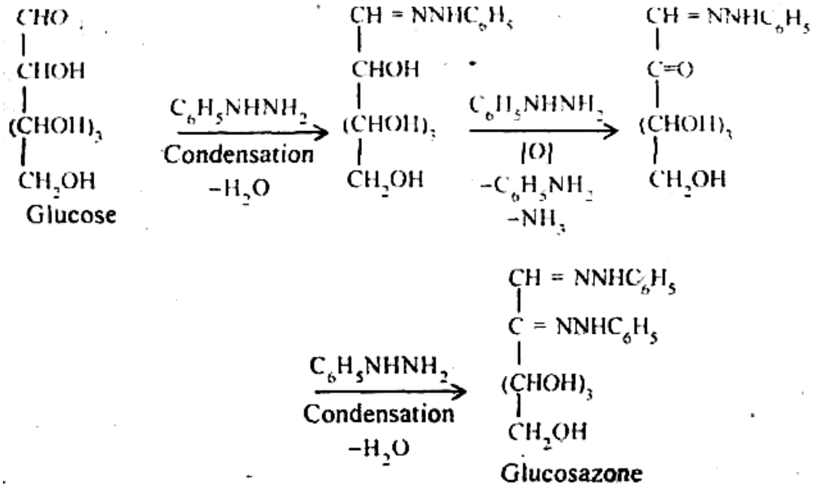
When treated with excess phenyl hydrazine, glucose gives osazone.

Mechanism: (Fischer)

i. One molecule of phenyl hydrazine condenses with the aldehyde group of glucose and forms the corresponding phenyl hydrazone.

ii. When glucose is warmed with excess phenyl hydrzone, a second molecule of the phenyl hydrazine oxidises the secondary alcoholic group on the carbon atom next to the aldehyde group. The corresponding ketone is formed.

iii. Now a third molecule of phenyl hydrazine condenses with this newly producted keto group giving the final product glucosazone.



Limitations of Fischer Mechanism:

i. Phenyl hydrazine is a well known reducing agent. But in this mechanism it is shown to oxidise the phenyl hydrazone of glucose.

ii. The oxidation process stops with the second carbon. The reason is not given.

Importance

1. Osazones are used to characterise the sugares.

2. The fact that both glucose and fructose give the same osazone helpsus to establish that the configurations of fructose with respect to C_3, C_4 and C_5 are the same as in glucose, because osazones formationinvolves C_1 and C_2 only.

c. Some other important reactions :

i. Fermentation*:*

When a solution of glucose is treated with yeast we get ethanol. The enzyme zymase present in yeast converts glucose into ethanol and carbon dioxide.

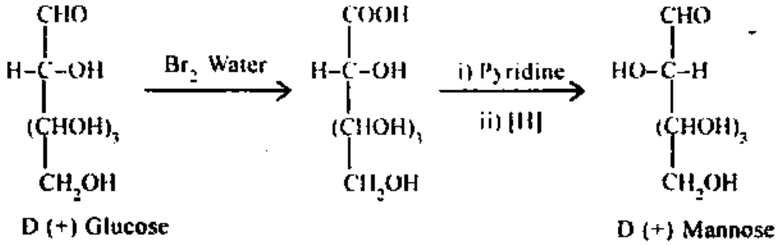
$$C_6H_{12}O_6 \xrightarrow[\text{(Zymase)}]{\text{Yeast}} 2C_2H_5OH + 2CO_2\uparrow$$

ii. With alkalis :.

When glucose is warmed with alkali it becomes yellow, turns brown and finally gives a resinous product.

iii. Epimerisation :

The change of configuration of one asymmetric carbon atom is known as epimerisation. Sugars having identical configurations on all their asymmetric carbon atoms except one carbon atom are known as epimers. E.g.

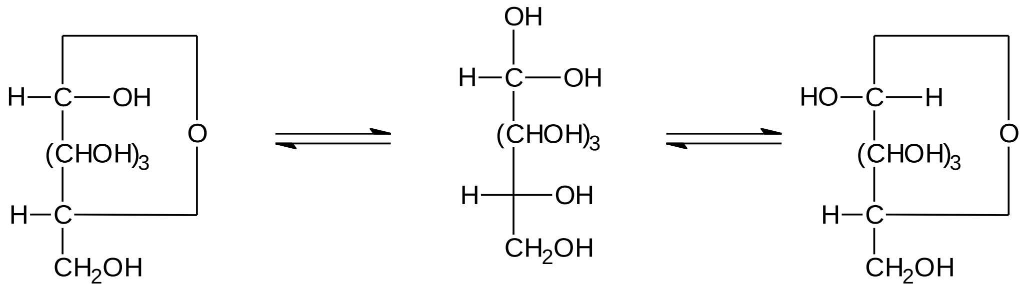


Muta Rotation

When a monosaccharide is dissolved in water, the specific rotation of the solution gradually changes and reaches a constant value. This change in the value of specific rotation is known as mutarotation. All reducing sugars except some ketoses undergo mutarotation. E.g., A solution of glucose has a specific rotation of +111° When it is freshly prepared. On standing the specific rotation decreases slowly and reaches the constant value of +52.5°

Mechanism (Lowry) :

Mutarotation takes place only in the presence of a solvent like water which behaves both as an acid and a base. According to Lowry, in presence of water, the ring structure of glucose opens. Then is recloses either in the original position or in the inverted position via an intermediate product aldehydrol.



α - Glucose Aldehydrol β - Glucose

$[\alpha]_D = +110^0$ $[\alpha]_D = +52.5^0$ $[\alpha]_D = +19.7^0$

Significance :

The fact that glucose shows mutarotation has helped to prove that glucose has cyclic structure and not an open chain structure.

Reason :

Glucose exists in two stereoisomeric forms viz. a and p glucose. Because of this is it shows mutarotation.

The specific rotation of α - glucose is + 110^o and that β - glucose is + 19.7° in aqueous solution, the specific rotation of α - glucose decreases slowly from +110° to +52.5° but the specific rotation of β - glucose increases from+ 19.7° to+52.5°. This shows that the following equilibrium is existing in solutions.

Uses of glucose :

1. If is used a sweetening agent in confectionery
2. It used in the preparation of vinegar.
3. It is used in silvering of mirrors.
4. It is used to reduce Indigo blue to Indigo white.
5. It is used a food for infants and invalids.
6. It is used for the preparation of vitamin - B, Vitamin - C and ethyl alcohol.

Tests:

- i. It reduces Fehling's solution and gives a red precipitate.
- ii. It reduces Tollen's reagent and forms a silver mirror.
- iii. It gives a yellow precipitate of glucosazone with excess phenyl hydrazine.
- iv. It gives violet colour with an alcoholic solution of α - Napthol and concentrated sulphuric acid. This test is known as Molische's test. This is answered by all carbohydrates.

Structure Elucidation of Glucose

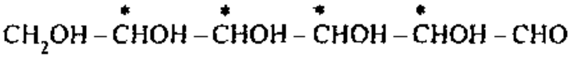
A. Open chain structure for glucose :

1. Molecular formula $C_6H_{12}O_6$.
2. a. On treatment with acetic anhydride it gives a penta acetyl derivative. Therefore it contains five 'OH' groups.

b. It is not easily dehydrated. Therefore each hydroxy group must be linked to different carbon atoms.

3. It forms a cyanohydrin with HCN and an oxime with hydroxyl amine. This shows the presence of a carbonyl group in glucose.
4. Glucose decolourises bromine water. It is oxidised to gluconic acid. Glucose and gluconic acid have the same number of carbon atoms. Therefore the carbonyl group present is an aldehydic group. Aldehyde group is monovalent. Therefore it must be present at one end of the molecule.
5. When glucose is reduced with concentrated hydriodic acid and red phosphorus at 100°C we get a mixture of 2-iodohexane and hexane. Thus all the six carbon atoms in glucose are in a straight chain.

From the above evidences Baeyer suggested an open chain structural formula for glucose.



$$CH_2OH-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-CHO$$

There are four asymmetric carbon atoms. Hence it must have $2^4 = 16$ optically active forms. All of them are known.

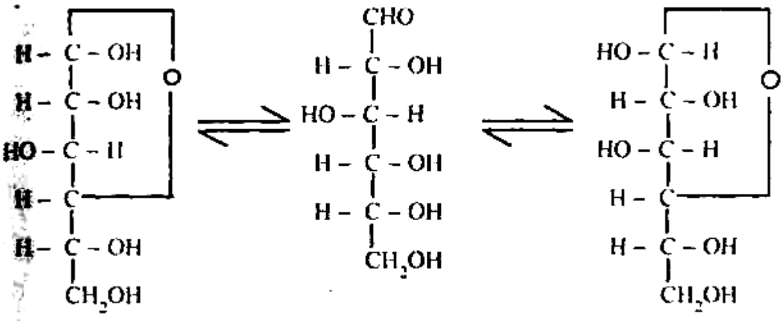
B. Cyclic structure for glucose:

The open chain structure of glucose does not explain the following reactions of glucose.

1. It does not add sodium bisulphite and NH_3. This raises a doubt whether the aldehyde group is actually present or not.
2. When glucose is crystallised form an alcoholic solution or from aceticacid solution we get a glucose with specific rotation +110°. But when glucose is crystallised from pyridine solutioin we get a glucose with specific rotation +19.7°. This shows that glucose exists in two stereoisomeric forms.
3. When an aqueous solution of glucese is allowed to stand, its specific rotation slowly decreases from 110° to +52.5°. This is called mutarotation.
4. When glucose is treated with methyl alcohol and dry HCl gas, we get two stereoisomeric methyl glucosides.

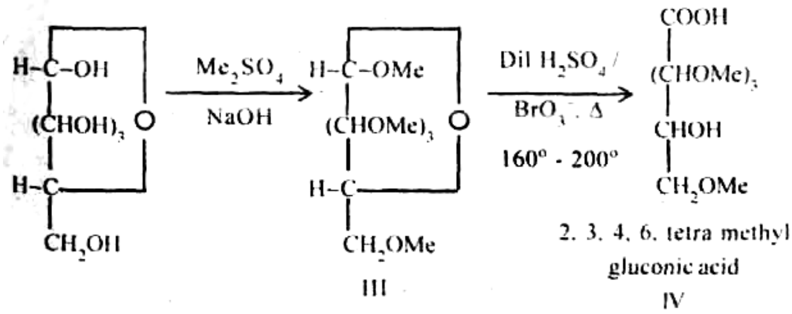
Furanose structure for glucose - Tollens

To account for the above observations the following ring structure have been assigned to glucose. Thus during the formation of the ring a new asymmetric carbon would be produced. This can exist in two configurations, i.e., in two forms. He assumed a five membered ring, i.e., a furanose structure glucose. The two forms of glucose are called α - D (+) glucofuranose (I) and β-D (+) gluco furanose (II).

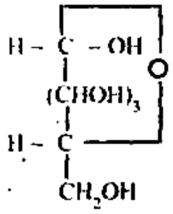


Pyranose structure for glucose (Haworth)

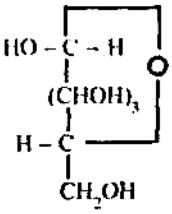
Haworth proposed a pyranose structure for glucose, i.e., six membered ring strucutre. This is shown by the following methylation studies. When glucose is heated with dimethyl sulphate in the presence of dilute sodium hydroxide solution it forms a penta methyl derivative (III). This is heated with bromite solution in presence of dilute sulphuric acid. We get 2, 3, 4, 6 tetra methyl gluconic acid (IV). This proves that the C_1 and C_5 are involved in the ring structure in glucose. In other words the ring in glucose is a pyranose ring. With carbon atoms C_1 to C_5. and one oxygen atom.



It is clear that 'OMe' on C_1 in HI has been hydrolysed and then oxidised. This reaction provides an evidence for the presence of a pyranose ring structure in glucose. Thus IV and V represent the pyranose ring structures for α - and β - glucose respectively.



α - Glucose
(α- D (+) - Glucopyranose)
IV



β - Glucose
(β- D(+) - Glucopyranose)
V

Fructose (Laevulose)

Fructose occurs in the free state along with glucose in most of the sweet fruits and honey. It is also found in inulin.

Preparation :

1. **From cane sugar***:*

A concentrated solution of cane sugar is hydrolysed with dilute hydrochloric acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

When the hydrolysis is over, the solution is treated with lime. Calcium fructosate $\mathbf{C_6H_{12}O_6.CaO}$ is precipitated. Calcium glucosate remains in solution. The precipitate is removed. It is suspended in water. Carbondioxide is passed through the solution. Calcium carbonate is precipitated. It is removed. The solution is concentrated. Fructose crystallises out.

2. From Inulin: (Manufacture) When inulin, a polysaccharide, is hydrolysed with dilute sulphuric acid fructose is got.

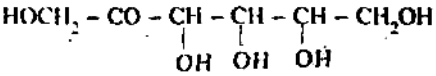
$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

When the hydrolysis is over, the solution is treated with barium carbonate. Barium sulphate is precipitated. It is removed. The solution is concentrated. Fructose crystallises out.

Properties:

1. It is a white crystalline solid.
2. It is sweeter than cane sugar. It is optically active.
3. It is laevo-rotatory. Therefore it is called laevulose.

The structural formula of fructose is



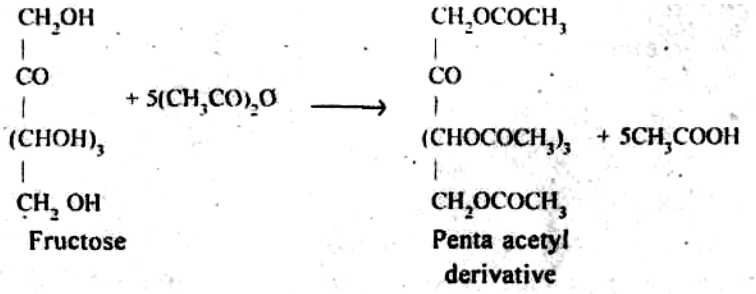
$$HOCH_2-CO-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2OH$$

It is contain a keto group, two primary alcohol and three secondary alcohol groups. Therefore it behaves as a ketone, primary alcohol and a secondary alcohol.

1. As on alcohol:

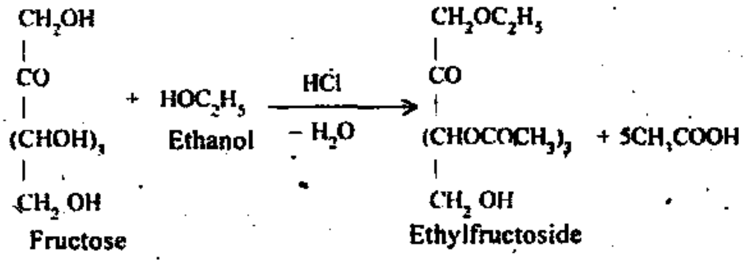
i. Acetylation

It reacts with acetic anhydride giving penta acetyl derivative of fructose.



ii. Formation of fructosides :

With monohydric alcohol in the presence of dry hydrochloric acid gas it gives fructosides.



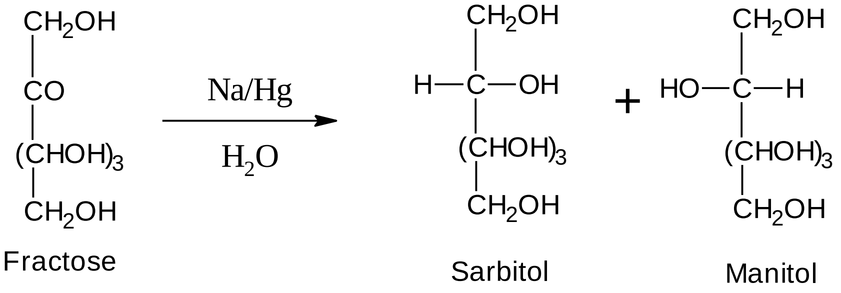
iii. Formation of fructosates:

Fructose reacts with metallic hydroxides giving fructosates. For example with calcium hydroxide it gives calcium fructosate. ($C_6H_{12}O_6CaO$).

b. As a ketone :

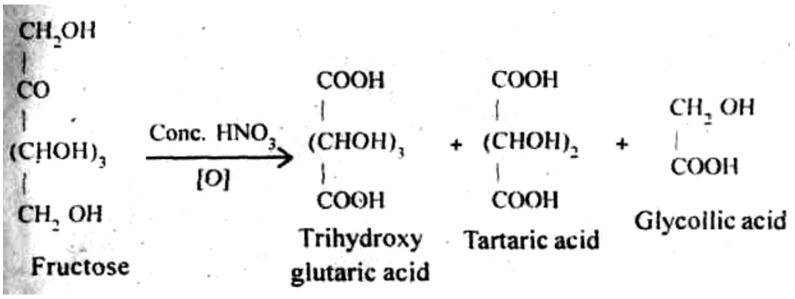
i Reduction:

When fructose is reduced with sodium amalgam in aqueous or alcoholic solution or using catalysts or even electrolytically we get a mixture of sorbitol and mannitol.

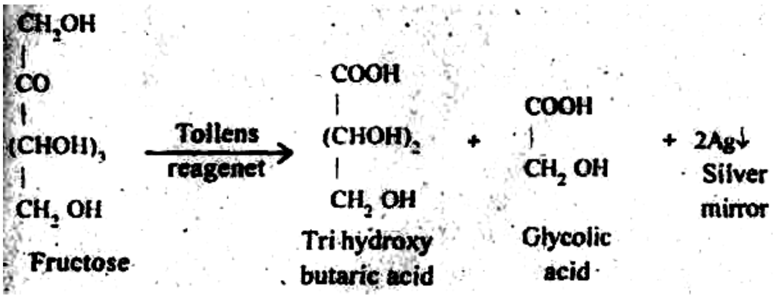


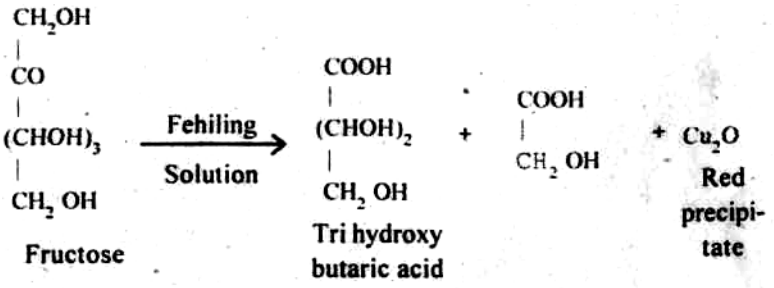
ii. Oxidation : .

It resists oxidation. On strong oxidation with nitric acid fructose gives a mixture of trihydroxy glutaric acid, tartaric acid and glycollic acid.

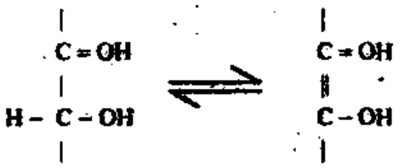


It reduces Tollens reagent and Fehling's solution. It decolourises bromine water readily. This can be explained as follows :



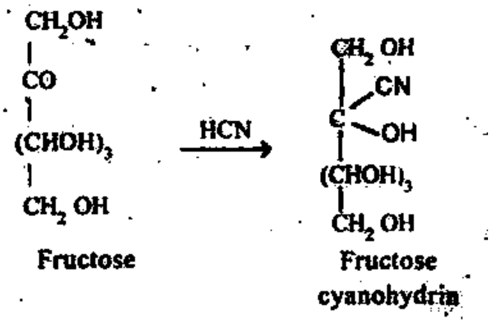


A keto group containing as α - CHOH group undergoes tautomeric change to form an ene - diol. This ene diol can easily get oxidised. This is why fructose shows the above reducing properties.



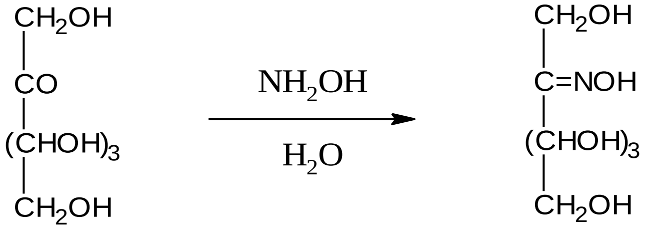
iii. Addition reactions :

It adds HCN giving the cyanohydrin of-the fructose.



iv. Condensation reactions:

It condenses with hydroxylamine giving the oxime of fructose.



$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \xrightarrow[H_2O]{NH_2OH} \begin{array}{c} CH_2OH \\ | \\ C{=}NOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

Fractose

Fractose hydroxy amir

Action with phenyl hydrazine:

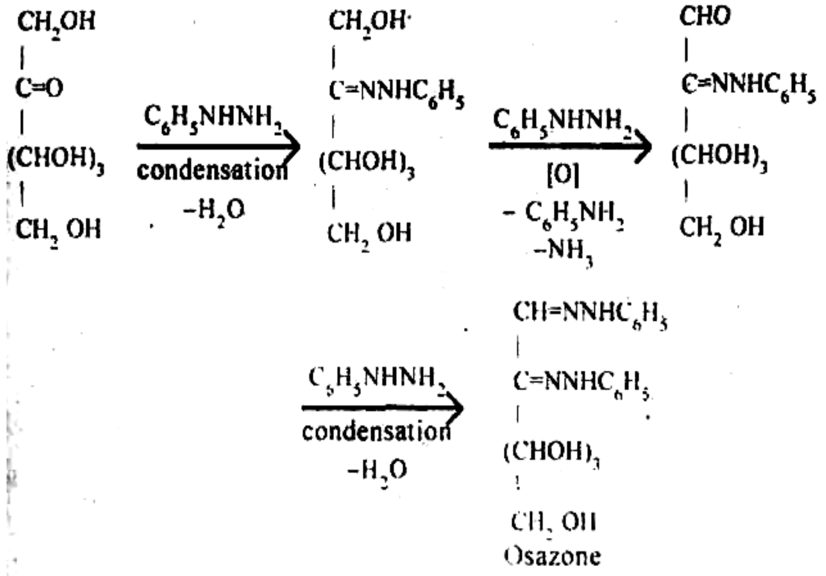
When treated with phenyl hydrazine, fructose gives an osazone. The osazone obtained in this reaction is the same as the one obtained from glucose.

Mechanism (Fischer):

i. One molecule of phenyl hydrazine condenses with the keto group of fructose and forms the corresponding phenyl hydrazine.

ii. When fructose is warmed with excess phenyl hydrazine, a second molecule of the phenyl hydrazine oxidises the adjacent primary alcoholic group into an aldehyde group.

iii. Now a third molecule of phenyl hydrazine condenses with this newly produced aldehyde group giving the final product osazone (same as glucosazone).



Thus both fructose and glucose give the same osazone because

1. In both reactions condensation with phenylhydrazine is followed by oxidation and then another condensation.
2. In both reactions only the first two caFbons are involved.
3. The configuration of C_3,C_4,C_5 and C_6 of both glucose and fructose are the same.

c. Some other important reactions

i Fermentation:

When a solution of fructose is treated with yeast we get ethanol. The enzyme zymase present in yeast converts fructose into ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow[\text{(Zymase)}]{\text{Yeast}} 2C_2H_5OH + 2CO_2\uparrow$$

ii. With alkalis :

When fructose is warmed with dilute alkalis no resin is formed. Instead, it undergose Lobryde Bruyn Van Ekensten rearrangement giving a mixture of glucose, mannose and fructose.

Uses :

It is used as sweetening agent. It is used by diabetic patients as a substitute for cane sugar.

Tests

i Pinoff's test:

A solution of fructose is treated with a solution of ammonium molybdate and a few drops of acetic acid. A blue colour is produced.

ii. Selivanoff's test:

Fructose when treated with a dilute solution of resorcinol in dilute hydrochloric acid, a reddish brown precipitate is formed.

iii. It reduces Fehling's solution and gives a red precipitate.

iv. It reduces Tollens reagent and forms a silver mirror.

v. It gives a yellow precipitate of osazone with excess phenylhydrazine.

vi. Furfural test:

To one ml of fructose solution one ml of 1% alcoholic solution of α-naphthol is added followed by six ml of hydrochloric acid and the mixture is boiled. A violet colour produced.

Comparison between glucose and fructose

Similarities:

i) With phenyl hydrazine both give the same osazone.

ii) Both reduce Tollen's reagent and Fehling's solution,

iii) On fermentation with yeast both give ethanol.

iv) Both are acetylated to give pentacetyl derivatives.

v) Both exhibit mutarotation.

Differences:

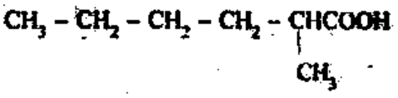
	Reaction	Glucose	Fructose
i.	Optical activity	Dextro-rotatory	Laevo-rotatory
ii.	With concentrated alkali	Resin is formed	No resin is formed
iii.	With lime	Forms glucosate soluble in water	Forms fructosate insoluble in water
iv.	Oxidation with bromine (mild	Oxidised. Gluconic acid is got. Bromine water is	No reaction

Structure Elucidation of Fructose

A. Open chain structure for fructose :

1. Molecular formula $C_6H_{12}O_6$.
2. a. On treatment with acetic anhydride it gives a penta acetyl derivative. Therefore it contains five 'OH' groups.

   b. It is not easily dehydrated. Therefore each hydroxy group must be linked to different carbon atoms.
3. It forms a cyanohydrin with HCN and an oxime with hydroxyl amine. This shows the presence of a carbonyl group in fructose.
4. On treatment with HNO_3 fructose is oxidised to a mixture of trihydroxy glutaric acid, tartaric acid and glycollic acid. All the above acids have fewer number of carbon atom than fructose. Therefore the carbonyl group in fructose is a ketonic group.
5. On treatment with HCN, fructose gives then cyanohydrine when this cyanohydrin is reduced with hydriodic acid we get, 2 - methyl hexanoic acid.

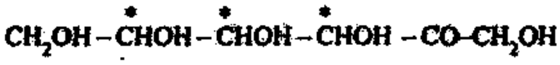


$$CH_3-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$$

This shows that the ketonic group is adjacent to one of the terminal cafbon atoms.

6. Fructose on reduction gives a mixture of sorbital and mannitol. These on reduction with concentrated hydriodic acid and red phosphorus at 100°C we get a mixture of 2-iodohexane and hexane. Thus all the six carbon atoms in glucose are in a straight chain.

From the above evidences Baeyer suggested an open chain structural formula for fructose.



$$CH_2OH-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-CO-CH_2OH$$

There are four asymmetric carbon atoms. Hence it must have $2^3 = 8$ optically active forms. All of them are known.

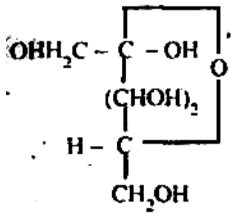
B. Cyclic structure for fructose :

The open chain structure of glucose does not explain the following reactions of fructose.

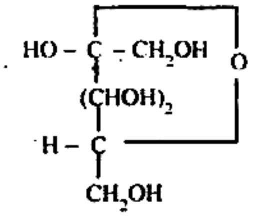
1. It does not add sodium bisulphite and NH_3 This raises a doubt whether the keto group is actually present or not.
2. An aqueous solution of fructose shows mutarotation. This suggests that it exists in two forms.
3. When fructose is treated with methyl alcohol and dry HC1 gas we get two stereoisomeric methyl fructoside.

Furanose structure for Fructose

To account for the above observations the following ring structure have been assigned to fructose.

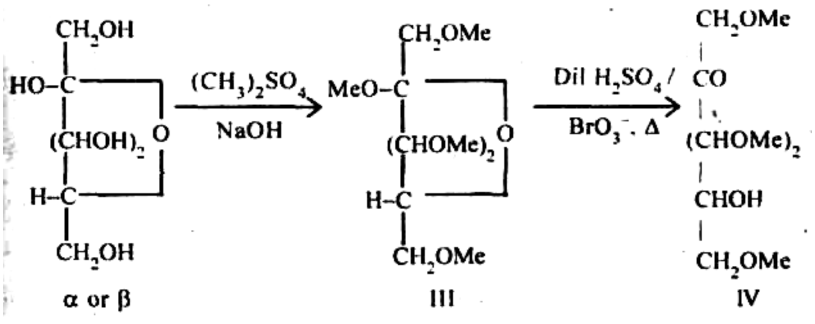


α- D (−) Fructofuranose
I



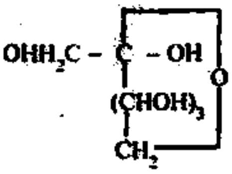
β- D (−) Fructofuranose
II

This structure is confirmed by the following methylation studies. When fructose is heated with dimethyl sulphate, it forms a penta - acetyl derivative (III). When III is heated with bromate solution in presence of dilute sulphuric acid IV is got. The formation of the free -OH group in C_5 indicates the furanose ring.

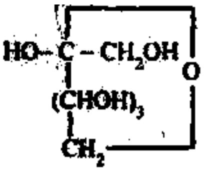


Pyranose structure for fructose

Fructose is assigned pyranose structure also.



α- D (–) Fructopyranose
V



β- D (–) Fructopyranose
VI

Sucrose

Occurrence

Sucrose occurs in sugarcane and beet.

Manufacture from of sucrose Sugar Cane

The sugarcane is cleaned. It is cut into bits. They are crushed in crushers. The juice is extracted. It is subjected to clarification by sulphonation and by carbonation. Clarification is done to avoid fermentation of sucrose into glucose and fructose and for removing unwanted matter. In sulphoxidation, the juice is treated with lime and then with sulphur dioxide. In carbonation, the juice is treated with lime and then with carbondioxide. Precipitates are removed. The clear juice is concentrated in a 'multiple' effect evaporator. The acidity of the solution is carefully maintained at a desired level in order to avoid loss of sucrose by inversion and destruction. The clear syrupy juice thus got is boiled in a vacuum pan. Sugar crystals begin to form. They are centrifuged out. They are dried and bagged.

Properties :

It is a colourless crystalline substance. It is sweet. It is dextrorotatory. It does not show mutarotation

Reactions :

a. Action of heat:

i. When heated with a small quantity of water, it melts and on cooling gives an amorphous glassy mass called barley sugar.

ii. When heated to about 200°C it loses water and gives a brown mass called caramel. Caramel is used in confectionery and colouring wine.

iii When heated to very high temperatures it carbonises to give sugarcharcoal.

b. Hydrolysis (Inversion of cane-sugar):

When warmed with dilute mineral acids it is hydrolysed to glucose and fructose

$$\underset{\substack{\text{Cane-sugar}\\\text{(Sucrose)}}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Cane-sugar has a specific rotation of +66.5°. On hydrolysis it - converted to glucose and fructose. Glucose has a specific rotation of + 52.5° and fructose has a specific rotation of -92°. Thus during hyrolysis the specific rotation, changes from a +ve value to a - ve value. This change, of dextro-rotatory sucrose into laevorotatory mixture of glucose and fructose is called **inversion of cane-sugar.**

c Oxidation:

When treated with concentrated nitric acid it is oxidised to oxalrc acid.

$$C_{12}H_{22}O_{11} + 18[O] \longrightarrow \underset{\text{oxalic acid}}{6(COOH)_2} + 5H_2O$$

d. Dehydration:

When treated with concentrated sulphuric acid, it is dehydrated giving sugar charcoal. This is called charring of sugar. A smell of sulphur dioxide is noticed due to reduction of sulphuric acid.

$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow \underset{\text{Sugar charcoal}}{12C} + [11H_2O + H_2SO_4]$$

$$C + 2H_2SO_4 \longrightarrow 2SO_2 + CO_2 + 2H_2O$$

e. Fermentation:

When a solution of sucrose is fermented with yeast we get ethanol. The enzyme invertase is the yeast converts sucrose into a mixture of glucose and fructose. The enzyme zymase present in yeast converts glucose and fructose into ethanol and carbon dioxide.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(yeast)}]{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\substack{\text{glucose}\\\text{or}\\\text{fructose}}}{C_6H_{12}O_6} \xrightarrow[\text{(yeast)}]{\text{Zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

f. Formation of sucrosates :

Sucrose reacts with metallic hydroxides giving sucrosates. For example with calcium hydroxide it gives calcium sucrosate ($C_{12}H_{22}O_{11}3CaO$)

g. Acetylation:

It reacts with acetic anhydride giving an octaacetyl derivative.

It does not reduce Tollen’s reagent of Fehling's solution. It does not, give resins with sodium hydroxide. It does not give any osazone with phenyl hydrazine. It does not exhibit mutarotation.

Uses

It is used

i. as an article of food.

ii. as a sweetening agent in sweet and drinks

iii. to preserve fruits.

iv. for the preparation of oxalic acid in the laboratory.

Tests :

i. When heated in a dry test tube the small of burnt sugar which is a characteristic smell, is noticed.

ii. On heating with conentrated sulphuric acid charring takes place. Smell of sulphurdioxide is noticed.

iii. It answers Molische's test,

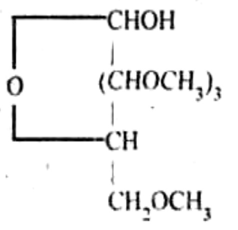
iv. It answers Salivanoff's test,

v. It answer furfural test.

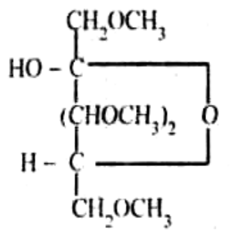
Structure:

1. Molecular formula $C_{12}H_{22}O_{11}$
2. On hydrolysis it gives a mixture of glucose and fructose. It shows that a molecule of glucose and a molecule of fructose, are linked through an oxygen atom in sucrose.
3. Sucrose is not a reducing sugar i.e., this does not reduce Tollen's reagent of Fehling's solution. This shows that the aldehyde group of glucose is absent in sucrose. That is why sucrose is a non - reducing sugar whereas glucose is a reducing sugar: Further it does not form an oxime or osazone. This shows that the ketonic group of fructose also is not present in sucrose. Sucrose does not undergo mutarotation. This also proves that neither the aldehyde group of glucose nor the ketonic group of fructose is free sucrose. Therefore both the monosaccharides must be linked through their respective reducing groups in sucrose.

4. On treatment with acetic anhydride it gives an octa - acetyl, derivative. It shows the presence of eight hydroxyl groups in sucrose.
5. On complete methylation it gives an octamethyl derivative this on hydrolysis gives 2,3,4,6 - tetramethyl δ - glucose (I) and 1,3, 4, 6 - tetramethyl γ - fructose (II).



I



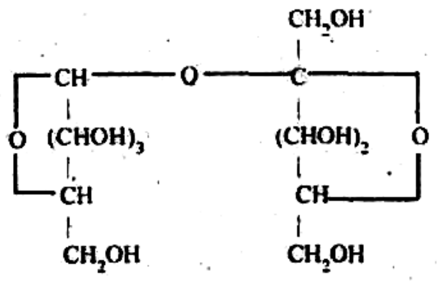
II

The above fact shows that C_5 in I and II have no -OH groups on them. This suggests that they must be involved in some ring formation in their molecules.

6. C_1 in 1 and C_2 in II have free hydroxyl groups on them. This suggests that the two parts are linked in sucrose through these carbon atoms only. This conclusion is supported by the fact that sucrose is a non reducing sugar.
7. Maltase hydrolyses sucrose. Therefore one reducing part of sucrose is a in character.
8. Kinetics of hydrolysis and optical rotation of sucrose have shown that glucose part is α - in character and fructose part is β – in character.

Therefore surcose is 1 - α - D - glucopyranosyl, 2 - β - D - fructose furanoside.

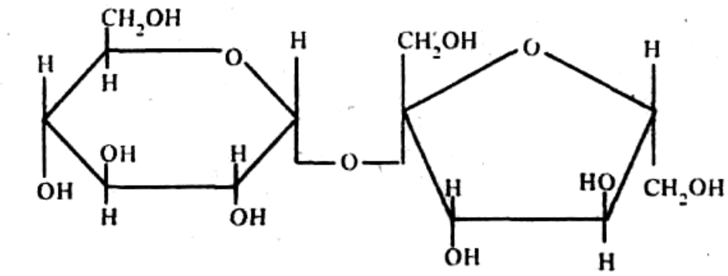
Plane diagram of sucrose



Sucrose

Polysaccharides

1. Starch



1 - α - D - Glucopyranosyl 2 - β - D - Fructofuranoside

It is a polysaccharide. It consists of a large number of molecules of glucose. It occurs in green plants. Maize, wheat, barley, rice, potato are some of the sources of starch.

Starch is a poiysaccharide the molecular formula is $(C_6H_{10}O_5)_{11}$. It occurs in rice, potatoes, wheat, maing barlly etc. Starch consists of two components namely amylose and amylopectin.

Amylose:

Starch consists of about 10 - 20 % of amylose. It is soluble in water. It gives blue colour with iodine. It consists of several glucose units in the form of linear chains. The glucose units are joined together with each other by a - glucosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit. The molecular weight of amylose ranges from 10,000 to 50,000 a single chain of amylose may contain about 60 to 300 D - glucose units. There is no cross link between the amylose chains.

Amylopectin :

Starch consists of about 80 - 90% amylopectin. Its molecular weight is very high. It is sparingly soluble in water. It consists of several glucose units linked together by a - glucoside linkage in the form of chains. There is cross link between the chains and has branched structure. Each chain consists of about 300 to 600 D - glucose units and the molecular, weight ranges from 50,000 to 1,000,000.

Occurrence:

It occurs in all green plants. Commercial sources of starch are maize, wheat, barley, rice, potato are some of the sources of starch.

Manufacture:

The starch material from which starch is to be manufactured is washed with water. It is disintegrated, mechanically. A paste like mass called pulp is obtained. It contains starch granules. This is contaminated with finely divided fibrous material. The mixture is washed with water and then sieved. The fibrous materials are thus seperated. The filtrate is allowed to stand. The heavier starch granules settle down. The supernatant liquid is decanted. The residue is centrifuged and dried slowly and then packed.

Properties :

Starch is tasteless, odourless, white amorphous powder. It is insoluble in water.

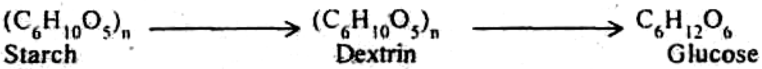
Reactions :

i. Action of heat:

On heating to 200 - 260°C starch changes into a gum like substance called dextrin. Dextrin is used in calicoprinting and as an adhesive. It chars at higher temperatures.

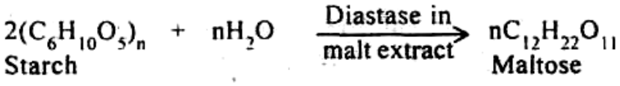
ii. Hydrolysis:

On hydrolysing starch with dilute mineral acids, it is converted to dextrine and finally to glucose



$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Dextrin}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}$$

When starch is hydrolysed with malt extract it gives maltose. The malt extract contains the enzyme diastase. This converts starch into maltose.



$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{malt extract}]{\text{Diastase in}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

iii. Action with iodine:

It gives a blue colour with iodine. The colour disapperas on heating and reappears on cooling. This is a sensitive test for starch.

iv. Formation of soluble starch : .

Ordinary starch is heated with 10% hydrochloric acid for 24 hours. It is converted into soluble starch. It is precipitated with alcohol and thus separated.

Uses :

i. It is one of the most valuable constituents of food as rice, breadcornflour, potato etc.

ii. It is used in the manufacture of glucose, alcohol, dextrin and adhesives.

iii. It is used in laundry as a stiffening agent,

iv. It is used in calico printing.

v. Starch acetate, a derivative of starch is used for making sweets,

vi. Nitro starch another derivatives of starch is used as an explosive for blasting.

2. Cellulose

Occurrence:

It occurs in the cell walls of plants and in certain animal tissues. It is the main structural material of trees and plants. Its main source is cotton and wood. Other sources are straw, corncobs, and similar agricultural wastes.

Preparation:

i. From Wood:

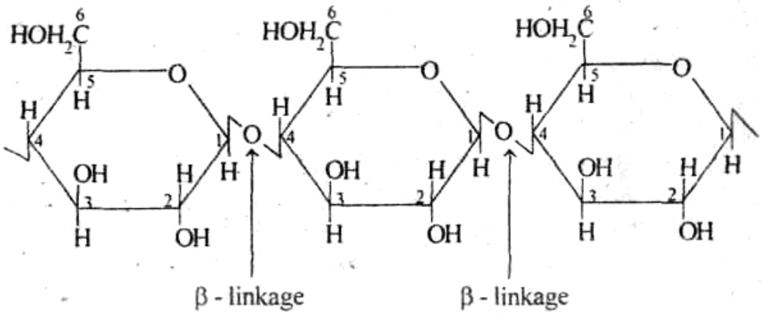
Wood shavings are successively treated with dilute alkaji, dilute acid, water alcohol and ether. All the other substances like lignin. resin, accompanying cellulose are removed by these treatments and cellulose is obtained as an amorphous mass. It may be bleached with hypochlorites to give a white amorphous powder of cellulose.

ii. From cotton :

The seed hairs of the cotton plant is the best source of cellulose. The fats and waxes present in it are extracted with organic solvents. The mineral matters present in it are removed from it with hydrofluoric acid. We get crude cellulose. It is bleached. We get pure cellulose.

Structure:

Cellulose is a straight - chain polysaccharide composed of D - glucose units. These units are jointed by β - glcosidic linkages between C - 1 of one glucose unit and C-4 of the next glucose unit. The number of D -glucose units in cellulose ranges from 300 - 2500.



Properties :

It is an amorphous white solid insoluble in water. It is soluble in Schewitzers reagent (ammoniacal copper hydroxide solutions). When acids, alcohols or salts are added to the solution it is precipitated. This property is made use of in the manufacture of rayon (artificial silk).

Cellulose on treatment with concentrated sodium hydroxide, becomes a gelatinous translucent mass. Cotton goods treated in this way get a silky lustre. Such cotton in known as mercerized cotton. The process is called mercerizing.

Reactions:

1. Action of concentreated sulphuric acid:

Cellulose dissolves in cold concentreated sulphuric acid. On dilutior. it is precipitated as amyloid. For example, when an ordinary paper is dipped in concentrated sulphuric acid for a few seconds and then washed with water, amyloid is precipitated on the surface of the paper and the surface of the paper become rough. Such a paper is called parchment paper.

ii. Hydrolysis:

When it is boiled with dilute acids it is hydrolysed to glucose.

iii. Acetylation:

On treatment with acetic anhydride it forms triacetate.

iv. Nitration:

On treatment with acetic anhydride it forms triacetate.

v. Formation of esters:

On treatment with acids like acetic acid, nitric acid etc., it gives esters. These esters are commercially important.

Uses :

1. Cellulose forms the raw material for the textiles and paper industries.
2. Cellulose nitrate is called gun cotton, Gun cotton is used in the manufacture of explosives like blasting gelatin and cordite.
3. Lower cellulose nitrates are called pyroxylins. Pyroxylin is used to manufacturecollodion which is used in-photography. It is also used to manufacture elluloid which is used for making toys, photographic films etc.
4. Cellulose is used for the preparation of artificial silk like viscose rayon.This is used in weaving cloth.
5. Cellophane is made from viscose and this is used as a protective film.
6. Cellulose nitrate when dissolved in proper solvents produce lacquers.

Derivatives of cellulose :

1. Cellulose nitrate (Nitro Cellulose)

The highest nitrate of cellulose theoretically possible is the trinitrate $(C_6H_7N_3O_{11})_3$. It contains 14.4% nitrogen. The nitrates are prepared by the reaction of cellulose with a mixture of nitric acid and sulphuric acid. The degree of nitration depends on the concentration of acids and the time of the reaction. Cellulose trinitrate is known as Gun - Cotton. It is used in the manufacture of blasting explosive and smokeless powders. The lower nitrates in the solid state are known as Pyroxylin. Pyroxylin mixed with camphor as plasticiser is converted into celluloid.

2. Cellulose acetate (celanese silk)

When acetylated with acetic anhydride in the presence of H_2SO_4 cellulosed is converted into cellulose triacetate. The triacetate is decomosed to diacetate by adding water. The diacetate is washed dried and dissolved in a mixture of organic solvents. From this solution fine threads of cellulose acetate are drawn.

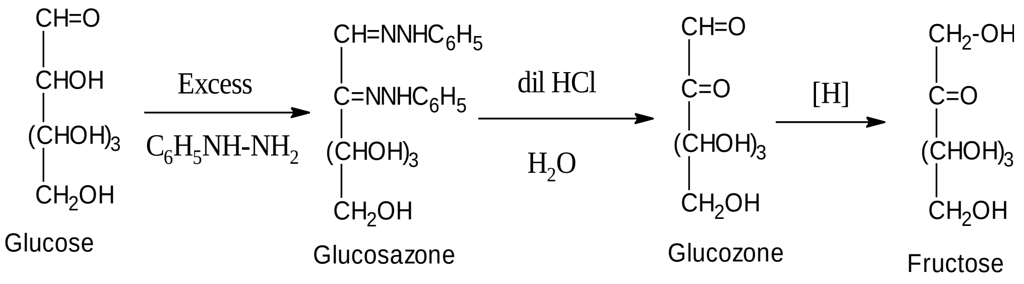
3. Ethyl cellulose

Cellulose may be treated with ethyl chloride in the presence of alkai to form ether groups out of the OH groups. We get ethyl cellulose. It is used for making plastic, textiles and films.

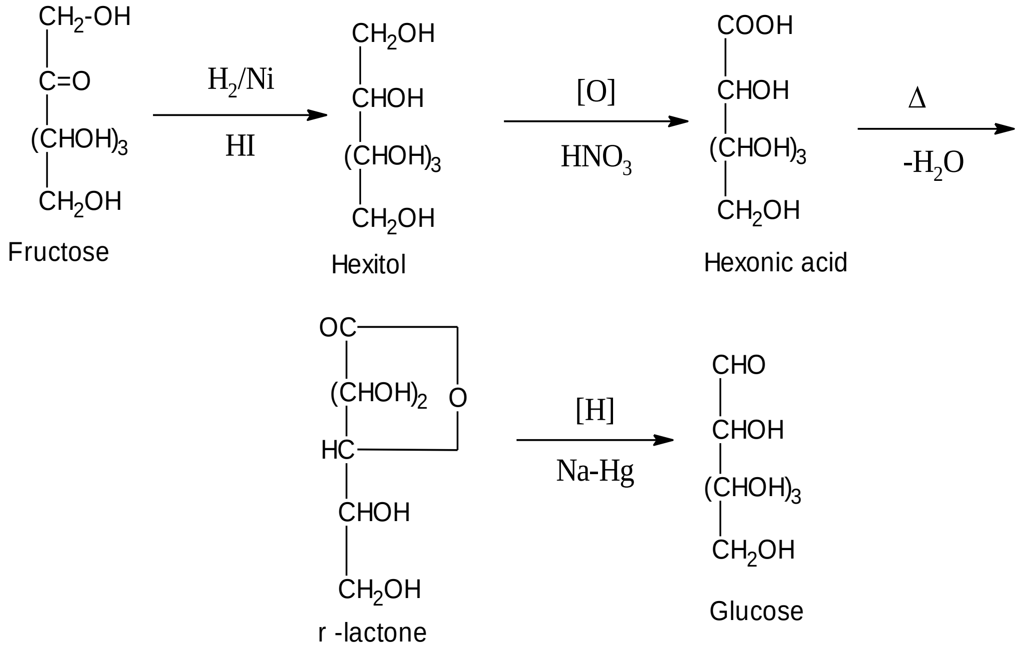
4. As a cattle Food :

Grazing animals like cattle, goats have in their digestive system, an enzyme called cellulase, which digests cellulose by hydrolysing it into glucose. So they can take grass, straw etc., directly as their food. But man and similar mammals donot have this cellulase in their digestive system. So they can not take directly grass and straw as their food. They have only the enzyme amylase, diastase and maltase in their digestive system. Diastase hydrolyses starch into maltose, which is then hydrolyse into glucose with the help of maltase.

Inter conversion of Glucose to Fructose:

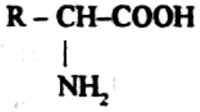


Inter conversion of Fructose to Glucose:



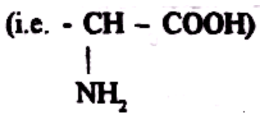
AMINO ACIDS

An amino acid, as the name implies, is a difunctional compound which contains both an amino and a carboxyl group. This may be regarded as a derivative of carboxylic acids in which a hydrogen atom has been replaced by an amino group. On the basis of the position of amino group with respect to the carboxyl group, these are classified as α, β and γ - amino acids. Most of the amino acids which occur as components of proteins are a - amino acids and have the general formula.



$$R-\underset{|\atop NH_2}{CH}-COOH$$

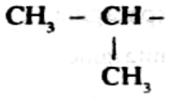
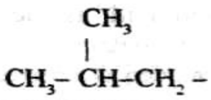
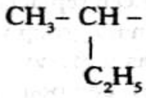
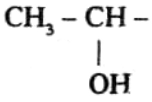
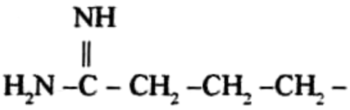
The chemical classification of the amino acids is based chiefly upon the. composition of the side chain or R-group. This is the feature which varies from one amino acid to another while the α-carbon, carboxyl and amino groups

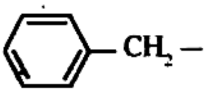
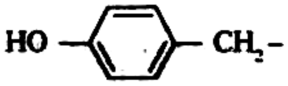
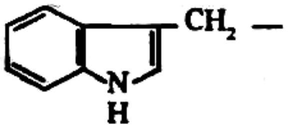
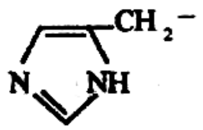


$$(i.e.\ -\underset{|\atop NH_2}{CH}-COOH)$$

are common to all.

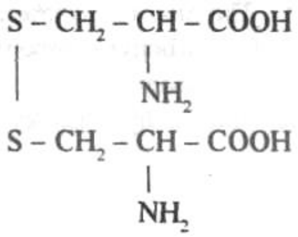
No single means of classification can be used for all amino acids. However, the classification based on the nature of R-group is given in the table.

Amino acid	***Structural formula for R – group***
(A) Simple or neutral amino acids	
1. Glycine	**$H-$**
2. Alanine	**CH_3-**
3. Valine	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-$
4. Norleucine	$CH_3-CH_2-CH_2-CH_2-$
5. Leucine	 $\overset{\overset{CH_3}{\vert}}{CH_3-CH}-CH_2-$
6. Isoleucine	 $CH_3-\underset{\underset{C_2H_5}{\vert}}{CH}-$
(B) Hydroxy amino acids	
7. Serine	$HO-CH_2-$
8. Threonine	 $CH_3-\underset{\underset{OH}{\vert}}{CH}-$
(C) Basic amino acids	
9. Lysine	$H_2N-CH_2-CH_2-CH_2-CH_2-$
10. Arginine	 $H_2N-\overset{\overset{NH}{\|}}{C}-CH_2-CH_2-CH_2-$
(D) Acidic amino acids	
11. Aspartic acid	$HOOC-CH_2-$
12. Glutamic acid	$HOOC-CH_2-CH_2-$
(E) Amide amino acids	
13. Asparagine	$H_2N-CO-CH_2-$
14. Glutamine	$H_2N-CO-CH_2-CH_2-$

(F) Aromatic amino acids	
15. Phenylalanine	
16. Tyrosine	
(G) Sulphur containing amino acids	
17. Cysteine	$HS - CH_2 -$
18. Methionine	$CH_3 - S - CH_2 - CH_2 -$
(H) Heterocyclic amino acids	
19. Tryptophan	
20. Histidine	

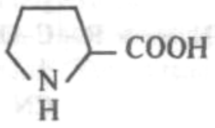
The amino acids which do not fit into the above classifications are given below:

21. Cystine

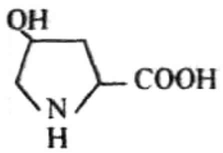


$$\begin{array}{l} S - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \\ | \\ S - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \end{array}$$

22. Proline



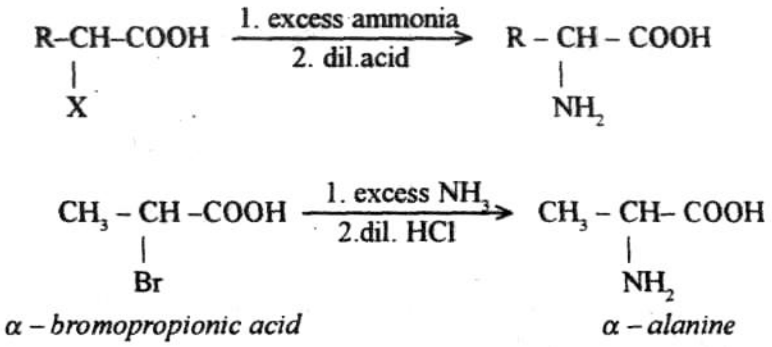
23. Hydroxyproline



The amino acids that can be synthesised from other compounds by the tissues of the body are called *Non-essential* amino acids. The amino acids that cannot be synthesised by the body and must be supplied in the diet are called *essential* amino acids. The essential amino acids are - valine, isoleucine. leucine, phenylalanine, tryptophan, threonine, lysine. arginine, histidine and methionine.

Preparation of amino acids

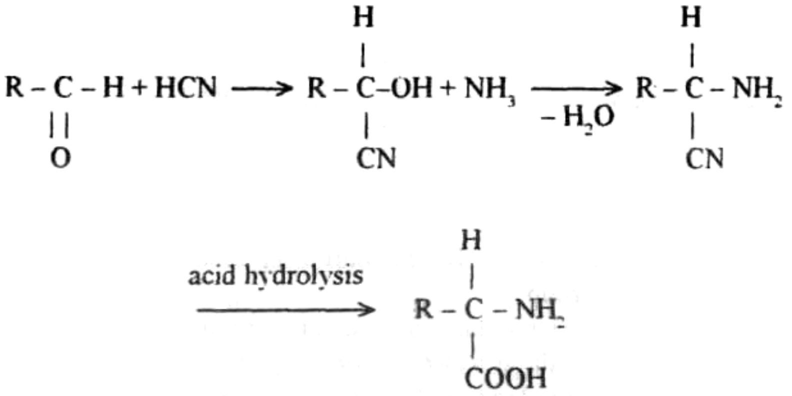
A) One of the several useful syntheses of α-amino acids involves the α-halo acids in the following way :



$$\underset{\substack{|\\X}}{R\text{–}CH}\text{–}COOH \xrightarrow[\text{2. dil.acid}]{\text{1. excess ammonia}} R-\underset{\substack{|\\NH_2}}{CH}-COOH$$

$$CH_3-\underset{\substack{|\\Br}}{CH}-COOH \xrightarrow[\text{2.dil. HCl}]{\text{1. excess }NH_3} CH_3-\underset{\substack{|\\NH_2}}{CH}-COOH$$

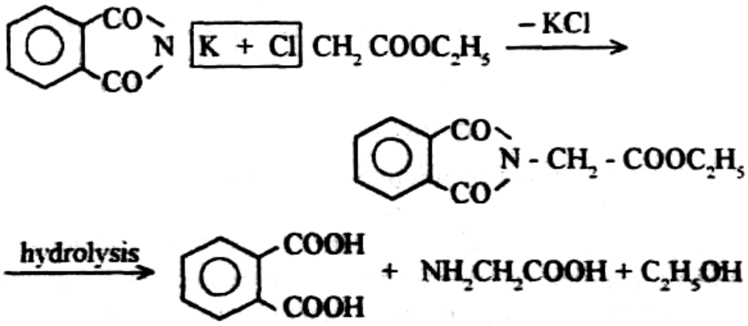
B) **The Strecker synthesis** of α - amino acids involves the reaction of a carbonyl compound with a mixture of ammonium chloride and sodium cyanide. These inorganic reagents react to form ammonia and hydrogen cyanide, the active ingredients in this process :



$$R-\underset{\substack{||\\O}}{C}-H+HCN \longrightarrow R-\overset{\substack{H\\|}}{\underset{\substack{|\\CN}}{C}}\text{–}OH+NH_3 \xrightarrow[-H_2O]{} R-\overset{\substack{H\\|}}{\underset{\substack{|\\CN}}{C}}-NH_2$$

$$\xrightarrow{\text{acid hydrolysis}} R-\overset{\substack{H\\|}}{\underset{\substack{|\\COOH}}{C}}-NH_2$$

C) In **Gabriel synthesis,** an ester of α-halo acid is treated with potassium phthalimide to form the corresponding substituted phthalimide which on hydrolysis yields an amino acid.



D) When hydrolysed by strong inorganic acids or by enzymes, proteins yield a mixture of α-amino acids which-can be separated more conveniently into individual amino acids either by *chromatography* or by *electrophoresis.*

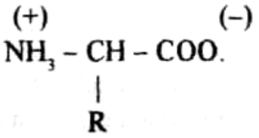
Properties of amino acids

1) Some of the physical properties of amino acids differ noticeably from other organic compounds:

For example, amino acids melt at relatively high temperatures. Decomposition usually accompanies the melting.

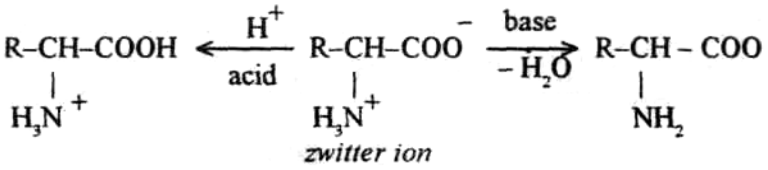
2) The majority of the amino acids are more soluble in water than in typical organic solvents.
3) When measured in aqueous solutions, the dipole moment of amino acids is found to have a large value.

To account for this large value, it has been suggested that amino acids exist in solution as an *inner salt.* This is readily explained by assuming an internal neutralisation achieved by the shift of a proton from the carboxyl to the amino group.



$$\overset{(+)}{NH_3}-\underset{\substack{|\\ R}}{CH}-\overset{(-)}{COO}$$

This is known, in addition to an inner salt, as a *zwitter ion, ampholyte* or a *dipolar ion.* Amino acids, in this form are amphoteric i.e. they react with both acids and bases:



$$\begin{array}{l} R-CH-COOH \\ \quad | \\ H_3N^+ \end{array} \xleftarrow[\text{acid}]{H^+} \begin{array}{l} R-CH-COO^- \\ \quad | \\ H_3N^+ \end{array} \xrightarrow[-H_2O]{\text{base}} \begin{array}{l} R-CH-COO \\ \quad\;\; | \\ \quad NH_2 \end{array}$$

4) Thus, in acidic solution amino acids exist as positive ions while in basic solutions they exist as negative ions. In acidic solution, an amino acid migrates towards the cathode and in basic solution it migrates towards the anode. At

certain pH, the amino acid molecule would not migrate to either electrode and exists as a neutral dipolar ion.

This pH is called the *isoelectric point* of that amino acid. Neutral amino acids have isoelectric points from **pH 5.5 to 6.3.** Acidic amino acids have them around **pH 3** whereas basic amino acids have them around **pH 10.**

Though the following reactions are typical of all a-amino acids, many reactions are illustrated taking glycine as example. *Reactions characteristic of the amino group*

1) Amino acids react with strong acids to give the corresponding salts.

$$H_3\overset{+}{N}-CH_2-\ CO\overset{-}{O}+HCl \longrightarrow \overset{-}{Cl}\ H_3\overset{+}{N}-CH_2-COOH$$

glycine hydrochloride

2) The amino group of amino acids can be acylated with acetyl chloride or acetic anhydride to form N-acylamino acids.

$$CH_3-CO-\boxed{Cl + H}\ NH\ CH_2COOH \longrightarrow CH_3-CO\ NH-CH_2-COOH+HCl$$

N-acetyl glycine (aceturic acid)

Similarly, with benzoyl chloride, glycine forms benzoyl glycine, *hippuric acid.*

$$C_6H_5CO-\ \boxed{Cl +H}\ \ NH-CH_2-COOH \longrightarrow C_6H_5\ CO-NH-CH_2-COOH +HCl$$

hippuric acid.

3) Like primary aliphatic amines, amino acids react with nitrous acid to form hydroxy acids.

$$H_2N-CH_2COOH +HONO \longrightarrow HO-CH_2-COOH +N_2 +H_2O$$

Glycollic acid.

4) Amino acids react with nitrosyl chloride (or bromide) to' form halo acids.

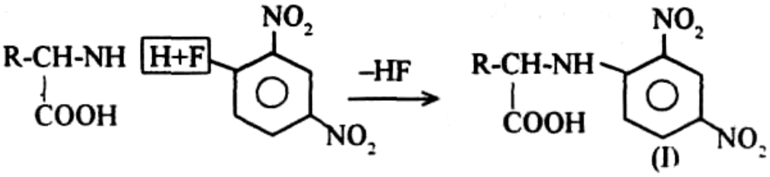
$$H_2N-CH_2-COOH +NOCl \longrightarrow Cl-CH_2-COOH + N_2 +H_2O$$

Chloroacetic acid

5) Amino acids react with formaldehyde to yield N- methyleneamino acids.

$$HCH\ \boxed{O+H_2}NCH_2\ COOH \longrightarrow CH_2=NCH_2\ COOH + H_2O$$

6) Amino acids react with *Sanger's reagent* (2.4 - dinitrofluorobenzene) to produce yellow coloured dinitrophenyl (DNP) amino acids (I)



Reactions characteristic of the carboxyl group

1) Amino acids react with alkalies to form salts.

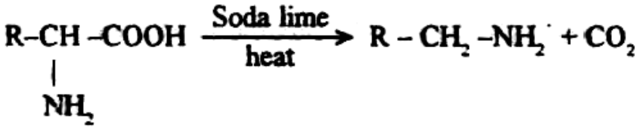
$$H_3\overset{+}{N}CH_2 - CO\overset{-}{O} + NaOH \longrightarrow NH_2 - CH_2 - COONa + H_2O$$

Sodium aminoacetate

2) Amino acids may be esterified by an alcohol in the presence of an inorganic acid.

$$H_2N - CH_2 - COOH + HOC_2H_5 \xrightarrow{HCl} \overset{-}{Cl}\ \overset{+}{N}H_3 - CH_2 - COOC_2H_5 + H_2O$$

3) When heated with soda lime, they decompose into atnine.



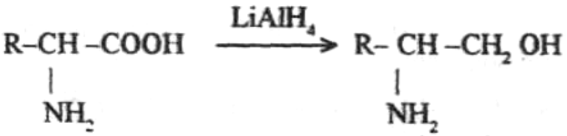
$$\underset{\substack{|\\NH_2}}{R-CH}-COOH \xrightarrow[\text{heat}]{\text{Soda lime}} R - CH_2 - NH_2 + CO_2$$

4) Amino acids react with metallic oxide or hydroxide in water to produce complex salts.

$$2\,NH_2 - CH_2 - COOH + Cu^{2+} \xrightarrow{\Delta} Cu\,(OOC - CH_2 - NH_2)_2 + 2H^+$$

cupric glycinate.

5. Amino acids **may be reduced to amino alcohols by lithium aluminium hydride (LiAIH$_4$)**



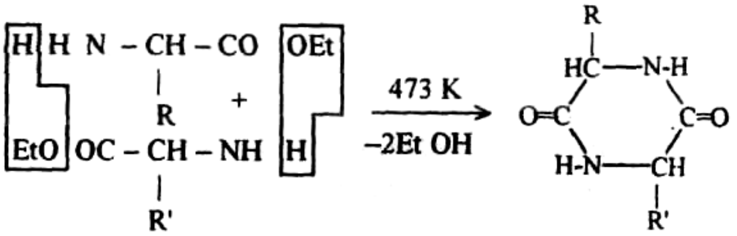
$$\underset{\substack{|\\NH_2}}{R-CH}-COOH \xrightarrow{LiAlH_4} R-\underset{\substack{|\\NH_2}}{CH}-CH_2\,OH$$

amino alcohol.

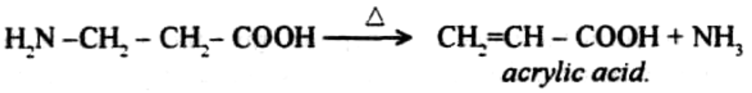
Reactions involving both the carboxyl and the amino groups

1) Action of heat on amino acids:

a) α-amino **acids** undergo **dehydration on heating to** give *diketopiperazines:*

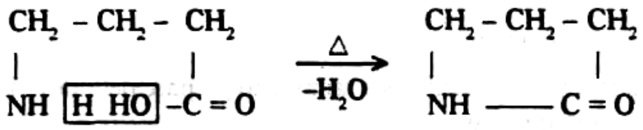


b) A β-amino acid on heating loses a molecule of ammonia to form an unsaturated acid. For example, β- ammo propionic acid on heating forms acrylic acid:



$$H_2N-CH_2-CH_2-COOH \xrightarrow{\Delta} \underset{\textit{acrylic acid.}}{CH_2=CH-COOH} + NH_3$$

c) γ -amino acids on heating eliminate water and form inner amides or lactams which are cyclic:



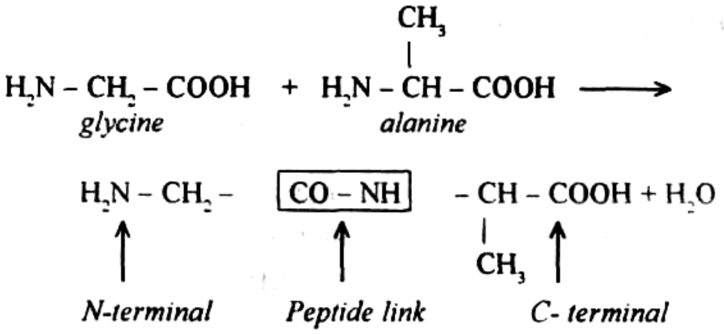
$$\begin{array}{l}CH_2-CH_2-CH_2\\ |\qquad\qquad\qquad |\\ NH\ \boxed{H\ HO}-C=O\end{array} \xrightarrow[-H_2O]{\Delta} \begin{array}{l}CH_2-CH_2-CH_2\\ |\qquad\qquad\quad |\\ NH ——— C=O\end{array}$$

2) All α-amino acids react with ninhydrin to produce thesame purple colour.

3) All α-amino acids (except glycine) are optically active.

PEPTIDES

Peptides are condensation products of amino acids. Structurally they occupy an intermediate position between the relatively simple α-amino acids and the considerably more complex proteins. If two amino acids condense between **the** carboxyl group of one amino acid and the amino radical of the other, a substituted amide of a particular type, commonly referred to a *peptide,* is formed.



$$\underset{\textit{glycine}}{H_2N-CH_2-COOH} + \underset{\textit{alanine}}{H_2N-\overset{\overset{CH_3}{|}}{C}H-COOH} \longrightarrow$$

$$\underset{\substack{\uparrow\\ \textit{N-terminal}}}{H_2N-CH_2-}\ \underset{\substack{\uparrow\\ \textit{Peptide link}}}{\boxed{CO-NH}}\ \underset{\substack{\uparrow\\ \textit{C- terminal}}}{-\underset{\underset{CH_3}{|}}{CH}-COOH} + H_2O$$

Thus, a ***dipeptide*** is formed from two amino acids. A three amino acids peptide is called *"**tripeptide**"* and so on. Compounds in which a large number of amino acids are linked to each other through **peptide bonds** are known as *"**polypeptides**"*. **Proteins** are polypeptides haveing very high molecular weight which range from about 10000 to many millions.

To form the name of a peptide give the names of the constituent amino acids in the order they appear in the molecule. The endings of all (except the amino acid with the free terminal carboxyl group) are changed from *"ine"* to *"yl"* . hi this way, the above peptide is named as *"Glycylalanine"*

Synthesis of polypeptide

There are many methods available to prepare peptides. Few of them are listed below:

(i) Azide synthesis	(ii) Carbobenzoxy method
(iii) Chloroacid chloride synthesis	(iv) Diketopiperazine method
(v) Ester condensation	(vi) Mixed anhydride synthesis
(vii) Phthalyl synthesis	(viii) Pyrophosphite synthesis.

All the methods generally consist of the following three steps -

(i) Protection of amino group in the amino acid

(ii) Formation of peptide linkage

(iii) Removal of the protecting group.

Bergmann Method:

In Bergman method, for amino group protection Benzyl oxy carbony group is used.

C_6H_5-CH_2-O-CO-Cl

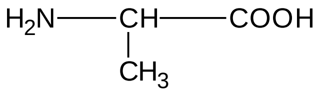
Benzyl oxy carbonyl chloric

Let us considered the synthesis of the following tripeptide.

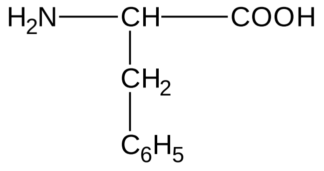
Gly – ala – phe

Here,

$$H_2N—CH_2—COOH \quad = \quad H_2N—A^1—COOH$$



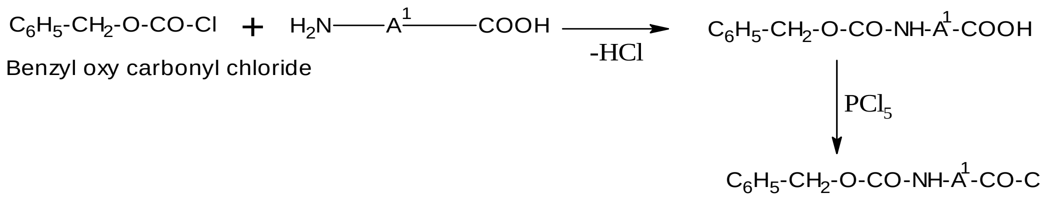
$$H_2N—\underset{CH_3}{\underset{|}{CH}}—COOH \quad = \quad H_2N—A^2—COOH$$



$$H_2N—\underset{C_6H_5}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}—COOH \quad = \quad H_2N—A^3—COOH$$

Stage – I

Protection of amino group



$$C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}Cl + H_2N\text{—}A^1\text{—}COOH \xrightarrow[\text{-HCl}]{} C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}COOH$$

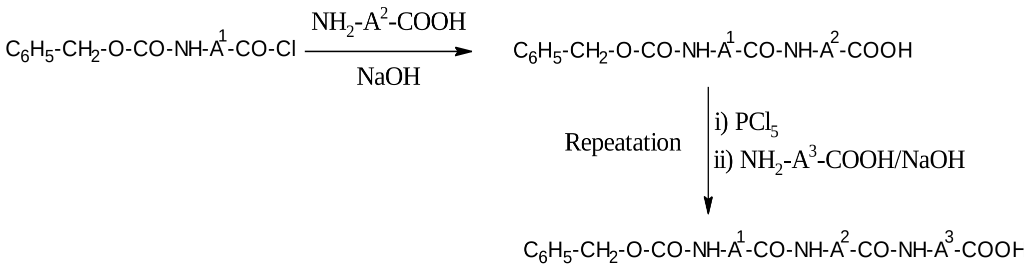
Benzyl oxy carbonyl chloride

$$\Big\downarrow PCl_5$$

$$C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}CO\text{-}C$$

Stage – II

Peptide bond formation



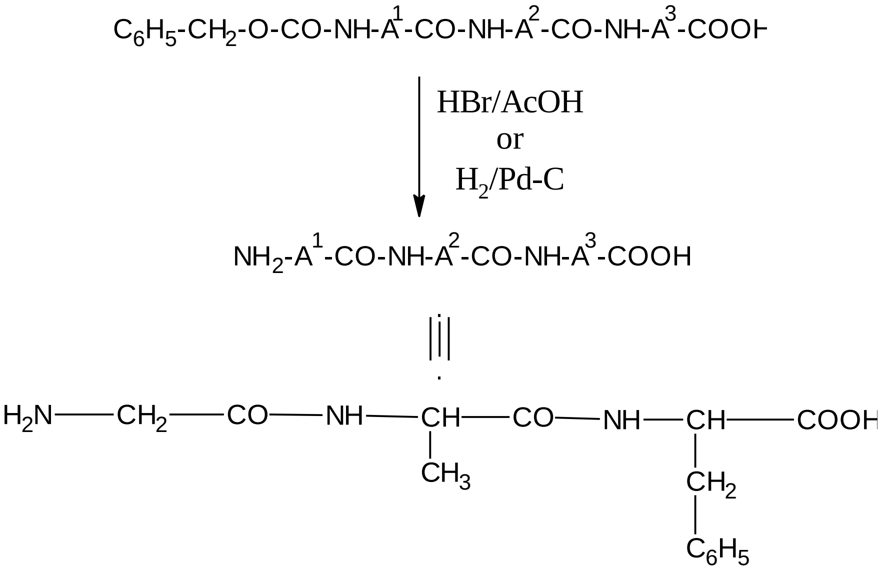
$$C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}CO\text{-}Cl \xrightarrow[\text{NaOH}]{NH_2\text{-}A^2\text{-}COOH} C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}CO\text{-}NH\text{-}A^2\text{-}COOH$$

$$\text{Repeatation}\ \Big\downarrow \begin{array}{l}\text{i) } PCl_5\\ \text{ii) } NH_2\text{-}A^3\text{-}COOH/NaOH\end{array}$$

$$C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}CO\text{-}NH\text{-}A^2\text{-}CO\text{-}NH\text{-}A^3\text{-}COOH$$

Stage - III

Removel of the protecting group



$$C_6H_5\text{-}CH_2\text{-}O\text{-}CO\text{-}NH\text{-}A^1\text{-}CO\text{-}NH\text{-}A^2\text{-}CO\text{-}NH\text{-}A^3\text{-}COOH$$

$$\Big\downarrow \begin{array}{c}\text{HBr/AcOH}\\ \text{or}\\ H_2/Pd\text{-}C\end{array}$$

$$NH_2\text{-}A^1\text{-}CO\text{-}NH\text{-}A^2\text{-}CO\text{-}NH\text{-}A^3\text{-}COOH$$

$$\equiv$$

$$H_2N\text{—}CH_2\text{—}CO\text{—}NH\text{—}\underset{\substack{|\\ CH_3}}{CH}\text{—}CO\text{—}NH\text{—}\underset{\substack{|\\ CH_2\\ |\\ C_6H_5}}{CH}\text{—}COOH$$

Gly – ala – phe

PROTEINS

As pointed out earlier in this chapter, proteins are polymers of amino acids. More specific structural studies have shown them to possess certain unique properties because of their giant size. The classification of proteins are given below :

Simple Proteins

Proteins which yield only amino acids or their derivatives on hydrolysis are called simple proteins. The *further classification based on their solubility* in various solvents is given below:

a) **Albumins** *:* Soluble in pure water and coagulable by heat. *Example:* serum albumin, egg albumin.

b) **Globulins***:* Insoluble in pure water, but soluble in NaCl solutions. *Examples:* serum albumin, (in blood), tuberin (in potato) arachin and conarchin (in peanuts).

c) **Glutelins:** Insoluble in all neutral solvents, but soluble in very dilute alkalies. The best known protein of this group is the glutelin of wheat.

d) **Prolamins:** Soluble in 70% alcohol. *Examples:* gliadin (in wheat) and zein (in maize).

e) **Histones***:* Soluble in water and insoluble in very dilute ammonia. On hydrolysis, they yield several amino acids among which the basic ones predominate. The important members of this group are the *thymus histones* and the globin of *haemoglobin.*

f) **Prolamins***:* Strongly basic proteins with low molecular weight are soluble in water, not coagulable by heat and on hydrolysis yield large amounts of basic amino acids. *Example: Salmine* from *Salmine sperm.*

Conjugated Proteins

Hydrolysis of conjugated proteins yield α-amino acids and a non-protein material. The non-protein material is known as *prosthetic group.* On the basis of the prosthetic groups present in the protein, they are classified in the following manner :

No.	*Conjugated protein*	*Prosthetic group*	*Example*
1.	**Nucleoproteins**	**Nucleic acid**	**Yeast, Chromosomes**
2.	**Glycoproteins**	**Carbohydrate**	**Mucin,Egg white**
3.	**Phosphoproteins**	**Phosphorus**	**Caseinogen, Ovovitelin**
4.	**Haemoproteins**	**Haem**	**Haemoglobin, Myoglobin**
5.	**Lipoproteins**	**Lipids**	**Lipovitelins in eggs**
6.	**Chromoproteins**	**Fe,Mg,Cu**	**Haemoglobin,** **Chlorophyll,** **Cyanocuprin**

Classification on the basis of the shape of the molecule

1) ***Globular Proteins:*** These proteins have relatively spherical shape. They are relatively soluble.

2) **Fibrous Proteins***:* Sclero proteins are chiefly fibrous proteins. These proteins resemble long ribbons or fibres in nature. These tend to be insoluble. They are found usually as components of the tougher types of tissues such as *keratins* of skin, hair and feathers. The collagens of tendons, elastins of ligaments and silk fibroin belong to this class. They are insoluble in water and other common solvents.

Denaturation of Proteins:

Proteins may be coagulated i.e., precipitated irreversibly. This irreversible precipitation of protein is called *denaturation.* This can be brought about by heat, strong acids or bases or various other agents. As a result of denaturation, the protein undergoes changes physically and chemically. Solubility, molecular shape size and the biological activity of the protein may change. The optical rotation of many proteins changes as a result of denaturation. Denaturation involves changes in the secondary structure of the protein.

BIOLOGICAL FUNCTIONS OF PROTEINS

Proteins are intimately connected with almost all the chemical and physical activities that constitute life. In fact, there is hardly an important physiological function in which proteins do not participate.

Some proteins called *enzyme* serve as catalysts to speed up the variety of chemical transformations which living cells are able to accomplish.

Other proteins function as *hormones* whose principal activity is to control processes which occur in living things. The growth hormone produced by the pituitary gland is an example of such a hormone. Likewise, haemoglobin, a protein in the blood serves as an oxygen carrier to transport oxygen from the lungs to the various tissues. Still another protein, *actomyosin* participates in muscular contraction. The much familiar hormone *insulin* produced in the pancreas controls sugar metabolism in the body.

Nucleoproteins, typical conjugated proteins composed of substances called nucleic acids and simple proteins, are the main constituents of genes, the carriers *of heredity.*

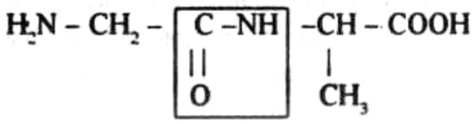
Antibodies, which are proteins, function to protect human beings against diseases.

Less spectacular are the proteins such as hair and finger nails which serve as important *structural elements* of the body.

STRUCTURE OF PROTEINS

Primary Structure

The main mode of linkage of the amino acids in proteins is the peptide bond formed by the reaction of the carboxyl group of one amino acid with the amino group of another as indicated in glycylalanine (gly-ala) below:



$$H_2N - CH_2 - \boxed{\underset{\underset{O}{\|}}{C} - NH} - \underset{\underset{CH_3}{|}}{CH} - COOH$$

The primary structure of proteins deals with the actual arrangement or *sequence* of various amino acids held together by peptide linkages in protein. If a peptide linkage is formed by two amino acids, there are two possible sequences :

Example:

(a) The two amino acids, glycine and alanine, give two (2!= 1 x 2 =2) possible sequences in the following way:

1) Glycylalanine (gly - ala) 2) Alanylglycine (ala - gly)

(b) If three amino acids (say, glycine, alanine and leucine) form peptide linkage, there are six (3! =1 x 2 x 3 =6) possible sequences as:

1) Ala-gly-leu 2) Ak-leu-gly 3) Gly-ala-leu

4). Gly-leu-ala 5) Leu-ala-gly 6) Leu-gly-ala

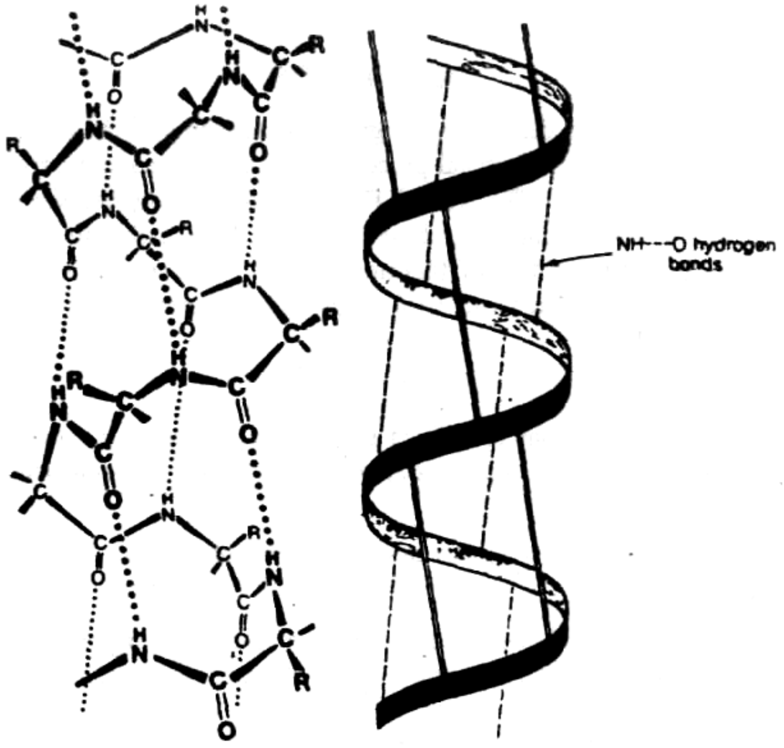
(c) Similarly, if there are "n" amino acids in a protein, they giverise to "n!" (n! = 1 x 2 x 3 x4...n) sequences.

It has been established from various studies that slight variations in the sequence of amino acids have marked effects on the chemical and physical properties of proteins and this aspect is dealt in the primary structure.

Secondary Structure

As discussed above, the primary structure deals with the actual arrangements of amino acids in protein. It fails to throw light on the shape, configuration and conformation of the molecule. The secondary structure of a protein deals with the shape in which the long amino acid chain exists, the way in which the protein chain is folded and the nature of the bonds which establishes this structure.

The proteins, especially globular proteins, indicate a coiled structure in which peptide bonds are folded in a regular manner. Much of the folding is the result of linking of the carboxyl and amide groups of the peptide chain by means of hydrogen bonds. Such foldings produced or maintained by hydrogen bonding is often called the secondary structure of the proteins. Present evidences suggest that in many proteins the hydrogen bonding produces a regular coiled arrangements called, α - *helix.* This secondary structure has been confirmed by X-ray studies and is shown in the figure.



Tertiary Structure

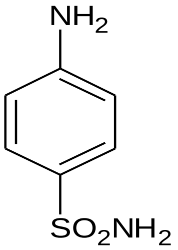
The tertiary structure deals with the way in which the poly peptide chains fold up into various shapes i.e.. globular or ellipsoidal. This folding involves hydrogen bonding, ionic and disulphide bonds. The tertiary structure is determined by temperature and pH.

CHEMOTHERAPY:

Ehrlich in 1909 introduced the term chemotherapy. It may be defined as the treatment of disease caused by bacterial invasion by chemical compounds. These chemicals selectively destroy the micro-organisms without affecting the host tissues. This definition excludes disinfectants like formaldehyde, phenol, iodine etc., because hey are applied externally and tend to destroy the tissues.

Sulpha drugs:

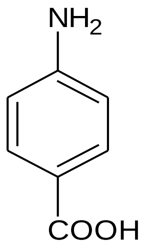
The parent compound of all sulpha drugs is Sulphonamide. Sulphonamides are antimicrobial compounds containing sulphonamide ((SO_2NH_2)) group. These are synthetic chemotherapeutic agents. These were the first of antibacterial drugs to be used successfully for the treatment of bacterial infections in human. These are active against certain gram positive and gram negative organisms. These are mainly bacteriostatic in action and are used in the treatment of many diseases like gonorrhoea, blood poisoning, scarlet fever, tonsillitis, sinus infections, urinary tract infections etc.



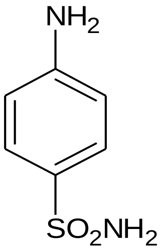
Sulphonamid

Mechanism of action of sulpha drugs:

These are bacteriostatic in action. The bacteriostatic nature of sulphonamides is due to their structural similarity to Para Amino Benzoic Acid (PABA), which is a compound for the normal functioning of some of the vital process in bacteria.



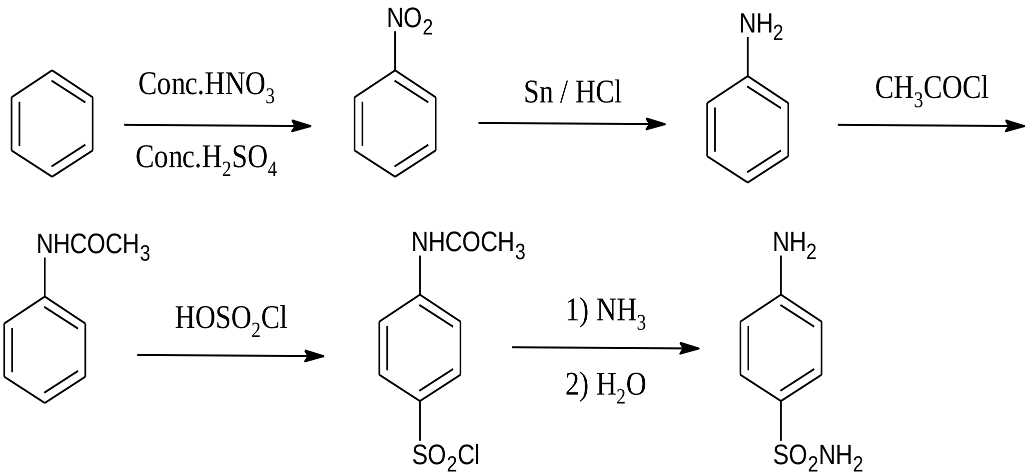
Para amino benzoic acid



Sulphonamid

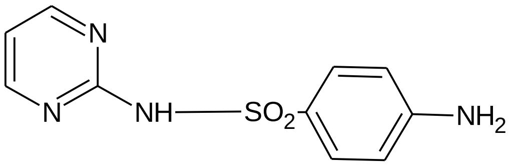
Folic acid derived from PABA is important for bacterial metabolism. Sulphonamides are antimetabolites of PABA, as due to structural similarity the bacteria takes up sulphonamide, which inhibit the enzyme folic acid synthetatase, that is involved in the conversion of PABA to folic acid. Thus the metabolism is blocked and the growth of bacteria stops.

The parent compound, sulphonamide, $p\text{-}NH_2\text{-}C_6H_4\text{-}SO_2NH_2$ is prepared from benzene in the following way.



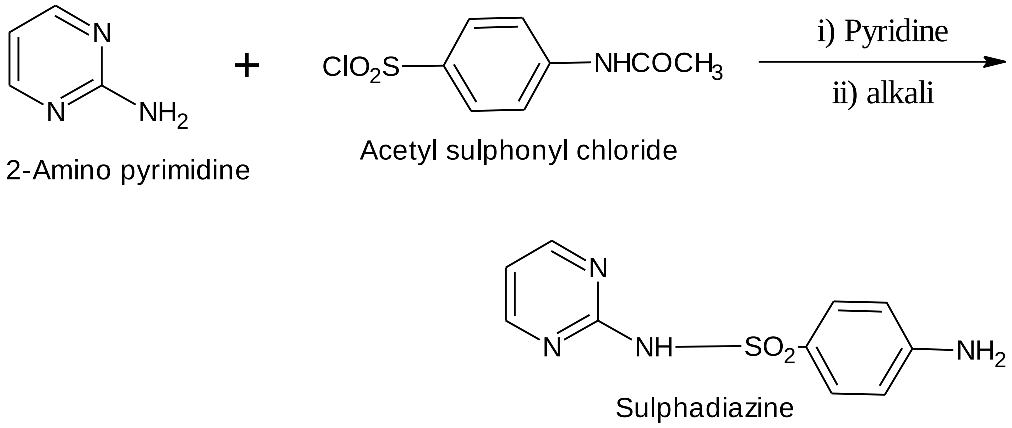
Sulphadiazine:

Structure:



Preparation:

It is prepared by condensing 2-amino pyrimidine with Acetyl sulphonyl chloride in the following manner.

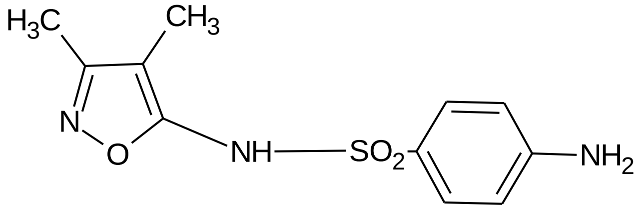


Uses:

i. It is used for general purposes as it is not toxic and is easily absorbed and excreted.
ii. It is a short acting sulpha drug.
iii. It is used for systemic infections and is usually administered orally.
iv. It is used in the treatement of meningococcai meningitis.

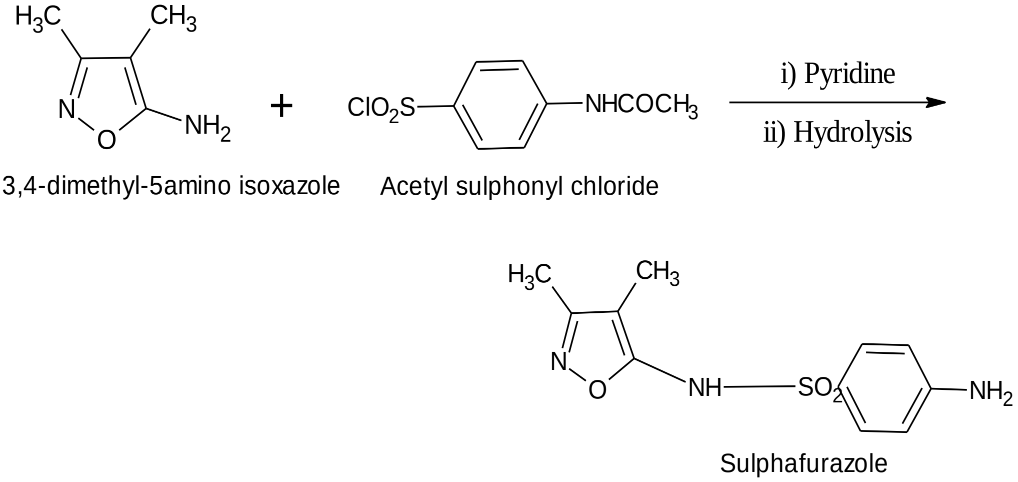
Sulphafurazole:

Structure:



Preparation:

It is prepared by condensing 3,4-dimethyl-5-amino isoxazole with Acetyl sulphonyl chloride(ASC).



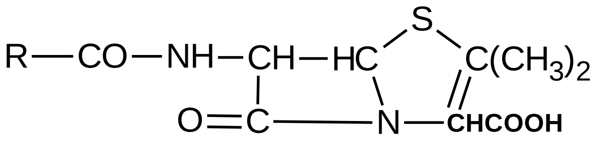
Uses:

i) It is a short acting sulphonamide derivative.

ii) It i used for urinary tract infections.

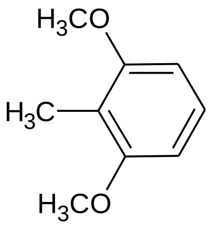
Pencillins:

These are the most potent antibacterial drugs. Fleming in 1929 discovered it from the mold penicillium species. Penicillin is the name given to the mixture of natural compound having the general molecular formula, $C_9H_{11}O_4N_2SR$ and differing only in the nature of r. Penicillin-G is the most commonly used one among the natural penicillin. The common structural formula is given below.



Penicillins

Classification based on the nature of R group is given in table.

No.	Penicillin	R =
1	F	$-CH_2-CH=CH-CH_2-CH_3$
2	G	$-CH_2-C_6H_5$
3	K	$-CH_2-(CH_2)_5-CH_3$
4	N	$-(CH_2)_3-CH(NH_2)-COOH$
5	X	$-CH_2-C_6H_4-OH(p)$
6	V	$-CH_2-O-C_6H_5$
7	Ampicillin	$-CH(NH_2)-C_6H_5$
8	Methicillin	

Penicillins are of two classes.

1. Biosynthetic and
2. Semisynthetic.

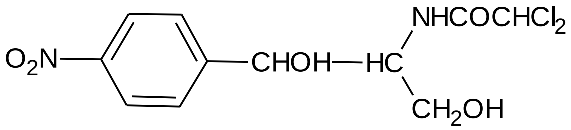
Biosynthetic types are formed during fermentation eg. Penicillin G, V. Semisynthetic types are made by adding certain compounds to 6-amino penicillaric acid.

Penicillin is active only against Gram positive organisms including staphylococci, pneumoccocci, meningococci, gonococci and against spirochetes. Penicillin is less toxic but it loses much of its activity when given orally and that it is excreted rapidly.

Methicillin is synthesised from minopenicillinic acid. Those micro-organisms resistance to penicillin are responsive to it.

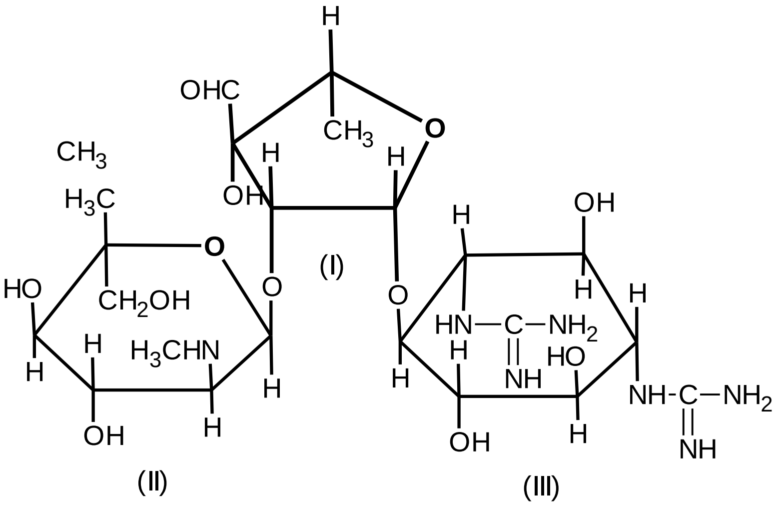
Chloramphenicol (Chloromycetin) $C_{11}H_{15}O_5N_2Cl_2$

The chlorine containing antibiotic, chloramphenicol was isolated in 1948 by Carter et al from a streptomyces venezuela, a micro-organism found in the soils of Venezuela, Illinois and Japan.



Chloromycetin is very effective against Gram negative bacteria especially those producing intestinal diseases such as typhoid fever, diarrhoea and dysentry. It is as effective as aureomycin and terramycin against typhus and virus pneumonia.

Streptomycin, $C_{21}H_{39}O_{12}N_7$



I - Streptose II - N-methylglucosamine III - Streptid

Streptomycin was isolated by Waksman et al from cultures of streptomyces griseus in 1944. It is composed of three units, streptose, streptidine and N-methylglucosamine. This antibiotic is very effective in the treatment of tuberculosis, meningitis, pneumonia, plague, tularemia, bactremia and streptococci. It is also used to treat other common infections like throat, lungs, ears and kidneys.

Prolonged use of this drug may lead to deafness.

Analgesics:

Analgesics are the drugs which relieve pain by acting on the central nervous system and they reduce pain without loss of consciousness.

Analgesics can be divided into two groups.

i) Narcotic analgesics.
ii) Non – narcotic analgesics.

i) Narcotic analgesics:

These drugs produce depression on the central nervous system and are mainly of two types.

a. Natural analgesics	:	Eg., Morphine, Codeine.
b. Synthetic analgesics	:	Eg., Pethidine, Methadone.

ii) Non – narcotic analgesics:

These drugs d not produce significant depression of the central nervous system. Unlike narcotic analgesics the non-narcotic analgesics possess anti – inflammatory and antipyretic effect. Eg., Salicylates.

Antipyretic Analgesics:

The analgesics also possess antipyretic and anti inflammatory property. Antipyretic agents reduce the elevated body temperature. The hypothalamus place an important role in regulating the body temperature.

Inflammation is a series of changes in tissues. The important aspect of inflammation is redness of the skin, edema and formation of granulation tissue. The anti – inflammatory agent reduces the conditions by controlling the cause of inflammation.

Example: Antipyretic analgesics:

1. The salicylic acid and its derivatives. Eg., Aspirin, Methyl salicylate.
2. The para-amino phenol derivatives. Eg., Para-acetamol, Phenacetin.
3. The pyrozole derivatives.
4. Indoyl and Aryl acetic acid derivatives.
5. Miscellaneous.

Tranquilizers:

Tranquilizers have been defined as drugs, which gives “peace of mind” without causing hypnosis or anesthesia.

Under the general heading of tranquilizers are included various drugs with widely differing types of pharmacological activity.

Requirements of an ideal tranquilizer:

1. Should not produce toxic effect.
2. Should not produce undesirable side-effects.
3. Should not impair unconsciousness.
4. Should be effective.

Tranquilizers are classified as:

1. Antipsychotics or Neuroleptic or major tranquilizers
2. Anti-anxiety agents or Minor tranquilizers.

1. Antipsychotic agents:

These are used mainly in major psychoses like Schizophrenia.

Example: Rauwolfia alkaloids, phenothiazene derivatives, butyrophenone derivatives, Diphenyl butyl piperidines and Indole derivatives.

2. Anti-anxiety agents:

They have a calming effect in anxiety states associated with neurotic personality, situational crisis or physical disease. In smaller doses they relieve anxiety, while in larger doses they induce sleep.

Example: Meprobamate, Benzodiazepine drugs, Diphenyl methane derivatives.

Sedatives and Hypnotics:

Hypnotics are CNS depressants that produce sleep which resembles natural sleep. A sedative calms down the nervous system and reduce excitement and induces sleep. But there is no definite line of demarcation among the various groups of sedatives and hypnotics.

Example:

Phenobarbitol - 25-30mg - mild sedative

Phenobarbitol - 100mg - hypnotic

In large doses it leads to anesthetic state and in some cases even death may result.

$$\text{Sedative} \rightleftharpoons \text{Hypnosis} \rightleftharpoons \text{Anaesthesia} \rightleftharpoons \text{Coma} \rightleftharpoons \text{Death}$$

There are some compounds exerting only one effect. Eg. Simple bromides are good sedatives having little or no hypnotic action whereas thiopentone is a powerful hypnotic but can not be used as sedative.

The most commonly used sedatives, hypnotics have been divided into the following classes.

Example:

1. Alcohols:
    a. Chloretone.
    b. Brometone
2. Aldehydes – Paraldehyde, Chlorall hydrate etc, ketones – Diethyl ketone, Acetophenone, phenyl ethyl ketone sulphones – Trional.
3. Amides or ureas – Declonal, Neuronal
4. Urethanes & Biurets – voluntal, hedonal
5. Barbiturates
6. Hydantoin derivatives
7. Heterocyclic compounds.

Anesthetics:

Drugs which produce loss of sensation are called anesthetics.

The most important aspect of anesthetics is that the loss of consciousness is reversible i.e., as soon as the concentration of the anesthetic is decreased, the effected organs return to the normal state.

An ideal anesthetics agent should have the following characteristics:

1. It should be able to give enough relaxation time for the surgery to be performed.
2. It should be inert, non-flammable and should be non-irritating to the mucous membrane.
3. It should not have any toxic effect on heart, brain, liver, kidney, etc.,
4. It should be stable to light and heat.
5. It should not reduce the blood pressure drastically.
6. It should not induce vomiting or drastically.
7. It should not give any adverse effect with the administration of other drugs.
8. It should have analgesic action and muscle relaxation.

Classification:

An anesthetic may produce unconsciousness all over the body or in a particular organ. The anesthetics could be classified as follows according to their mode of action.

1. General anesthetics

Volatile general anesthetics or Inhalation general anesthetics.

Non-volatile general anesthetics or Intravenous anesthetics.

Eg. Thiopental sodium, Metho hexitone.

2. Local anesthetics:

Eg. Cocaine, Benzocaine.

1. General anesthetics:

The anesthetics belonging to this group produce unconsciousness all over the body by depressing the central nervous system to such an extent that the sensitivity to pain or feeling is lost.

Eg. Ether, Nitrous oxide.

2. Local anesthetics:

These agents abolish the sensation of pain in localized area, i.e., they do not affect the whole body, but only a part of the body becomes insensitive to any pain or feeling. These drugs affect the peripheral nervous tissues and block nerve conduction and thus abolish all sensation in the part supplied by the nerve.

Eg. Cocaine, Benzocaine.

NOTES

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

UNIT - IV

Nuclear Chemistry

4.1. Fundamental particles of Nucleus – nuclide, isotopes, isobars and isotones

4.2. Natural radioactivity-radioactive series including Neptunium series-Group displacement law.

4.3. Nuclear Binding energy, mass defect-Calculations.

4.4. Nuclear Fission and Nuclear Fusion-differences – Stellar energy.

4.5. Applications of radioistopes-C-14 dating, rock dating,isotopes an tracers, study of Reaction mechanism (ester hydrolysis) radiodiognosis and radiotherapy

4.6**. Photochemistry**: Grotthus-Draper law and Stark-Einstien's law of photochemical equivalence. Quantum yield. Example for photochemical reactions- Hydrogen-Chlorine reaction (elementary idea only) photosynthesis.

4.8. **Phase Rule:** Phase rule and the definition of terms in it. Application of phase rule to water system. Reduced phase rule and its application to a simple eutetic system (Pb-Ag) Freezing mixtures.

NUCLEAR CHEMISTRY

The subject that deals with nucleus of an atom with special emphasis on its chemical aspects is known as nuclear chemistry.

During nuclear reactions tremendous amount of energy is liberated. This fact is to the discovery of atom bomb a hydrogen bomb etc.

FUNDAMENTAL PARTICLES OF NUCLEUS:

Once upon a time the nucleus was considered to be made up of protons and neutrons only. They were collectively known as nucleons. Today it is supposed to be made up of several particles called fundamental particles. Some of these fundamental particles are stable; and some are unstable. The stable particles are electrons, protons, antiprotons, positrons, nutrino, photons and gravitons. Of these the first four are mass particles, and the other three are energy particles. The unstable particles are neutrons, mesons and V-particles.

Besides these several other particles have been detected during nuclear reactions. We can say that nucleus consists of only protons and neutrons. All other particles are produced during nuclear reactions in which mass is converted into energy or vice versa.

Nuclides:

An atomic nucleus characterised by the numbers of protons and neutrons is often referred to as a nuclide and is denoted by ${}_{Z}X^{A}$. Where, X is the chemical symbol of the element with Z protons.

A is the total number of protons and neutron in the nucleus and also, known as the mass number

$$A=Z + N$$

Examples:

For ${}_{92}U^{235}$

$$A = Z + N$$

$$N = A – Z$$

$$N = 235 – 92 = \mathbf{143}$$

Isotopes:

Atoms having the same atomic number but different mass number or atomic masses are called isotopes.

Since isotopes have the same atomic number, these can also be defined as different atoms of the same element which have the same number of protons but different number of neutrons in their respective nuclei.

Example:

Isotopes of Hydrogen:

There are three isotopes of hydrogen (At. No Z=1) with mass number (A) 1,2 and 3

These are

i. Ordinary hydrogen or protium ${}_{1}H^{1}$
ii. Heavy hydrogen or deuterium ${}_{1}H^{2}$ (or) D
iii. Tritium ${}_{1}^{3}H$ or T

Isobars:

Definition:

The atoms of different elements which have the same mass number but different atomic number are called isobars.

For example, argon, potassium and calcium have atoms of same mass number 40: ${}_{18}Ar^{40}$, ${}_{19}K^{40}$, ${}_{20}Ca^{40}$. But their atomic numbers are 18, 19 and 20 respectively.

Isotones:

Atoms having same number of neutrons but differing in their mass number as called isotones. The difference in mass number is due to the difference in the number of protons present in them. Isotones are different elements with different physical and chemical properties.

Example:

$_{14}Si^{30}$ $_{15}P^{31}$ $_{16}S^{32}$

$_{6}C^{14}$ $_{7}N^{14}$ $_{8}O^{16}$

Each contain 16 neutrons in their nucleus in the first set while the second set has 8 neutrons.

Radio Activity:

Radioactivity is of two types

1. Natural Radioactivity:

We have seen that the naturally occurring elements like Uranium, Polonium, Radium etc. are constantly undergoing a spontaneous change and as a result of this they are emitting α,β and γ rays and thus changes into other elements. This spontaneous change is called natural radio activity.

2. Artificial or induced radioactivity:

Artificial or induced radioactivity is a process by which an element is converted into a new radioactive isotope of a known element by artificial means.

Radioactive Series:

Atoms of heavy elements like uranium, thorium, polonium and radium etc are constantly breaking up into fresh radioactive atoms with the emission of α,β and γ rays from their nuclei. In the process, the original (or parent) atom disappears and gives rise to new (daughter) atom. These new atoms are also in general. Radio active and hence spontaneously break up in their turn, there by leading to a long chain of different radioactive elements in the form of a series until an inactive element is reached.

The series of elements thus obtained by the successive disintegration of the new atoms in known as radioactive disintegration series and the spontaneous breaking up of the nucleus is known as radioactive disintegration.

(i) Uranium series [(4n+2) series]

(ii) Thorium series [4n series]

(iii) Actinium series [(4n+3) series]

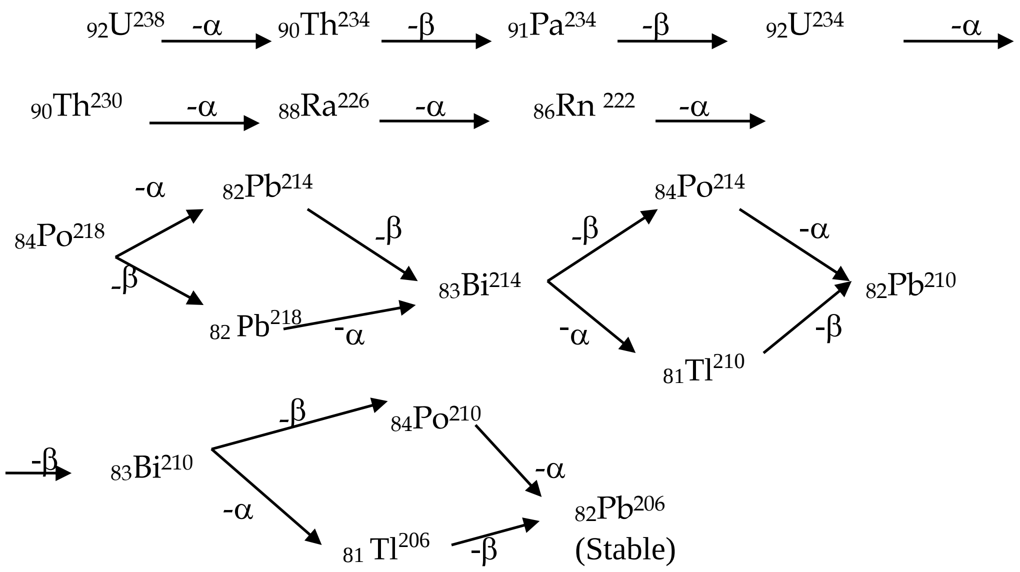
These series have been named after the name of the element at or near head of the respective series. All the three series which are also called natural radioactive series end with a stable isotope of lead.

Some elements of the each series emit α - particles whereas some other elements emit β - particles.

1. Uranium series [(4n+2) series].

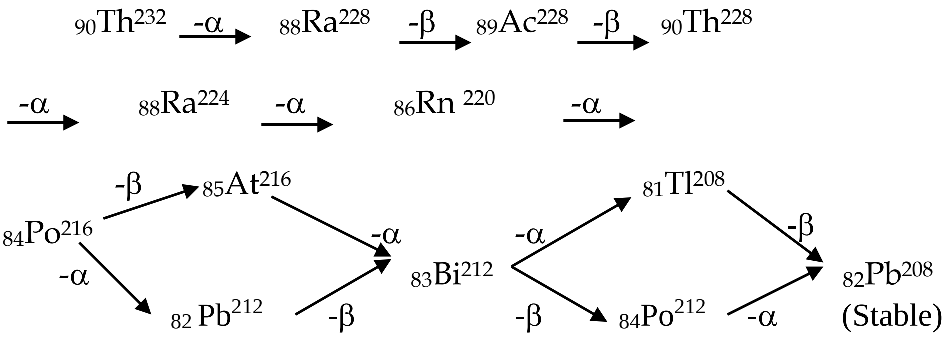
This series is also called (4n+2) series because the mass number of the elements of this series are given by this expression in which n is an integer whose value increases by unity when we go from one radioactive element to the next one below it.

The mass numbers of the members of this series give a remainder of 2 when devided by 4. In $_{92}U^{238}$ is the parent element and through the successive disintegrations it is finally transformed into a stable isotope of lead $_{82}Pb^{206}$.



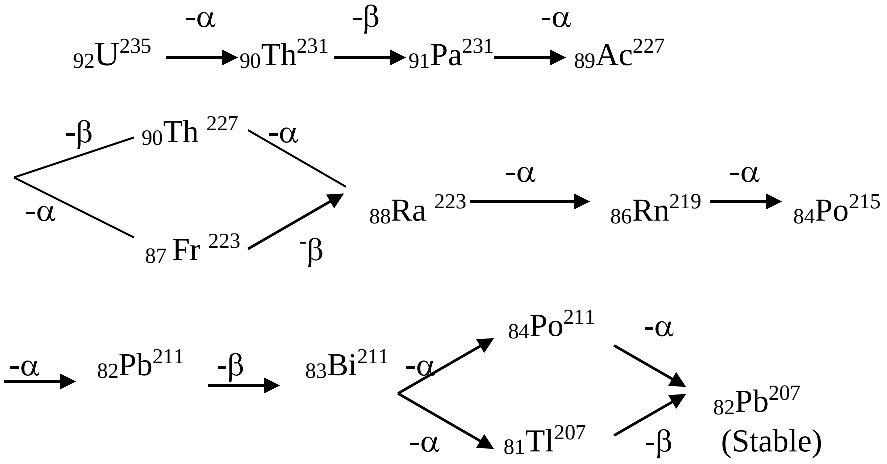
2) Thorium Series: (4n series)

This series is also known as 4n series because mass numbers of the members of this series are divisible by 4. This series starts with $_{90}Th^{232}$. As shown in fig. 1 by a successive trans mutation or disintegration it ends up in a stable isotopes of lead $_{82}Ph^{208}$



3. Actinium series [(4n+3) series]

This series is also known as (4n+3) series because the mass numbers of the members of this series give a remainder of 3 when divided by 4. Actinium was one time thought to be the starting element of this series, but now it is known that the true starting element is $_{92}U^{235}$ which by successive transformations ends up in a stable isotope of lead, $^{207}Pb_{82}$, the whole chain of elements.

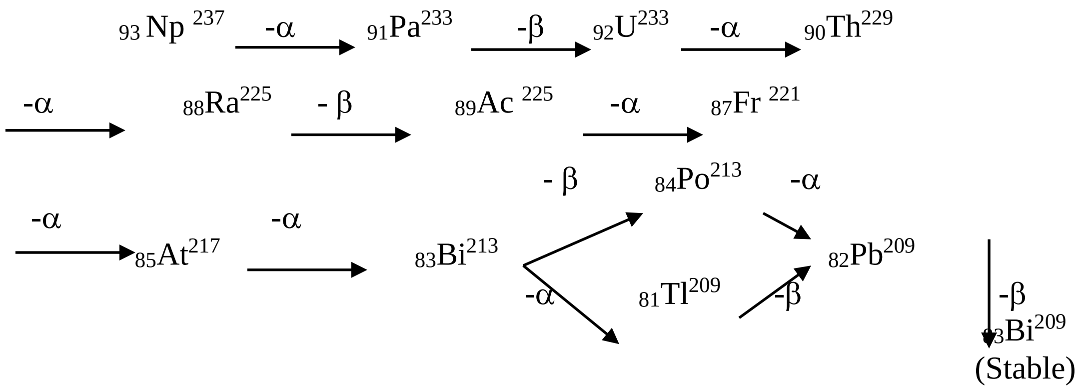


Similarities between radioactive series:

1. In all series a product is formed which disintegrates in a branching process by emitting either α or -β particle. The two substances thus produced are then transformed in such a way as to give a common product.
2. In all there is an element of atomic number 86 which has the properties of an inert gas and is called emanation.
3. The stable end – product in all the three series having an atomic number of 82 is an isotope of lead Pb^{206}

Neptunium series [(4n+1) series]

In addition to the three series described above, there is a fourth series which has been obtained from an artificially produced radioactive material. The first element in the series is ${}_{93}Np^{237}$ after which it has been named and the stable end product is the ordinary bismuth, ${}_{83}Bi^{209}$ rather than an isotope of lead as in the uranium actinium and thorium series. This series is also known as (4n+1) series.



Group displacement law:

When an α -particle is emitted from a radioactive element (i.e. parent element), the new element (i.e. daughter element) formed has atomic number two units less than that of the parent element. It is consequently displaced two places to the left in the periodic table.

When an β -particle is emitted, the daughter element will have atomic number one unit more than that of the parent element and will thus belong to the next group to the right in the periodic table. This is termed as Group displacement law.

Example:

Polonium (${}_{34}Po^{215}$) is in group VIA of the periodic table. On losing an α -particle, it is transformed into radioactive Lead, ${}_{32}Pb^{211}$, which belongs to group IVA, ie. two places left to the parent element Polonium.

$$ {}_{34}Po^{215} \xrightarrow{\qquad\qquad} {}_{32}Pb^{211} + \alpha $$

Nuclear binding energy and mass defect

It has been observed that the experimental value of atomic mass (A) of an isotope of an element is invariably less than the sum (M) of the masses of protons neutrons (called nucleons) and electrons present in the atom of the element. The difference between the two masses is called mass defect and is denoted by ΔM.

$$\text{Mass defect} \quad (\Delta M) \quad = \left\{ \begin{array}{l} \text{Sum of the masses of protons and} \\ \text{neutrons (M) – Experimental} \end{array} \right\}$$

Value of atomic mass of the isotope (A)

$$\Delta M = M - A$$

Binding energy:

When the nucleons are allowed to combine together to form the nucleus, some mass disappears in the form of energy. In the combination of nucleons to form the nucleus, some amount of energy is released.

The energy released in the formation of a nucleus from its constituent nucleons is called binding energy of the nucleus. If ΔM is the mass defect in a.m.u, the binding energy of the nucleus in Mev is equal to ΔM x 931 Mev, since 1 a.m.u = 931 Mev of energy. The greater the mass defect, the greater is the binding energy of the nucleus. The binding energy of a nucleus divided by the total number of nucleons (i.e neutrons + protons) is called the binding energy per nucleon in the atom.

$$\text{Binding energy per nucleon} = \frac{\text{Binding energy}}{\text{Neutrons + Protons}}$$

Calculation of Binding Energy :

Example:

Calculate the binding energy of lithium nucleus given that

Mass of proton = 1.00814 amu

Mass of neutron = 1.00893 amu

Mass of lithium nucleus = 7.01822 amu

Solution:

Obliviously the lithium isotopes considered is $_{3}\text{Li}^{7.}$ It contains 3 protons and (7-3) = 4 neutrons.

Mass of 3 protons = 3 x 1.00814 = 3.02442 amu

Mass of 4 neutrons = 4 x 1/00893 = 4.03572 amu

Total mass of 7 nucleons = M = 7.06014 amu

Mass of the lithium nucleus , A = 7.01822 amu

Mass defect ΔM = M-A = 7.06014 – 7.01822

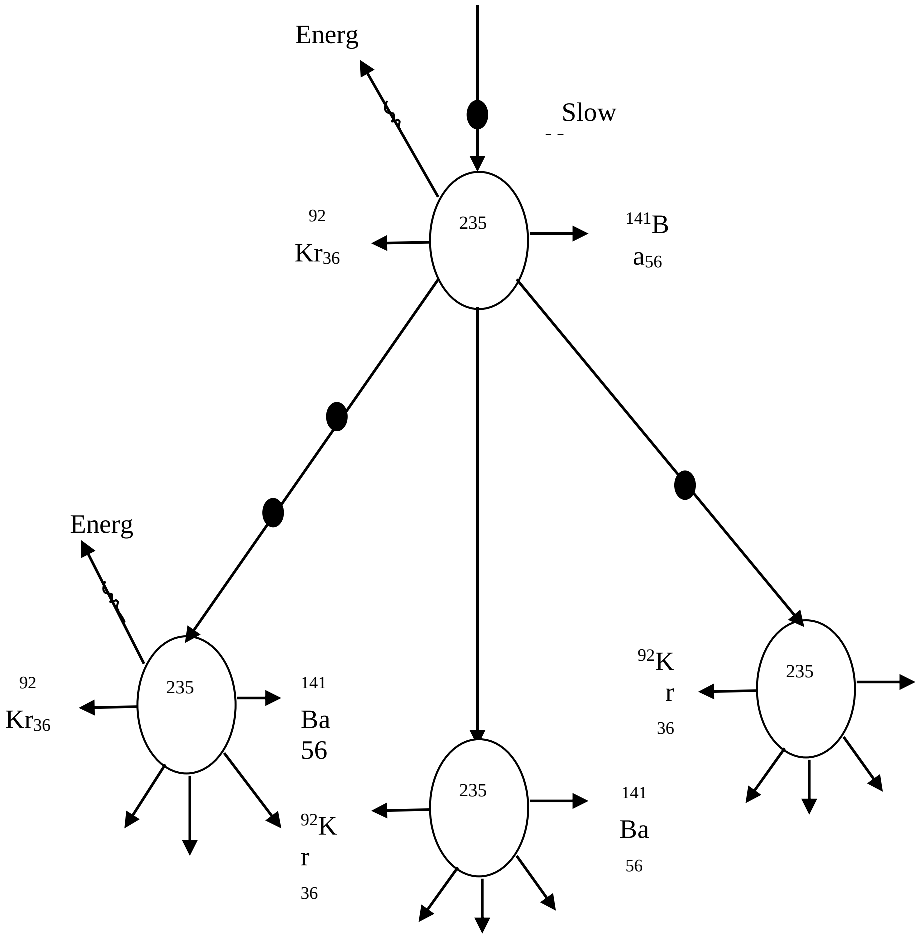
= 0.04192 amu

∴ Binding energy = 931 x 0.04192

= 39 Mev

Nuclear Fission Reaction:

The nuclear reactions in which one heavier nucleus is split up into two lighter nuclei of almost equal size with the release of a huge amount of energy is called nuclear fission or atomic fission.



$^{235}U_{92}$ with slow moving neutrons and observed that ^{235}U nucleus, after capturing neutron, gave ^{236}U nucleus which was radioactive and hence had broken up to from ultimately a pair of stable products (called fission products) consisting of $^{141}Ba_{56}$ and $^{92}Kr_{36}$ and liberated three neutrons (called secondary neutrons) in addition to a huge amount of energy, called fission energy.

$$^{235}_{92}U + {}^{1}n \longrightarrow {}^{236}_{92}U \longrightarrow \underbrace{{}^{141}_{56}Ba + {}_{36}Kr^{92}} + 3\,{}_{0}n^{1} + \text{Energy}$$

Nucleus Products (Fission products)

In the nuclear fission reaction a huge amount of energy is also liberated. One $^{235}U_{92}$ nucleus by one neutron obtained either by cosmic rays or by some radioactive source. In this fission process, each $^{235}U_{92}$ nucleus suffering fission will liberate three neutrons. These three neutrons will in turns caches the fission of other three $^{235}U_{92}$ nuclei and will liberate three more neutrons in the fission of each $^{235}U_{92}$ nucleus. The nine neutrons will be obtained so on. This chain reaction continues till the whole of $_{92}U^{235}$ has undergone fission. The chain reaction is also accompanied by the liberation of a huge amount of energy which is called fission energy or atomic energy.

Approximately 200 Mev of energy is released by the fission of one $_{92}U^{235}$ nucleus.

Nuclear Fusion:

Two or more nuclei have a tendency to combine or fuse together to give the nucleus of higher mass number and higher binding energy or stability. Such a nuclear reaction in which two lighter nuclei are combined or fused together to form a heavier nucleus is called nuclear fission.

In this respect, nuclear fusion is the opposite of nuclear fission in which one heavier nuclear is split up to two lighter nuclei. In nuclear fusion also, large amount of energy is released because the mass of the product nucleus is less than the masses of the two nuclei which are fused together.

Nuclear fusion occurs at reasonable rates only at very high temperatures. Because of this that nuclear fusion reactions are also called thermonuclear reactions. ie. Temperature – dependent reactions.

Nuclear fusion of two hydrogen isotopes

$$_1H^1 + {}_1H^1 \longrightarrow {}_2H^1 + {}_{+1}e^0 + 0.42\ \text{Me}$$

$$_1H^2 + {}_1H^1 \longrightarrow {}_2He^3 + 5.50\text{Mev}$$

$$_6C^{13} + {}_1H^1 \longrightarrow {}_7N^{14} + 7.55\text{Mev}$$

$$_1H^2 + {}_1H^2 \longrightarrow {}_2He^3 + {}_0n^1 + 3.3\text{Mev}$$

$$_1H^2 + {}_1H^3 \longrightarrow {}_2He^4 + {}_0n^1 + 17.6\text{Mev}$$

Difference between Nuclear fission and Nuclear fusion

S. No	Nuclear fission	Nuclear fusion
1	The process occurs only in the nuclei of heavy elements.	The process occurs only in the nuclei of light elements.
2	In this process heavy nuclei splits of into two lighter nuclei	In this process heavy nuclease is formed.

3	This process is carried out at room temperature.	The process is takes place at higher temperature (108^0c).
4	Nuclear fission the process can be controlled for useful purpose.	The process can't be controlled.
5	It is a chain Process.	It is not a chain process.
6	In this process higher amount of energies liberated (200Mev)	In this process less amount of energies is liberated (3.25 Mev)
7	Nuclear waste is formed.	No nuclear wastes.

Steller Energy:

Steller energy is the energy of the sun and other stars of the main sequence. Van weizsacher and Hans Beth (1932) proposed that steller energy is due to a series of nuclear reactions involving carbon-hydrogen nitrogen cycle which operates through the following steps.

$${}_{6}C^{12} + {}_{1}H^{1} \longrightarrow {}_{7}N^{13} + 1.94\text{ Mev}$$

$${}_{7}N^{13} \longrightarrow {}_{6}C^{13} + {}_{+1}e^{0} + 1.20\text{ Mev}$$

$${}_{6}C^{13} + {}_{1}H^{1} \longrightarrow {}_{7}N^{14} + 7.55\text{Mev}$$

$${}_{7}N^{14} + {}_{1}H^{1} \longrightarrow {}_{8}O^{15} + 7.29\text{Mev}$$

$${}_{8}O^{15} \longrightarrow {}_{7}N^{15} + {}_{+1}e^{0} + 1.74\text{Mev}$$

$${}_{7}N^{15} + {}_{1}H^{1} \longrightarrow {}_{6}C^{12} + {}_{2}He^{4} + 4.96\text{ Mev}$$

on adding the above nuclear reaction,

$$4\,{}_{1}H^{1} \longrightarrow {}_{2}He^{4} + 2\,{}_{+1}e^{0} + 4.96\text{ Mev}$$

Nuclear reaction(1) indicates that the steller energy is produced due to the fusion reaction in which four H-atoms (or protons) are fused together to produce one helium nucleus and two positions on the sun the fusion of four H-Nuclei into helium nucleus does not take place through a single step but takes place through deutrium (${}_{1}H^{2}$) are shown below.

$${}_{1}H^{1} + {}_{1}H^{1} \longrightarrow {}_{1}H^{2} + {}_{+1}e^{0} + 0.42\text{ Mev}$$

$${}_{1}H^{2} + {}_{1}H^{1} \longrightarrow {}_{2}He^{3} + 5.50\text{Mev}$$

$${}_{2}He^{3} + {}_{2}He^{3} \longrightarrow {}_{2}He^{4} + {}_{1}H^{1} + 12.80\text{Mev}$$

On adding the above equations,

$$4\,{}_{1}H^{1} \longrightarrow {}_{2}He^{4} + 2\,{}_{+1}e^{0} + 24.64\text{Mev}$$

Applications of Radio Isotopes

(i) Carbon 14 dating :

The age of recent objects such as those of animals or vegetable origin like a piece of wood or animal fossil can be determined by radio-carbon dating method, since rock dating method is useful only for the minerals or rocks of considerable age.

The determination of the age of a sample of wood (i.e. the time which elapsed after the death of the living plants) consist of determining the ratio of the amount of ${}_{6}C^{14}$ to that of ${}_{6}C^{12}$ in both the pieces of wood, i.e, in fresh (living) piece and dead (act) piece.

We know that the atmospheric carbon dioxide is a mixture of $C^{14}O_2$ and $C^{12}O_2$ which are present in a fixed ratio. Plants absorb carbon dioxide from the atmosphere and prepare cellulose (wood). As long as the plant is alive, the ratio of ${}_{6}C^{14}$ to ${}_{6}C^{12}$ atoms in the wood of the plant is the same as the atmosphere but when the tree is cut (ie when the plants dies), the ratio of ${}_{6}C^{14}$ to ${}_{6}C^{12}$ begins to decrease continuously due to continuous decrease in the amount of ${}_{6}C^{12}$ in the plant this decrease in the amount of ${}_{6}C^{14}$ is due to its continuous disintegration emitting of β– radiations as shown,

$$ {}_{6}C^{14} \xrightarrow{\hspace{2cm}} {}_{7}N^{14} + \beta \text{ Particle} $$

Now,

$$ N = N_o.e^{-\lambda t} $$

$$ t = \frac{2.303}{0.693} \log_{10} \frac{N_o}{N} $$

No = C^{14}/C^{12} ratio in the living (fresh) plant

N = C^{14}/C^{12} ratio in the dead (cut) plant

(ii) Rock – Dating :

The age of a rock (i.e., the time that elapsed since the rock crystallized from the molden state) given an approximate idea about the age of the earth, provided it is assumed that the rock or the mineral under examination is as old as the earth. Let us consider a rock containing U^{238} isotope formed many years ago. The age of this rock can be determined by considering its radioactive disintegration which as we have already seen, is governed by relation.

$$N = No,\ e^{-\lambda t}$$

Where,

No = Amount of U-238 isotope originally present in a small quantity of the rock or mineral at the time the rock was formed.

N = Amount of U-238 still left undulated after the lapse of time, t, which represents the age of the rock, and

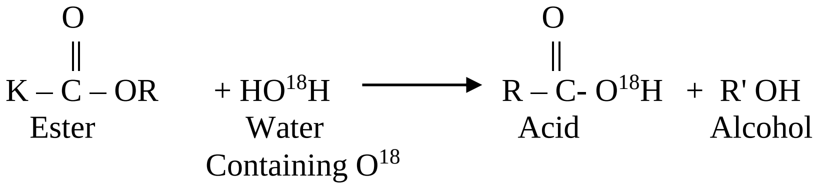
λ = disintegration constant of U-238.

Isotope Tracers :

`Radio active isotopes have a property due to which they can easily be detected and estimated quantitatively. Further, they reach almost exactly as the corresponding non-radioactive isotopes do. As such, if we want trace the course of an atomic species in a chemical or a physical change, we mix a small quantity of the radioactive isotope with non-radioactive isotope is acting as a radioactive tracer or radioactive indicator or simply labelled or tagged element.

Study of Reaction Mechanism (ester hydrolysis)

Mechanism of ester hydrolysis has been studied by using O^{18} isotope. It is observed that when an ester is hydrolyzed by water containing O^{18} (i.e. H_2O^{18}), the alcohol formed does not have any) O^{18} while the acid has the whole of it. The presence of O^{18} in the acid proves that the – OR' group in the ester is wholly replaced by – $O^{18}H$ group in H_2O^{18}. Thus the hydrolysis should correctly be shown as:



$$\underset{\text{Ester}}{K-\overset{\overset{\displaystyle O}{\|}}{C}-OR} \quad + \underset{\substack{\text{Water}\\ \text{Containing } O^{18}}}{HO^{18}H} \longrightarrow \underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\ O^{18}H} \ + \underset{\text{Alcohol}}{R'\,OH}$$

Radiodiognosis P:

Radio isotopes have proved very useful in the diagnosis and understanding many of the diseases.

(a) Location and detection of brain tumour.

Labelled Iodine has been used to locate and detect the presence of tumour. To locate it a small quantity of radioisotope of iodine mixed with an organic dye injected into the body of the patient. Dye with radioisotope is strongly absorbed by the tumour and radiations are produced. Detection of these radiations gives valuable information regarding the limits of the growth and location of the tumour.

(b) Functioning of thyroid gland :

Radioisotope of iodine, I^{131} with T = 8 days is given to a patient with thyroid disorders. It decays β - rays. Detection of these rays gives information regarding the functioning of the thyroid gland.

1. Disorders associated with pregnancy: Tracer iron has been used in studying the disorder associated with pregnancy.
2. Test of cancer growth: ^{50}Co emits high energy γ - rays which are used for testing deeply seated cancer growth.
3. Circulation of blood: Radio sodium Na^{24} (T = 15 hours, β - particle emitter) has been used to study causes of restricted circulation of blood.

Radiotherapy:

The treatment of diseases by the use of radioisotopes is called Radiotherapy.

(a) Treatment of thyroid complaints:

Radioactive iodine I^{131} has been used for the treatment of certain thyroid complaints. Stable iodine and radioactive iodine are preferentially absorbed by the thyroid gland. This fact is utilized in the treatment of hyperthyroidism and cancer of the thyroid. Radioactive iodine destroys abnormal tissues in the thyroid gland more rapidly and in this way checks the abnormal growth.

(b) Treatment of blood disorders:-

Radioactive phosphorus in the form of phosphate is widely used in the treatment of certain blood disorder.

(c) Treatment of cancer growth: -

Radio cobalt (Co^{60}) produced by the action of neutrons from a nuclear pile. T = 5.3 days, Υ - rays emitter are used in the treatment of some forms of cancer Co^{69} has been called poor man's radium

(d) Treatment of leukaemia.

Radioisotope of phosphorus is being used for the treatment of leukaemia.

(e) Treatment of skin diseases:

Radio phosphorus (p^{30}), T = 14.3 days, β - emitter is found good for skin diseases.

PHOTOCHEMISTRY:

The absorption of light and photochemical processes:

In ordinary chemical reactions the activations energy is supplied by thermal energy. Such reactions are called thermal reactions or dark reactions. An alternate way in which the necessary activation energy can be acquired is through the absorption of quanta of visible or ultraviolet radiations. Such reactions are called photochemical reactions. When light falls on matter, it may be transmitted, reflected, refracted, scattered or absorbed. In photochemistry we are concerned only with the light absorbed.

Grothus-draper law:

According to this law, chemical change is produced in a system only by those radiations which are absorbed. In other words there can not be a photochemical reaction unless the radiation is absorbed.

It does not mean that all the absorbed radiation cause the chemical reaction. A part of it may be converted into heat energy or may be re-emitted as radiations of same or different frequency. If the absorbed light is re-emitted with the same frequency or with some other frequency, it is called fluorescence if the emission of radiation continues for some time after the removal of the light source, it is called phosphorescence. Grothus Draper law is also called the first law of photochemistry.

Stark-Einstein law of photochemical equivalence:

This is the second and most important law in photochemistry. According to this law "each molecule taking part in a photochemical reaction absorbs one quantum of radiation".

If ν is the frequency of absorbed radiation, then each molecule absorbs energy equal to hν. Where h is the Planck's constant. Therefore the energy absorbed by one mole of the substance will be Nhν. Where, N is the Avogadro number ($6.023X10^{23}$). The quantity Nhν is called one Einstein.

$$E = h\nu$$

$$E = Nh\nu$$

$$Nh\nu$$

$$E = \frac{\quad}{4.185X10^{7}} \text{ calories per mole } (1cal = 4.185X10^{7} \text{ ergs})$$

We know that $\gamma = C/\lambda$. Where λ is the wavelength and C is the velocity of light = $3 X 10^{10}$ cm/sec.

Quantum yield

We have seen that the energy absorbed per mol of the reacting substance is called one Einstein. The number of mole reacting for each einstein of radiation is studied under quantum yield. Otherwise quantum yield or quantum efficiency is the ratio between the number of moles of the substance reacting chemically and the number of einstein of light energy absorbed.

$$\varphi = \frac{\text{Number of moles substances reacting chemically}}{\text{Number of einstein absorbed}}$$

If we consider he reacting substance is number chemically

$$\varphi = \frac{\text{Number of molecules reacting chemically}}{\text{Number of quanta of light absorbed}}$$

One Quantum:

The energy absorbed by one molecule of the reactant during photo chemical reaction is called one quantum. It is denoted as,

$$E = h\nu$$

Where,

E = Energy in ergs

h = Plank's constant ($6.625 X 10^{-27}$ ergs sec)

ν = frequency of reaction

One Einstein:

The energy absorbed by one mole of the reactant during photochemical reaction is called one Einstein.

$$E = Nh\nu$$

Where,

E = Energy in ergs

N = Avagadro Number ($6.023X10^{23}$)

h = Plank's constant ($6.625 X 10^{-27}$ ergs sec)

ν = frequency of reaction

Photochemical reactions:

A chain reaction is one in which the products carry on the reaction on the part of the reacting molecules and thus a long series of self-repeating steps is started.

These reactions were first proposed by Bodenstein to account for the high yield of photochemical reaction between hydrogen and chlorine. In this case the quantum yield is abnormally high. In such reactions it is proposed that they proceed via chain mechanism.

Primary and Secondary processes:

The study of photochemical reaction gives an idea about the mechanism of the reaction. A photochemical reaction may be considered to be consisting of two stages.

1. Primary process and
2. Secondary process

Primary process:

In the primary process, light is absorbed by an atom or a molecule. 'A' giving rise to the formation of an excited atom or a molecule A*.

$$A + h\nu \longrightarrow A^*$$

The excited molecule may give atoms or free radicals.

Secondary processes:

The products of primary process, namely the excited atom or molecule A* may undergo any of the following three steps.

1. The excited atoms or molecules may give the products.
2. The excited molecules may collide with the reactants and lose energy.
3. The excited molecules may emit energy and return to their normal state. This process is called fluorescence.

Hydrogen – Chlorine reaction:

This is a well known example of a photochemical chain reaction. A mixture of hydrogen and chlorine is exposed to light of wavelength less than 4000A^0.

Hydrogen an chlorine combine photo chemically to give HCl.

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

The quantum yield of this reaction is in the order of 10^5.

The mechanism of this reaction is as follows.

i) Primary process:

A chlorine molecule absorbs a quantum of light and becomes atoms. The; quantum yield of this process is one [φ = 1]

$Cl_2 + h\nu \longrightarrow 2Cl^{\bullet}$ (Chain initiation)---------------(

ii) Secondary process:

The Chlorine radical produced in the above step combines with H_2 producing HCl.

$Cl^{\bullet} + H_2 \longrightarrow HCl + H^{\bullet}$ ---------------(

In turn hydrogen radical combines with Cl_2 produce HCl and Chlorine radical.

$H^{\bullet} + Cl_2 \longrightarrow HCl + Cl^{\bullet}$ ---------------(

Step (3) has produced another Chlorine radical. Hence steps (2) and (3) take place indefinitely resulting in a high quantum yield φ. Such a reaction, which proceeds by a series of successive process is called a chain reaction. The free radicals $Cl^{\bullet}$ and $H^{\bullet}$ produced in steps (s) and (3) respectively are called chain carriers. The chain will continue until whole of the hydrogen or chlorine has been used up. Some chain terminating steps also take place.

Example:

$H^{\bullet} + H^{\bullet} \longrightarrow H_2$ (Chain terminating)-----------

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$ (Chain terminating)-----------(

$H^{\bullet} + Cl\cdot \longrightarrow HCl$ (Chain terminating)-----------(

The quantum efficiency of this reaction high (=10^5 to 10^6), because the steps (2) and (3) are repeated several times before the chain termination reaction (4) to (6) could occur.

Photosynthesis:

Photosynthesis is a light driven process in which CO_2 is fixed to yield carbohydrates (CH_2O).

$$CO_2 + H_2O \longrightarrow (CH_2O) + O_2$$

This process, in which both CO_2 and H_2O are utilized to yield carbohydrate and O2, is essentially the reverse process of oxidative carbohydrate metabolism. Photo synthetically produced carbohydrates therefore serve as an energy source for the organism produced them as well as for non-photosynthetic organisms that directly or indirectly consume photosynthetic organisms. Ultimately life on the earth depends on solar energy. Therefore, the important aspect of photosynthesis is the ability to capture solar energy for the reduction of carbon. It is estimated that photosynthesis annually fixes ~10^{11} tons of carbon, which represents the storage of over 10^{18} kJ of energy. Moreover, photosynthesis is responsible for the production of oxygen in the earth's atmosphere.

PHASE RULE

Meaning of the Terms

Phases (P)

A heterogeneous system consists of two or more homogeneous parts separated from each other by distinct boundaries. These homogeneous, physically distinct and mechanically separable parts of a heterogeneous system are called phases. For a system containing pure water in equilibrium with its vapour is said to have two phases. A solution of sugar in water is a one phase system. As immiscible mixtures of carbon tetra chloride and water represents a system with two phases.

Components (C)

The number of components in a system at equilibrium is the minimum number of chemically distinct constituents by means of which the composition of each phase can be expressed. E.g.,

I. Water exists in three phases which can be in equilibrium. Ice, liquid water and water vapour. Though there are three phases one component is enough to define the whole system. The component is H_2O
II. In the dissociation of PCl_5, the system contains PCl_5, PCl_3 and Cl_2 . Three species are present but there are only two components. This is because when we alter the concentration of any two of these, the concentration of the third is automatically fixed.

Degrees of Freedom (F)

After specifying the phases and components one has to specify a number of additional variables are pressure, temperature, energy content, entropy, concentration of the components etc., so, the degrees pf freedom is defined as the minimum number of independent variables such as pressure, temperature, composition of phases etc., which must be arbitrarily fixed in order to describe the system completely.

Examples:

i) A system containing a pure gas: We know that for a given mass of gass PV=nRT. So any two of the three variables P, V and T will define the system completely. So this system has two degrees of freedom.

ii. Water $\rightleftharpoons$ Water vapour system. This system has only one degree of freedom because if we specify the temperature of the system the aqueous tension (i.e., pressure of vapour) is automatically known and vice-versa.

DERIVATION OF GIBB'S PHASE RULE

Thermodynamic derivation

Consider a heterogeneous system having P phases and C components. The degree of freedom F of the system is equal to the minimum number of independent variables, which must be fixed to define the system. Otherwise the degree of freedom is equal to the total number of variables minus the total number of relations in equilibrium.

Total numbers of Variables:

1. **Temperature:** At equilibrium each phase has the same temperature. So there is one temperature variables for the whole system.
2. **Pressure:** At equilibrium each phases has the same pressure. So there is one pressure variables for the whole system.
3. **Composition**: Suppose there are two components A and B in a phase. If the mole fraction (Concentration) or A is 0.4 then that of B is known to be 1 – 0.4 = 0.6. Thus with two components, concentration of one component is enough to define the system. In a phase, if there are 3 components is enough to define the system. In (3-1) =2 components, the concentrations of C-1 components are necessary to define the system. If these 'C' components present in 'P' phases, for each phase we require, the concentrations of C-1 components. So the total composition variable is P(C-1)

$$\text{Total number of Variables} = 1 + 1 + P\,(C–1)$$
$$= P\,(C-1) + 2$$

Number of relations at equilibrium:

According to thermodynamics, for a system in equilibrium the chemical potential of a component is the same in all the phases. Suppose we have a component A in three phases 1, 2 and 3.

$$\mu_{1A} = \mu_{2A}$$
$$\mu_{2A} = \mu_{3A}$$

So if we have three phases we will have two equations (relations) if we have ‘P’ phases, then the number of relations will be P-1. This is for one component A. If we have ‘C’ components then the total number of relations will be C (P-1).

$$\left(\begin{array}{c}\text{The degree}\\ \text{of}\\ \text{Freedom F}\end{array}\right) = \left(\begin{array}{c}\text{Total}\\ \text{number}\\ \text{of variables}\end{array}\right) - \left(\begin{array}{c}\text{Total}\\ \text{number}\\ \text{of relations}\end{array}\right)$$

Thus,

$$F = P\,(C – 1) + 2 – C\,(P-1)$$
$$= P\,C – P + 2 – PC + C = C – P + 2$$

So, $\mathbf{F = C – P + 2}$

This equation is the Gibbs phase rule.

The Reduced Phase Rule Equation for two component condensed systems :

In a two component system when P = 1. F has the highest value 3.

$$F = C – P + 2$$
$$= 2 – 1 + 2 = 3$$

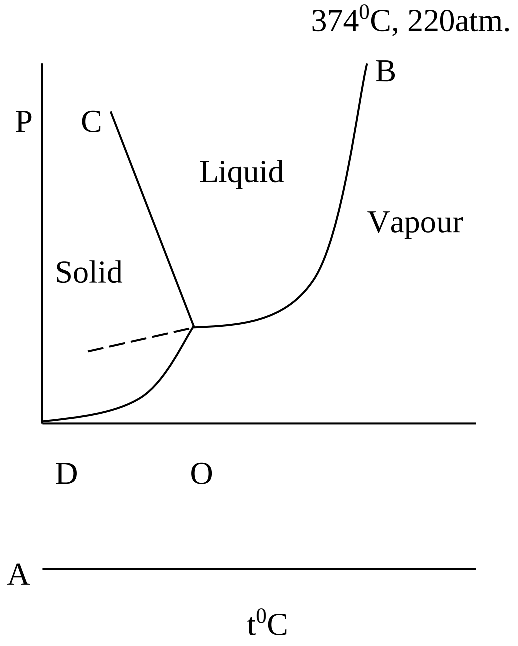
Thus three variables pressure, temperature and the concentration of one of the components must be specified in order to describe the system. A set of three co-ordinate axes at right angles to one another would be required to represent these relations graphically. However the usual practice is to disregard the vapour phase and to fix an arbitrary pressure of 1 atmospheric pressure. The experimental work is then done in an open vessel at 1 atmospheric pressure. Of course, the pressure under these conditions will not be the equilibrium pressure. However for solid liquid equilibria the effect of pressure is negligible since the vapour pressures of solids are small. Thus the results obtained are substantially the same as if the system were in true equilibrium with its vapour. Such systems in which only liquid and solid phases are considered are known as condensed systems. If pressure is kept constant then

$$\mathbf{F = C - P + 1}$$

This is known as the **Reduced Phase Rule or Reduced Phase Rule Equation.** In all the discussions of two component systems it is assumed that the pressure is kept constant and the reduced phase rule equation only will be used.

One component systems

1. Water System



Water system is a one component system. Liquid water contains a larger number of chemical species. E.g., H_2O. $(H_2O_2)_2$, $(H_2O)_3$…. In addition to this we have vapour phase (water vapour) and solid phase (ice). It has only one component H_2O. The phase diagram for water is shown in Figure 16.

The Areas: Solid, liquid and vapour can exist in the areas AOC, COB, and AOB respectively.

That is in each area only one phase is present.

Thus it is necessary to specify two degrees of freedom which are temperature and pressure in this case.

The lines: On each line two phases co-exist in equilibrium.

So, $F = 1 - 2 + 2 = 1$

To define any point along a line it is enough if we specify only one degree of freedom, namely, either temperature or pressure.

AO is the sublimation curve of ice. Along this curve ice and water vapour co-exist in equilibrium. The lower limit of this curve is absolute zero. (We know that sublimation is a process in which a solid becomes a liquid. Along AO we field that only solid and vapour can co-exist. This account for the property of sublimation).

OB is the vapour pressure curve of vapourisation curve of water. Along the curve liquid water and water vapour co-exist in equilibrium. B is the critical point (P_c=220 atm ; T_c = 374°C). Above this point is not possible to distinguish between water and water vapour.

OC is the fusion curve of ice. This curve shows the temperature at which the two phases ice and water are in equilibrium at various pressure. This curve shows that the effect of pressure. This curve OC slopes slightly towards the pressure axis. It means that the melting point is lowered slightly by the increase of pressure.

Triple point: 'O' is the triple point. We have seen that water and vapour are in equilibrium along OB and vapour and ice, are in equilibrium along OA. Therefore three phases namely ice, water and vapour co-exist 'O'. So this is called the triple point. If phase rule is applied to the triple point,

$$F= 1 - 3 + 2 = 0$$

This is a non variant point. The three phases co-exist at the temperature 0.00098°C and pressure 4.58 mm. It means that it can have no degree of freedom.

Meta-stable equilibrium:

Fahrenheit observed that under certain conditions water can be cooled to -9°C without separation of ice. This is called super-cooled water. Such an equilibrium is called meta-stable equilibrium. Curve OD represents this meta-stable equilibrium.

Application of Clapeyron equation H_2O systems:

The slope of fusion curve is negative (slopes towards the pressure axis) in the water system. In the case of water the molar volume of solid ice is greater than the molar volume of liquid water, so ΔV of H_2O is negative.

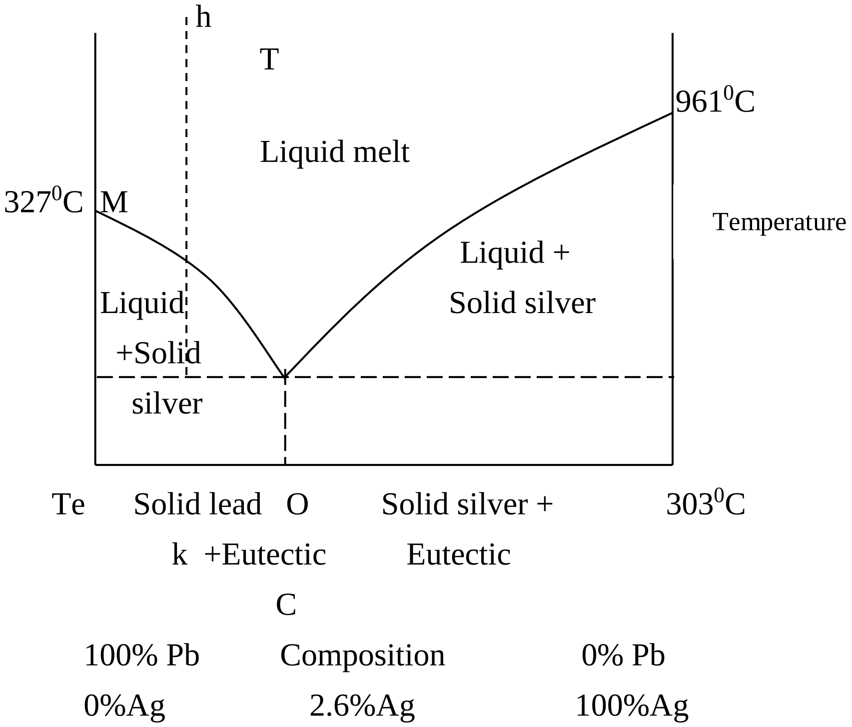
From Clapeyron equation,

$$\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V}$$

ΔS is always positive. The slope of the curve $\Delta P/\Delta T$ will depend upon the value of ΔV only. It is negative in the case of water.

Lead – Silver Systems

It is two component systems. The two components do not react chemically but mix in the liquid state. The vapour is negligible and hence the three phases of the systems are solid silver, lead and solution of Ag and Pb.



In the diagram N represents the melting point of Ag and M melting point of pure Pb. The curve NO shows the variation of the melting point of Ag on addition of Pb. Similarly MO shows the variation of melting point of Pb on addition of Ag.

O is the point at which solid Ag. Solid Pb and liquid are in equilibrium. This is called the eutectic point. For this point F=2-3+1=0. So eutectic point is a non- variant point. Above MON only the liquid can text

So, $F = C - P + 1$

$= 2 - 1 + 1 = 2$

The system above MON is bivariant. Below the line POQ no liquid can exist

The two solid phases namely pure silver and pure lead are present. In the area NOQ solid silver and liquid are in equilibrium and on MOP solid lead and liquid are in equilibrium.

NOTES

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

UNIT - V

5.1. Solutions: Liquid in liquid type-Raoult's law for ideal solutions. positive and negative deviation from Raoult's law-Reasons and examples, Fractional distillation and Azeotropic distillation.

5.2. Colligative properties: Review of colligative properties of dilute solutions-lowering of V.P, elevation of B.Pt and depression of F.Pt and osmotic pressure. Reverse osmosis. Abnormal molecular weights-van't Hoff factor-degree of dissociation and association-problems.

5.3. Chromatography: principle and application of column, paper and thin layer chromatography.

5.4. Electro Chemistry: Kohlrausch law -measurement of conductance, pH determination. Conductometic titrations. Hydrolysis of salts.

Derivation of K_h. pH and buffer action in living system. Galvanic cells-EMF-standard electrode potentials, reference electrodes, electrochemical series and its applications. Principle of electroplating, pH determination

Solutions

A solution is defined as a homogeneous mixture of two or more chemically no-reaction substances. Therefore, a solution forms a single phase. A solution may be gaseous, liquid or solid.

Binary solution:

A binary solution consists of two constituents. The constituents of a solution are classified as solvent and solute. A solvent is that constituent, which is present to a larger extent in the solution. A solute is that constituent, which is present to a smaller extent in the solution. The following are some examples for this kinds of solutions.

Types of binary solutions:

1. A liquid dissolved in a liquid. eg. Alcohol in water.
2. A solid dissolved in a liquid. eg. NaCl in water, Sugar in water.
3. A gas dissolved in a liquid eg. CO_2 in water.

Liquid in liquids:

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another the following three cases are possible.

i) Completely miscible: Where the two liquids are soluble in each other in all proportions. eg. Benzene in toluene, alcohol in water etc.,

ii) Partially miscible: In which liquid is soluble in another to some extent only. The resulting mixture separates into two layers each being a solution one in the other. eg. Phenol and water, Nicotine and water.

iii) Immiscible: In this case, the two liquids do not at all dissolve in each other and remain separated in the mixture. eg. CCl_4 and water, benzene and alcohol, carbondisulphide and water etc.

Raoult,s law:

Law:

The partial vapour pressure of any volatile constituent of a solution at a given temperature is equal to the product of vapour pressure of the pure constituent and its mole fraction in solution.

Explanation:

Let us consider a solution of liquid 2 at a given temperature T

$$P_1 = X_1 P_1^O$$

Where P_1 = Partial pressure of pure liquid 1 in solution

P_1^O = Vapour pressure of pure liquid 1

X_1 = Mole fraction of liquid 1 solution 1 solution.

Similarly $P_2 = X_2 P_2^O$

P_2 = Partial pressure of liquid 2 in solution

P_2^O = Vapour Pressure of pure liquid 2

X_2 = Mole fraction of liquid 2 in solution

Ideal Solution:

A solution is said to be an ideal solution if the molecules in it attract one another with equal force irrespective of the nature. This if we have an ideal solution of B in A, the forces between A and A, B and B and A and B should be the same. An ideal solution obeys Rauolt,s law .

Example:

i) Benzene and toluene

ii) Cyclohexane and Carbon Tetra Chloride these are completely miscible binary liquid systems.

Let us discuss the Benzene-Toluene system. This system behaves ideally to a good degree of accuracy. The partial pressure of benzene and toluene are linear function of the mole fraction of benzene. In this system the total vapour pressure is always equal to the sum of the vapour pressure of pure components. So this is called the ideal system.

Non-ideal solutions:

The solutions which deviate from ideal behaviour to a smaller or a greater extent is said to be non-ideal solutions. For a non-ideal binary solution none of the components follows Raoult's law over the entire range of concentrations.

Definition:

A solution which does not obey Raoult's law at all concentrations and at all temperature is known as a non-idea solution.

Example:

1. Acetone – CS_2
2. Ethyl alcohol – Chloroform.

Deviation from ideal behaviour-non-ideal solutions:

Non-ideal solutions deviate from ideal behaviour. The deviation may be either positive or negative from Raoult's law. Based on the nature of deviation, the non-ideal binary solutions are classified into two types.

i) Non-ideal solution showing positive deviation from Raoult's law.

ii) Non-ideal solution showing negative deviation from Raoult's law.

1.Positive deviation from Raoult's law:

Acetone-carbon disulphide system

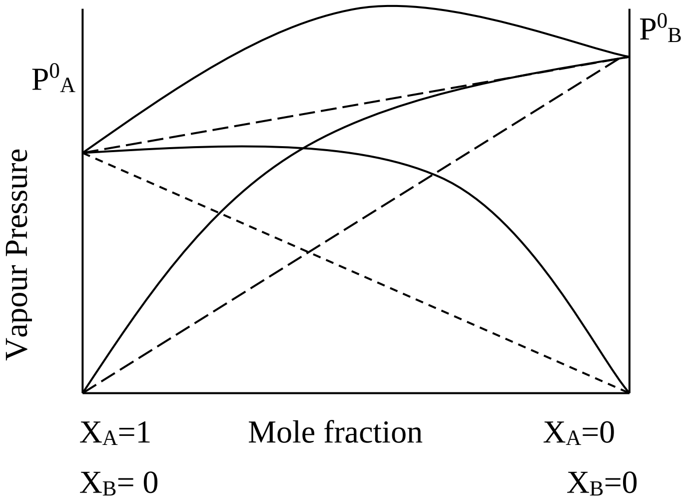
In this solutions there is a weaker inter molecular attraction between A and B than A-A and B-B.

In this system the individual partial pressure curves fall well above the ideal line that is the partial pressures are more than those calculated from Raoult's law . So this system exhibits positive deviation from Raoult's law. The Raoult's law prediction are shown by the dashed lines. The total vapour pressure shows a maximum.

Ex: Acetone-carbon disulphite

Ethyl alchohol-water

Chloroform – Ethyl alcohol



Reasons for positive deviation:

The two liquids have different

i) Polarizability
ii) internal pressure
iii) molecular association
iv) molecular structure.

Negative deviation from Raoult's law

Acetone-chloroform system:

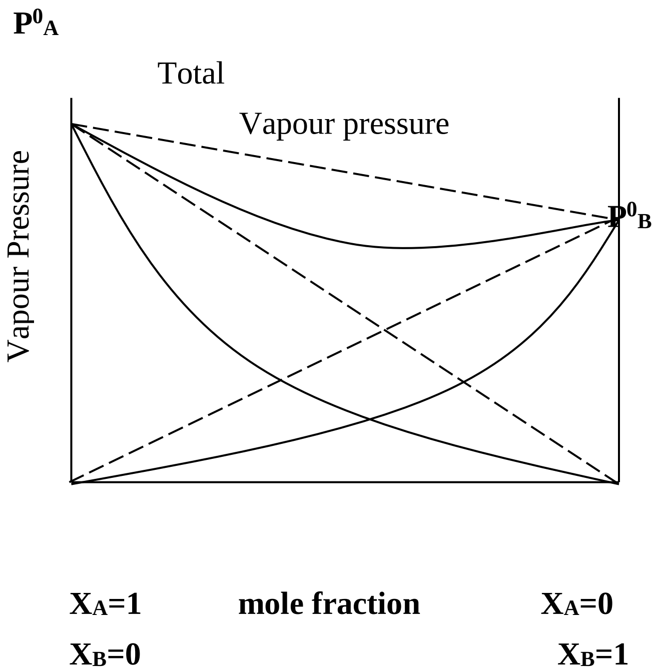
In this solutions there is a greater inter molecular attraction between A and B than A-A and B-B.

In this system the vapour pressure curves fall below the Raoult's law predictions. The system exhibits negative deviation from Raoult's law. The total vapour pressure has a minimum value which lies below the vapour pressure of either of the pure components.

Ex: Acetone-Chloroform

Pyridine-Acetic Acid

Hydrochloric Acid-Water



Reason for negative deviation:

i) The two liquids react to form ions that cannot be evaporated.

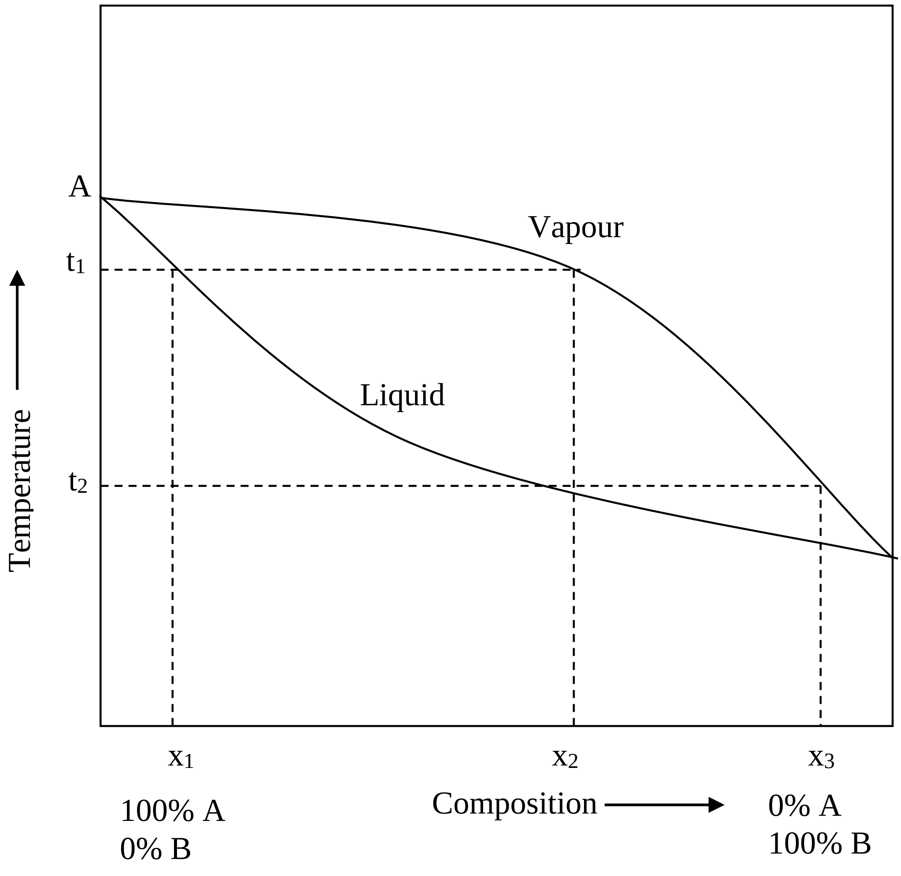
ii) Hydrogen bond also form in the solution.

Fractional Distillation:

Principle of fractional distillation:

The components of an ideal binary liquid system can be separated repeated step-wise distillation. The principle of this process called fractional distillation, can be explained by the boiling-point-composition curves of the system.

When an binary liquid mixture(AB) of composition X_1 is distilled, it boils at t_1. At this temperature, the vapour in equilibrium with the solution will have the composition X_2 in which the more volatile component B is in greater porportion.



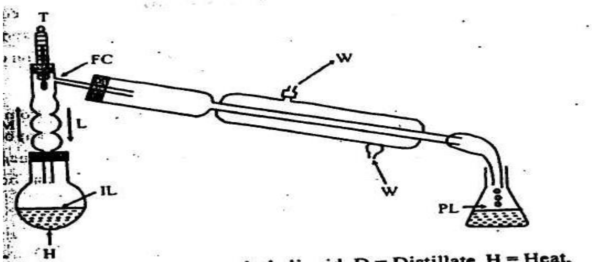
The vapour is removed and condensed. If the condensed liquid or distillate so obtained is redistilled. It will boil at t_2 and the vapour in equilibrium will have the composition X_3. On removing this vapour and condensing, a second distillate is obtained. This has greater proportion of B than the first one. If the process is repeated several times, pure B is obtained as the distillate. Consequently, the component A remains as the residual liquid. This method is used to separate ideal solutions like

i) Benzene and toluene

ii) Benzene and ether etc.,

2. Method of fractional distillation:

The apparatus used for the separation of mixture of ideal or non-ideal solutions is shown in the figure.



Impure liquid, M = More volatile liquid, D = Distillate, H = Heat,
Less volatile liquid, FC = Fractionating column, W = Water

The apparatus consists of a long tube called fractionating column containing a side tube fitted to a water condenser and receiver. The fractionating column is fitted with a thermometer at the top and flask having ideal solutions at the bottom.

When the liquid mixture is heated in the flask, the vapours consisting more of the volatile component rises up and posses through the condenser and collected in the receiver. The less volatile component remains in the flask below. In this way almost complete separation is achieved for ideal solutions. But for non-ideal solutions non-azeotropic mixture or constant burling mixture is obtained.

Non-ideal solutions – Azeotropes:

Azeotropic distillation:

The complete separation of the components of a non-ideal binary liquid system is not possible by fractional distillation. At best, it can be resolved into one pure component and a constant boiling mixture of the two components. Hen the resulting mixture is heated; it distills over without any change in composition. Mixture of this type is known as constant boiling mixtures or azeotropic mixtures or azeotropes.

Fractional distillation which results in the formation of an azeotropic mixture is called azeotropic distillation.

Example:

Ethanol and water mixtures offer a good example of this type. Ethanol – water mixture containing 95.6% ethanol boils at the minimum temperature 78.13^0. Thus, it is very difficult to obtain pure absolute alcohol by distillation. This difficulty has however been overcome by adding benzene, which form a low boiling mixture with water and on distillation it comes over, leaving pure ethanol behind.

Significance of azeotropic mixtures:

1. Azeotropic mixtures indicate that they cannot separated by fractional distillation.
2. It indicates separate methods have to be adopted to obtain one of the components in a pure state.

Colligative properties:

Review of colligative properties of dilute solutions:

Colligate properties of a dilute solution are those properties which depend entirely upon the number of particles of the solute present in a given volume of a solvent .and not upon the nature of the solute. The solute should be non-volatile.

The various cogitative properties are:

i) Lowering of vapour pressure.
ii) Osmotic Pressure
iii) Depression o freezing point
iv) Elevation of boiling point.

Colligative properties are the properties of only dilute solutions which are supposed to behave as ideal solution.

Lowering of vapour pressure:

The vapour pressure of a solvent in a solution containing a non-volatile solute at a given temperature will be less than the vapour pressure of the pure solvent at the same temperature. Let pure solvent at the same temperature. Let p^o be the vapour pressure of the pure solvent, P be the vapour pressure of that solvent in solution. Then P will be less than p^o. $(P-p^o)$ is called the lowering of vapour pressure.

Raoult's law:

Raoult's law gives the relationship between the lowering of vapour pressure of a solution and the mole fraction of a non volatile solute.

According to Raoult's law the vapour pressure of a solvent (P) in an ideal solution is given by

$$P_1 = X_1 \, p^o_1 \quad \text{--------(1)}$$

Where,

p^o_1 is the vapour pressure of the pure solvent and

X_1 is the mole fraction of the solvent in the solution.

We know that,

$X_1 + X_2 = 1$

$X_1 = 1 - X_2$

Substituting the value of X_1 in equation (1),

$$P_1 = (1 - X_2)P_1^0$$

$$\frac{P_1}{P_1^0} = 1 - X_2$$

$$X_2 = 1 - \frac{P_1}{P_1^0}$$

$$X_2 = \frac{P_1^0 - P_1}{P_1^0}$$

$\frac{P_1^0 - P_1}{P_1^0}$ is called the relative lowering of vapour pressure and X_2 is the mole fraction of the solute.

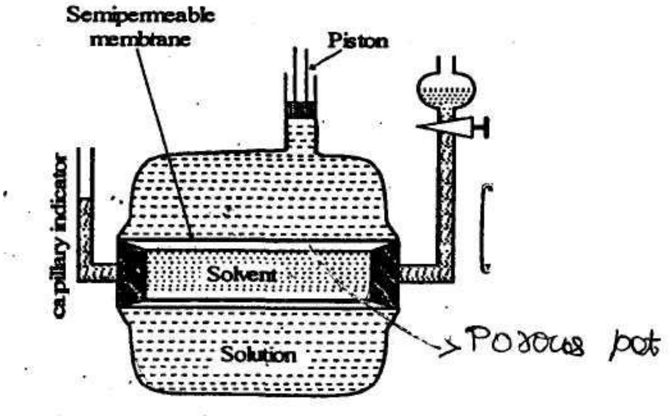
Osmotic Pressure:

Osmotic pressure may be defined as the external pressure applied to the solution in order to stop the osmosis of solvent into solution separated by a semipermeable membrane.

Measurement of Osmotic pressure:

Barkeley and Hartely's Method:

The apparatus consists of a porous pot containing copper ferrocyanide deposited on its walls. The porous pot is surrounded by a bronze cylinder filled with a piston. Solvent is taken in the porous pot and the solution is taken in the jacket. Water placed in the porous pot tends to pass into the solution through the semipemeable membrane. Due to this the water level in the capillary indicator tends to fall. Now sufficient pressure is applied on the piston So that the level of water in the capillary is maintained at the original level. The maximum pressure applied is the osmotic pressure of the solution.



Figure

Elevation of Boiling point:

The boiling point of a solution is more than the boiling point of the pure solvent this is consequence of the lowering of the vapor pressure. We can derive an expression for the relationship between the elevation of boiling point (ΔT_b) and the mole fraction of the solute (X_2)

Thermodynomic derivation of elevation of boiling point

(or)

Relationship between molality and elevation of boiling point

The clausius – clapeyron equation is,

$$\ln \frac{P_2}{P_1} = \frac{\Delta Hv}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad (1)$$

In this equation T_1 and T_2 may be replaced by T_0 and T, the boiling points of the solvent and solution respectively. P_2 and P_1 may be replaced by P_0 and P, and vapour pressures of the solvent and the solution respectively.

$$\therefore \ln \frac{P_0}{P} = \frac{\Delta Hv}{R}\left[\frac{T - T_0}{T T_0}\right] \qquad (2)$$

When the solution is dilute T will be rearly equal to T_0 then $TT_0 = T_0^2$.

So, $$\ln \frac{P_0}{P} = \frac{\Delta Hv}{R}\left[\frac{T - T_0}{T_0^{\,2}}\right]$$

ie, $$\ln \frac{P_0}{P} = \frac{\Delta Hv}{R}\frac{\Delta T_b}{T_0^2} \qquad (3)$$

Where,

ΔH_v is the molar heat of vapourisation

ΔT_b is the elevation of boiling point

equation (3) can be written as,

$$-\ln\frac{P}{P_0} = \frac{\Delta Hv}{R}\frac{\Delta T_b}{T_0^2} \tag{4}$$

From Raoult'n law,

$$\frac{P}{P_0} = x_1 = 1 - x_2 \tag{5}$$

Substituting the value of P/P_0 from equ (5) in equation (4)

$$-\ln(1 - X_2) = \frac{\Delta Hv}{R}\frac{\Delta T_b}{T_0^2} \tag{6}$$

Expansion of –ln(1-X2) in this series,

$$-\ln(1 - X_2) = X_2 + \frac{X_2^2}{2}\frac{X_2^3}{3} + ...$$

Neglecting the higher powers in the series,

$$-\ln(1 - X_2) \approx X_2 \tag{7}$$

Substituting equation (7) in equ (6)

$$X_2 = \frac{\Delta Hv}{R}\frac{\Delta T_b}{T_0^2}$$

$$\therefore \Delta T_b = \frac{X_2 R T_0^2}{\Delta Hv} \tag{8}$$

We know that,

$$X_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{W_2 M_1}{M_2 W_1}$$

Substituting the value of X2 in equ (8)

$$\Delta T_b = \frac{W_2}{M_2}\frac{M_1}{W_1} = \frac{R T_0^2}{\Delta Hv} \tag{9}$$

$\frac{\Delta H_v}{M_1} = l$, the latent heat of vapourisation of one gram of the solvent.

Then equation (9) becomes,

$$\Delta T_b = \frac{W_2 R T_0^2}{M_2 W_1 x l} \tag{10}$$

Multiplying and dividing, the equation (10), by 1000,

$$\Delta T_b = \frac{W_2}{M_2}\frac{1000}{W_1}\frac{RT_0^2}{1000xl} \qquad (11)$$

$$\therefore T_b = mk_b \qquad (12)$$

Where,

'm' is the molality of the solution

K_b is the molal elevation constant or ebulioscopic constant.

From equation (11), the molecular weigh of the dissolved soluti can be determined as,

$$M_2 = \frac{K_b W_2 1000}{\Delta T_b W_1}$$

Depression of freezing point:

The freezing point of a solution is less than the freezing point of pure solvent. This is a consequence of lowering of vapour pressure.

We can derive an expression for the relationship between the depression of freezing point (ΔT_1) and the mole fraction of the solute (X_2)

Thermodynomic derivation of depression of freezing point

(or)

Relationship between molality and depression of freezing point

The clausius – clapeyron equation is,

$$\ln\frac{P_2}{P_1} = \frac{\Delta Hv}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad (1)$$

When this is applied to a solution

$$\ln\frac{P_0}{P} = \frac{\Delta Hf}{R}\left[\frac{T_0 - T}{TT_0}\right] \qquad (2)$$

ΔHf is the molar heat of fusion

P_0 and P are vapour pressures of the solvent and solution

T_0 and T are the freezing points of the solvent and solution.

For a dilute solution,

$$T_0 = T$$

$$\therefore TT_0 \approx T_0^2$$

So, equation (2) becomes,

$$\ln\frac{P_0}{P}=\frac{\Delta Hf}{R}\left[\frac{T_0-T}{T_0^2}\right]$$

$$\text{ie .}\qquad \ln\frac{P_0}{P}=\frac{\Delta Hf}{R}\left[\frac{\Delta Hf}{T_0^2}\right]\tag{3}$$

Where, ΔHf is the depression in freezing point equation (3) can be written as,

$$-\ln\frac{P}{P_0}=\frac{\Delta Hf}{R}\left[\frac{\Delta fT}{T_0^2}\right]\tag{4}$$

From Raoults law,

$$\frac{P}{P_0}=x_1=1-x_2\tag{5}$$

Substituting equation (5) in equation (4)

$$-\ln(1-X_2)=\frac{\Delta Hf}{R}\left[\frac{\Delta Tf}{T_0^2}\right]\tag{6}$$

Expansion of $-l_n(1\text{-}X_2)$ is,

$$-\ln(1-X_2)=X_2+\frac{X_2^2}{2}+\frac{X_2^3}{3}+\ldots\ldots$$

Neglecting the higher powers in the series,

$$-\ln(1-X_2)=X_2\tag{7}$$

Substituting equation (7) in equ (6)

$$X_2=\frac{\Delta Hf}{R}\frac{\Delta Tf}{T_0^2}$$

$$\therefore \Delta Tf=\frac{X_2RT_0^2}{\Delta Hf}\tag{8}$$

We know that,

the mole fraction of solute $X_2=\dfrac{n_2}{n_1+n_2}=\dfrac{n_2}{n_1}$

$$\therefore X_2=\frac{W_2M_1}{M_2W_1}\tag{9}$$

Substituting equation (9) in equation (8)

$$\Delta Tf = \frac{W_2 M_1 R T_0^2}{M_2 W_1 \Delta Hf}$$

(ie) $$\Delta Tf = \frac{W_2 R T_0^2}{M_2 W_1 l} \qquad (10)$$

Where,

'l' is the latent heat per gram = $\frac{\Delta Hf}{M_1}$

Multiplying and dividing the equation (10) by 1000, we get,

$$\Delta Tf = \frac{W_2 R T_0^2}{M_2 W_1 l} x \frac{1000}{1000}$$

On rearranging

$$\Delta Tf = \frac{R T_0^2 W_2 1000}{1000 x M_2 W_1 x l}$$

So, $$\Delta Tf = \frac{K f W_2 1000}{M_2 W_1} \qquad (11)$$

$$\Delta Tf = Kfm$$

where,

'Kf' is the molal depression conslant (or)

Cryoscopic constant

'm' is the molality of the solute

From equation (11), we can calculate the molecular weight of solute as,

$$M_2 = \frac{K f W_2 1000}{\Delta Tf W_1}$$

Abnormal molecular weights:

Since osmotic pressure and other properties studied in this chapter are colligate properties, i.e, properties which depend upon the number of particles, the molecular weights determined by measuring these properties give abnormal results in some cases. When the solute associate or dissociates in solution such abnormal results are obtained.

1. Association:

Many organic solutes undergo association in non-aqueous solutions. Due to association two or more molecules of the solute form a bigger molecule. So the number of effective molecules or particles in the solution decreases. Thus the measured osmotic pressure the elevation of boiling point or the depression in freezing point is less than the calculated values. The molecular weights of solutes in such cases will be higher than the true molecular weights as indicated by their formulas.

E.g

Solute	**Solvent**	**Observed Mol .wt**	**calculated Mol .wt**
Acetic acid	Benzene	118	60
Benzoic acid	Benzene	242	122.0

2. Dissociation:

Many inorganic acids, bases and salts undergo dissociation in aqueous solutions. Due to dissociation the molecules break down into positively and negatively charged ions. So number of effective particles in the solution increases.

Thus, the measured osmotic pressure, the elevation of boiling point or the depression in freezing point is more than calculated values. The molecular weights of solutes in such cases will be less than the true molecular weight as indicated by their formulas.

E.g.

Solute	**Solvent**	**Observed Mol. wt.**	**Calculated Mol. wt.**
KCl	Water	38.75	74.5
Na_2SO_4	Water	49.84	142.0

Van’t Hoff Factor:

The ratio between the experimental value of a colligate property and the theoretical value is known as the Van’t Hoff factor.

$$i = \frac{\text{Experimental colligative property}}{\text{Theoretical colligative property}}$$

(or)

$$i = \frac{\text{Theoretical molecular weight}}{\text{Experimental molecular weight}}$$

Calculation of ‘i'

Let 1 mole of an electrolyte be dissolved in a given quantity of water. Let α be the degree of dissociation. When 1 mole dissociates let ‘n’ moles of ions will be formed. Since α is the degree of dissociation ‘$n\alpha$’ moles of ions will be formed. Therefore after ionization the total ions will be after ionization the total ions will be

$$= 1 - \alpha + n\alpha$$

$$= 1 + (n-1)\,\alpha$$

The ratio of number of moles after dissociation to the number of moles expected.

$$i = \frac{1 + (n-1)\,\alpha}{1}$$

From this equation we can also find if i is known using (1)

$$\alpha = \frac{i - 1}{n - 1}$$

Degree of dissociation of a solute is the ratio between the number of molecules dissociated and total number of molecules taken.

Thus, the degree of dissociation α is given by

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Number of molecules dissolved}}$$

$$\text{i.e,}\quad \alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles dissolved}}$$

Let one mole of a uni–uni valent electrolyte like potassium chloride be dissolved in a given volume of water. Let α be the degree of dissociation. Then the number of moles of KCl left undissociated will be $1 - \alpha$. At the same time α moles of K^+ and α moles of at will be produced as shown below.

$$\underset{1-\alpha}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl^-}$$

Thus, the total number of effective moles will be

$$\mathbf{1 - \alpha + \alpha + \alpha = 1 + \alpha}$$

Hence the Van’t Hoff factor, i is given by

$$i = \frac{\text{Observed colligative property}}{\text{Calculated Colligative property}}$$

$$= \frac{1 + \alpha}{1}$$

Degree of association

By degree of association in meant the fraction of the total number of molecules which combine to form bigger molecules.

Consider one mole of a solute dissolved in a given volume of a solvent suppose, n simple molecules combine to form an associated molecule.

ie. $nA \rightleftharpoons (A)_n$

Let α be the degree of association, then

The number of unassociated moles = $1 - \alpha$

The number of un associated moles = α/n

$\therefore$ The number of effective moles = $1 - \alpha + \alpha/n$ Since osmotic effect is proportional of the number of moles, therefore, the Van’t Hoff factor i is given by.

$$i = \frac{\text{Observed Osmotic effect}}{\text{Calculated Osmotic effect}} = \frac{1- \alpha + (\alpha/n)}{1}$$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{1- \alpha + (\alpha/n)}{1}$$

Thus, knowing n, i.e the number of simple molecules, which combine to give one degree of association, the Van’t Hoff factor can be easily calculated.

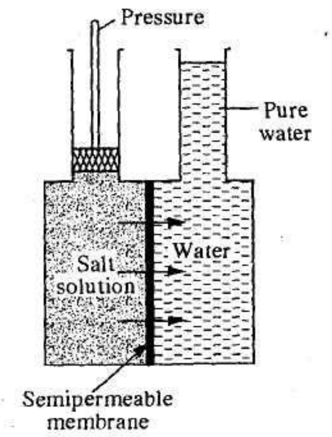
Reverse Osmosis:

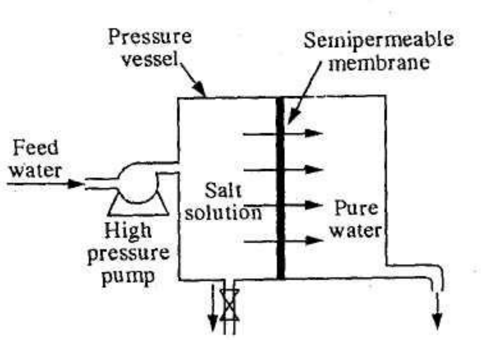
When a solution is separated from pure water by a semi permeable membrane **(SPM),** the solvent will start flowing from pure solvent to solution side. This phenomenon is called Osmosis.

If we consider again a solution separated from pure solvent by a semi permeable membrane and **if pressure applied** on the solution is more than the osmotic pressure, then solvent will start flowing from the solution side towards the pure solvent. This phenomenon is called Reverse Osmosis.

Reverse Osmosis (RO) technique is now being employed extensively for getting potable water from sea water.

In actual practice sea water is pumped into a pressure vessel fitted with a suitable semi permeable membrane (SPM). Under the influence of high pressure, water from the sea water passes out through the semi permeable membrane as shown.





Depending upon the salt concentration, the osmotic pressure of sea waters generally vary from 4000 to 5500 **kPa** (Pa= Pascal = 0.009 atm). For RO, the pressure applied should be about 1400 kPa. For continuous conversion of sea water to potable water the pressure to be applied in RO plant is in the range of 5400 to 6900 kPa. This is a quite high pressure. The problem is the selection of apt SPM for this purpose.

Cellulose acetates are used as SPM’s. There are two defects with this membrane and the methods to avoid are

- They are susceptible to degradation from biological attack. To avoid this the feed water should be properly chlorinated
- Cellulose acetate hydrolyses to cellulose under acidic and high pressure conditions. To minimize this, the pH of the system kept in the range of 4.5 to 7.5

Aromatic Poly amides are now a days used as special SPM. These membranes are stable in the pH range of 4 – 11 and are immune to biological attack. However they get degraded in presence of chlorine.

A properly designed Reverse Osmosis plant reduces the salt concentration of sea water from 35,000 to 42, 000 mg per litre to about 500 to725 mg per litre.

Sea water purification by RO is highly economical since the energy consumption is very low. The energy consumption is 25 – 30 kWh per 1000 gallons of water.(1 gallon = 3.785litre)

Chromatography:

The chromatographic methods of separation are useful for separating complex mixtures of substances which are not otherwise readily separated. The important chromatographic methods are,

1. Column chromatography
2. Thin-layer chromatography
3. Paper chromatography

Chromatography is based upon the principle of phase distribution. It involves selective removal of the components from the stationary phase by the mobile phase. The whole process centers on the distribution of the components of the mixtures differentially between two phases (solid-liquid or gas-solid). This differential distribution is because of differences in the capacities of the components of the mixture of adsorption on the stationary phases. For example, a mixture of Ni(II) and Co(II) in aqueous solution is passed through a tube filled with on adsorbent (cellulose). The cobalt ion will move down the column and reach the bottom faster than the Ni(II)ions. This is because Ni(II) ions is more strongly adsorbed on cellulose than Co(II) ion. The strongly adsorbed Ni(II) tends to stay on the column longer than the weakly adsorbed Co(II) ion. This leads to separation of these two ions.

1. Column chromatography:

Principle

A glass tube (column) is packed with in active solid. The solid is called the stationary phase and its active in absorbing substances. Alumina, silicagel, sucrose, cellulose, charcoal, calcium carbonate and resins (natural and synthetic) are the common adsorbents used for column chromatography.

The mixture to be separated is dissolved in a solvent and the solution is poured at the top of the absorbent in the column. Then the pure solvent is made to flow through the column slowly. The solvent thus used is called the eluent. As the solvent flows through the column, the components of the mixture will emerge through the tip of the column successively. This process is known as elution. Each solution fraction is collected in a separate flask and the solvent is removed by distillation to obtain the pure compound. Like the bus passengers getting off from the bus at different points, the compound of the mixture adsorbed on the column gets off the column at different points of elution.

No two compounds have the same tendency to be absorbed by the solid in the column no two compounds have the same solubility in the solvent. This is the basis for successful separation of mixture by chromatography.

Straight chain paraffins the C-27, C-29, C-31 and C-33 compounds are produced in all plants. Their physiological role in the life of the plants in mystery these four compounds can be separated from the petroleum ether extract of spincach. These compounds separate from the column as colourless solutions leaving the other plant materials on the column.

The best solvents for separating a mixture is found only by trail and error. Sometimes, a mixture of two solvents may be used. The solvent itself should not be absorbed column and it should not be more polar than the component of the mixture. The eluting powers of various solvents i,e., their ability.

To bush a given substance column differ. For example, the highly polar water has much greater eluting power than the non polar solvent carbon tetrachloride.

2. Thin layer chromatography:

Thin layer chromatography is based on the same principles as column chromatography. It is a type of solid liquid adsorption chromatography, but in this case, the solid adsorbent is spread as a thin layer on a piece of a glass plate. The mixture is dissolved in a solvent and tiny drop of this solution is placed near one edge of the plate. The plate is then placed in a container with sufficient solvent whose level comes just below the spot of the solution of mixture. The solvent migrates up the plate and carries with its components of the mixture at different rates. After some time, before the solvent front reaches the upper edge of the plates removed. The components of the mixture will then be located at different places of the plate but falling on a line.

The same solid adsorbents used for column chromatography may be used for TLC, silica and alumina being the most commonly used. A small amount of binder is usually mixed with the adsorbent for proper adherence of the adsorbent to the plate.

Advantages of TLC:

1. This method is easy and rapid to perform.
2. A small amount of a mixture is sufficient for analysis (as low as 10^{-9}g)
3. This method is suitable for routine analysis of mixture compositions.

Detection of spots on the chromatogram (plate) is easy for coloured substances. Spots of colourless substances may be developed (located) by spraying on the plate a reagent which produces colour with the components of the mixture. For example, spots of metal ions can be located with dilute aqueous hydrogen sulphide solution. Placing the plate in a closed champer containing iodine vapour will make the organic compound visible. The organic compounds adsorb iodine and therefore brown spots are produced on the chromatogram. Sometimes, irradiation of the plate with UV light will permit the location of the spots of compounds that fluorescence.

3. Paper chromatography:

Paper chromatography is similar to TLC. In this method, a specially made paper is used in the place of glass plate. The paper always contains moisture strongly adsorbed on the cellulose fibres of the paper.

A small spot of the mixture to be separated is placed near the bottom of strip of paper after drawing a pencil line on the two edges of the paper, this paper is gently placed inside a champer cotaining a solvent. The solvent level should be below the spot. As the solvent ascends up the paper by the capillary action, the compounds of the mixture move on the paper at different speeds and thus are separated into individual spots. Paper chromatography involves distribution of the substances between a polar liquid phase (water in the paper) and an eluting (moving) solvent. It is an example of liquid- liquid chromatography a compound is partitioned (distributed) between two liquids.

Advantages of paper chromatograpy :

1. This method is in expensive.
2. It is rapid.
3. Minute quantities of sample are enough for analysis.

Kohlraush's law :

Examination of equivalent condutance at infinite dilution of solutions of two salts having an ion in common reveals certain regularities. For example, in the case of pairs of potassium and sodium salts with a common ion, a constant difference of 21.1 in the conductance is noted. More examples are also given in table.

Table

Electrolyte	A°	Differences
KCl	130.0	
NaCl	108.9	21.1
KNO_3	126.3	
$NaNO_3$	105.2	2.1.1
NaBr	110.9	
NaCl	108.9	2.0
KBr	132.0	

Therefore the difference in the equivalent conductances of potassium and sodium ions or bromide and chloride, ions are independent of the nature of the other ion. This was observed by Kohlraush and a law was stated which read as follows: At infinite dilution, each ion contributes a definite amount to the total conductance of the electrolyte, irrespective of the nature of the other ion. This law is also known as the law of independent migration of ions. It may be represented as,

$$\boxed{\Lambda^\circ = \lambda^\circ_+ + \lambda^\circ_-}$$

It is strictly correct only if the electrolyte is at infinite dilution λ°+ and λ° - are the equivalent ionic conductances at infinite dilution of the cation andanion respectively.

Applications of Kohlrausch's law:

1. The absolute mobilities of ions can be determined.
2 The solubility of sparingly soluble salts can be determined.
3. Ionic product of water can be calculated.
4. An important use of Kholrausch's law-is to determine the equivalent conductance at infinite dilution of weak electrolytes. The Λ^0 of the weak electrolytes cannot be evaluated from direct experimental data. The extrapolation to infinite dilution of the graph obtained by plotting the equivalent conductivities and the concentrations of the solution is not possible for a weak electrolyte. But it can be evaluated using Kohlrausch's law. For instance, the equivalent conductance of acetic acid at infinite dilution can be obtained from the knowledge of equivalent conductances at infinite dilution of hydrochloric acid, sodium acetate and sodium chloride.

It can be computed as

$$\Lambda^{o}_{HAc} = \Lambda^{o}_{NaAc} + \Lambda^{o}_{HC\ell} - \Lambda^{o}_{NaC\ell}$$

It **is** because

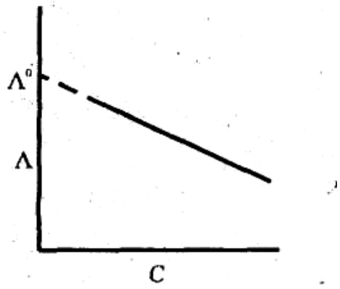
$$
\begin{aligned}
{}_{Na^+} + \lambda^{o}_{Ac^-} + \lambda^{o}_{H^+} + \lambda^{o}_{C\ell^-} - \lambda^{o}_{Na^+} + \lambda^{o}_{C\ell^-} \\
= \lambda^{o}_{H^+} + \lambda^{o}_{Ac^-} \\
= \Lambda^{o}_{HAc}
\end{aligned}
$$

Applications of Conductance Measurements

1. Determination of Λ° of a strong electrolyte

As described under heating measurement of conductance, In page number 7 the specific conductance of the given strong electrolyte is determined. The same experiment is repeated for different concentrations of the strong electrolyte. From the specific conductance values the equivalent conductance for the various concentrations of the strong electrolyte is calculated using the formula

$$\Lambda = \kappa \frac{1000}{c}$$



Figure

Λ = Equivalent conductance
Λ° = Equivalent conductanc
at infinite dilution
C = concentration

A graph is plotted between concentration of the electrolyte and equivalent conductance. The shape of the curve obtained is shown in figure. Extrapolation of the curve meets the axis at Λ°, which gives the value of the equivalent conductance at infinite dilution of the electrolyte.

2. Determination of dissociation constant K_a of Acids

To determine the dissociation constant of an organic acid we have to first find the degree of dissociation of the weak organic acid. From the degree of dissociation we can calculate the dissociation constant.

i. To find the degree of dissociation (a)

The equivalent conductivity (Λ) of the solution of weak organic acid is determined at a given concentration. Using the wheatstone bridge the resistance is measured and from that the equivalent conductance is computed as explained earlier. The equivalent conductance at infinite dilution (Λ^0) of the organic acid cannot be found[1] by the extrapolation of the graph since it is a weak electrolyte. The A is calculated from ionic conductances as described under Kohlrausch's law. Knowing Λ and Λ° Values, the degree of dissociation

α is calculated using the relation $\alpha = \frac{\Lambda}{\Lambda^{\circ}}$

ii. To find the dissociation constant K_a

Let HA be the organic acid which dissociates as H^+ and A^-

$$HA \rightleftharpoons H^+ + A^-$$

If c moles per litre of HA are taken and if α is the degree of, dissociation then the active masses of the different species at equilibrium will be

$$[HA] = c(1-\alpha)$$

$$[H^+] = c\alpha$$

$$[A^-] = c\alpha$$

So the equilibrium constant $K_a = \frac{[H^+][A^-]}{[HA]}$

$$K_a = \frac{c\alpha\ c\alpha}{c(1-\alpha)} \quad ; \qquad K_a = \frac{c^2\alpha^2}{(1-\alpha)}$$

$$\boxed{K_a = \frac{c^2\alpha^2}{(1-\alpha)}}$$

This equilibrium constant is called the dissociation constant of the weak organic acid. Knowing the value of α, the value of K_a can be calculated.

3. Determination of solubility product of a sparingly soluble salt

Substances like $BaSO_4$, AgCl, $PbSO_4$ Agl, Pbl_2, Ag_2CrO_4 are examples for sparingly soluble salts. Since they are sparingly (slightly) soluble their solutions may be considered as solutions at infinite dilution. The equivalent Conductance measured for this solution may be taken as equivalent conductance at infinite dilution.

A saturated solution of the sparingly soluble salt in water is prepared And its equivalent conductance measured. Now $\Lambda = \kappa V$

Where *K* is the specific conductance and V is the volume in cc containing 1 gram equivalent of the electrolyte. Knowing Λ and k, the, volume containing one gram equivalent V is calculated. From V the amount of the solute present in one litre can be calculated. This gives the solubility of the substance.

From the solubility (S) of the sparingly soluble substance, the solubility product (K_{SP}) may be calculated. Suppose we consider AgCl as the sparingly soluble salt, it ionises as

$$AgC\ell \rightleftharpoons Ag^{+} + C\ell^{-}$$

and the equilibrium constant

$$K = \frac{a_{Ag^{+}} \cdot a_{C\ell^{-}}}{a_{AgC\ell}}$$

Since the salt is sparingly soluble a_{AgCl} may be taken as 1..

Then, $K_{Sp} = a_{Ag^{+}} a_{C\ell^{-}}$

Since the solution is dilute the concentration of the ions may be considered instead of activity.

Then, $K_{Sp} = C_{Ag^{+}} C_{C\ell^{-}}$

$$\boxed{K_{Sp} = S\,S = S^{2}}$$

4. Determination of ionic product of water

The H_3O^+ ion concentration of a standard solution of alkali like NaOH is determined with the help of a cell as in the measurement of p^H. The concentration of OH^- ions is calculated from the strength of NaOH and its degree of dissociation in the solution. Then the value of $K_w = [H_3O^+] [OH^-]$ can be calculated.

The cell used is as follows :

Pt, H_2 (1 atm) 1 NaOH (m_1) || NaCl (m_2) | AgCl (s), Ag.

The e.m.f, of this cell is given by,

$$E = E^{\circ} \frac{RT}{F} \ln a_{H}^{+} a_{Cl}^{-}$$

Since $a_{H}^{+} . a_{OH}^{-} = K_w$.

$$E = E^{\circ} - \frac{RT}{F} \ln \frac{a_{Cl}^{-} . K_w}{a_{OH}^{-}}$$

Putting the activity as the product of molality and activity coefficient putting $E^{\circ} = 0.2224$ Vat 298.15 K, we get, $$E = 0.2224 - 0.0591 \log \frac{m_{Cl^-}\gamma_{Cl^-}K_w}{m_{OH^-}\gamma_{OH^-}}$$

or $$E = 0.2224 - 0.0591 \log \frac{m_{Cl^-}}{m_{OH^-}} - 0.0591 \frac{\log\gamma_{Cl^-}}{\gamma_{OH^-}} - 0.0591 \log K_w$$

or $$E = 0.2224 - 0.0591 \log \frac{m_2}{m_1} - 0.0591 \log \frac{\gamma_{Cl^-}}{\gamma_{OH^-}} - 0.0591 \log K_w$$

or $$E - 0.2224 + 0^{a}0591 \log \frac{m_2}{m_1} = -0.0591 \log K_w - 0.0591 \log \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

The value of the L.H.S of from the measured E values, is plotted against the ionic strength of the solution (i.e., m_1) and on extrapolation to zero ionic Istrength, gives the value of the intercept equal to - 0.0591 Kw

At 298.15 K, the value of Kw is equal to 1.004×10^{-14}

$$[H^+] = 1.01 \times 10^{-4}\ \text{mol m}^{-3} = 1.01 \times 10^{-7}\ \text{mol dm}^{-3}$$

$$[OH^-] = 1.01 \times 10^{-4}\ \text{mol m}^{-3} = 1.01 \times 10^{-7}\ \text{mol dm}^{-3}$$

$$K_w = [H^+][OH^-] = 1.01 \times 10^{-7}\ \text{mol dm}^{-3} \times 1.01 \times 10^{-7}\ \text{mol dm}^{-3}$$

$$= 1.02 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \approx 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}\ \text{at } 25^\circ\text{C}.$$

The pH and its determination

Water is a weak electrolyte and is known to be slightly ionised as:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \ldots (1)$$

Applying law of mass action to the above equilibrium

$$K = \frac{[H^+][OH^-]}{[H_2O]} \qquad \ldots (2)$$

Where, K is the equilibrium constant. As the concentration of un-ionised water is considered to be a constant, the above equation (2) becomes,

$$K = \frac{[H^+][OH^-]}{k} \qquad \ldots (3)$$

or, $$Kk = K_w = [H^+][OH^-] \qquad \ldots (4)$$

K_w is the *ionic product of water* and its numerical value at 298 K is lxl0^{-14}. In the case of pure, neutral water,

$$[H^+] = [OH^-] = 1 \times 10^{-7}\ \text{mole / lit.} \qquad \ldots (5)$$

If the concentration of hydrogen ion is *more than* 10^{-7}, the solution is acidic. If it is *less than* 10^{-7}, the solution is *alkaline.*

This way of expressing hydrogen ion concentration is cumbersome. A more convenient way, without the use of negative exponent is desirable. Sorenson, a Danish biochemist in 1909, introduced a new scale called, pH scale to express the hydrogen ion concentration. According to him, *pH of a solution is the negative logarithm of the hydrogen ion concentration.*

$$\mathrm{pH} = -\log[\mathrm{H}^+] = \log\frac{1}{[\mathrm{H}^+]} \qquad \ldots (6)$$

For pure water, $[H^+] = 1 \times 10^{-7}$ and hence, pH = 7.

If the value of pH is *less than seven,* the solution is *acidic.*

If pH is *greater than seven, it is alkaline.*

As pH expresses the scale of acidity, just in the same way, pOH expresses the scale of alkalinity. It may be given as

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = \log\frac{1}{[\mathrm{OH}^-]} \qquad \ldots (7)$$

$$\text{and} \quad \mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14 \qquad \ldots (8)$$

Conductometric Titrations

These titrations have the following advantages:

1. The titrations which cannot be carried out by ordinary methods can be carried out successfully under conductometric method.
2. Even titrations with turbid and coloured solutions where indicators cannot be used can be done:
3. Reactions in which precipitates are formed can also be titrated.
4. A weak acid can be titrated against a weak base.
5. Very dilute solutions can also be titrated.

Procedure

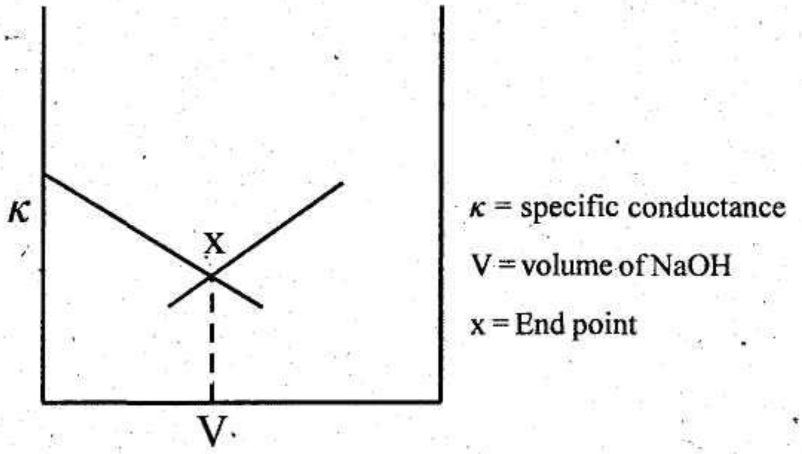
In the conductometric titrations, the variation of electrical conductivity of a solution during the course of the titration is measured. It is not necessary to measure the actual specific conductivity; and quantity proportional to conductivity can be measured and used. An electrolyte is taken in a small beaker and a conductivity cell is immersed in the electrolyte. The titrant is added from the burette and the corresponding conductance readings are taken. The conductance readings are-plotted against the volume of titrant added. The break in the cure gives the end point. The titrant should be atleast 10 times stronger than the solution being titrated in order to keep the volume change small (negligible).

1. Strong acid against strong base:

The titration of HCl against NaOH can be taken as an example. Usually the acid is taken in the beaker and the base is added from the burette. To start with we take a strong acid namely *HCl* in the beaker. It will have high value of conductance. During the titration the following reaction takes place. We find that H^+ions are replaced

$$H^+ + C\ell^- + Na^+ + OH^- \longrightarrow H_2O + Na^+ + C\ell^-$$

By Na^+ ions during the titration. The speed of the Na^+ ions is less than that of H^+ ions. Therefore conductance decreases when more and more of NaOH is added. When all of H^+ ions are replaced by Na^+ ions the conductance reaches a minimum value. At this point namely the end point we have Na^+ and Cl^{-1} ions only. If we add any more amount of NaOH the conductance increases rapidly. It is because NaOH is a strong electrolyte and the addition of it causes an increase of Na^+ and OH^- ions. The OH^- ions have high mobility and so conductance increases rapidly. The curve obtained in a titration is shown in figure. The break in the curve gives the neutralisation (end) point.

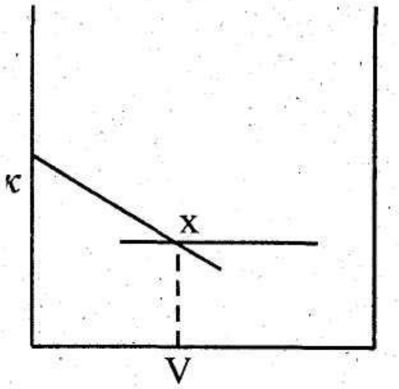


2. Strong acid against weak base

The titration of HCl against NH_4OH can be taken as an example. To start with we take strong acid HCl in the beaker. It will have a high value of conductance. During the titration the following reaction takes place.

$$H^+ + Cl^- + NH_4OH \longrightarrow NH_4 + Cl^- + H_2O$$

We find the H^+ ions are replaced by NH_4^+ ions during the titration. The speed of the NH_4^+ ions is less than H^+ ions. Therefore conductance decreases when more and more of **NH_4OH** is added.



When all the H^+ ions are replaced by NH_4^+ ions the conductance reaches **a** minimum value. If we add any more amount of NH_4OH there is no considerable change in the conductance. It is because NH_4OH is a weak electrolyte. It ionises to a very small extent. So addition of NH_4OH does not cause addition of any more ions. Thus the conductance remains almost constant.

The curve obtained in such a titration is shown in figure. The break in the curve 'X' gives the neutralisation point.

3. Weak acid against strong base:

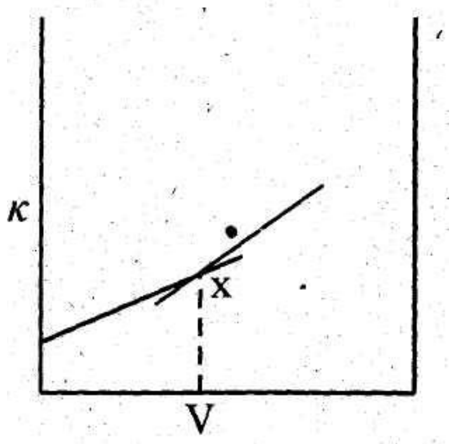
The titration Of CH_3COOH against NaOH can be taken as an example. To start with, we take the weak acid namely CH_3COOH in the beaker. The weak acid has a low ionisation.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

So it will have a low conductance. During the titration the following reaction takes place.

$$CH_3COOH + Na^+ + OH^- \longrightarrow Na^+ + CH_3COO^- + H_2O$$

Addition of NaOH produces sodium acetate salt which totally ionises to give Na^+ and CH_3COO^- ions. So during the course of the reaction more of Na^+ and CH_3COO^- are produced and hence conductance increases. At the end point, the conductance is due to Na^+ and CH_3COO^- ions only. If We add any more amount of NaOH the conductance increases rapidly. It is because NaOH is a strong electrolyte and the addition of it causes an increase of Na^+ and OH^-ions. The OH^- ions have high mobility and so conductance increases rapidly. The curve obtained in such a titration is shown in figure. The break in the curve 'x' is the neutralisation point.



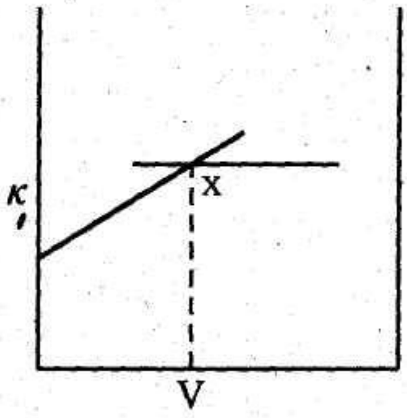
4. Weak acid against weak base :

The titration of CH_3COOH against NH_4OH can be taken as an example. To start with we take the weak acid namely CH_3COOH in the beaker. The weak acid has low ionisation.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

So it will have a low conductance. During the titration the following : reaction takes place.

$$CH_3COOH + NH_4OH \longrightarrow NH_4^+ + CH_3COO^- + H_2O$$



Addition of NH_4OH produces ammonium acetate salt which totally ionises , to give NH_4^+ and CH_3COO^- ions. So during the course of the reaction more and more of NH_4^+ and CH_3COO^- are produced and hence conductance increases. At the end point the conductance is due to NH_4^+ and CH_3COO^- ions only. If we add any more amount of NH_4OH there is no considerable change in the conductance. It is because NH_4OH is a weak electrolyte. It ionises to a very low extent. So addition of NH_4OH does not cause addition of any more ions.

Thus the conductance remains almost constant. The curve obtained in such a titration is shown in figure.

5. Mixture of strong acid and weak acid against strong base:

The titration of a mixture of HC£ and CH_3COOH against NaOH can be taken as an example. In the beaker we take the mixture of acids. The strong acid namely HCl ionises totally to give H^+ and Cl^- ions. So it will have high value of conductance. During the titration the strong acid (HCl) first reacts with NaOH. The following reaction takes place.

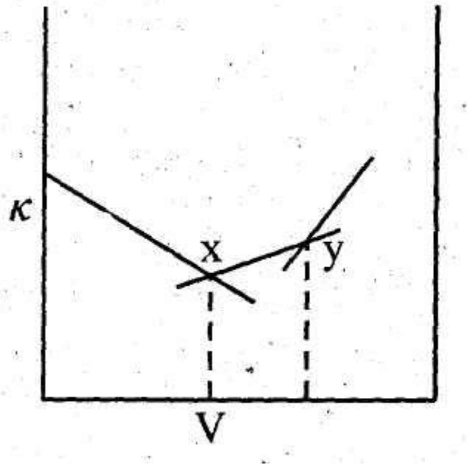
$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

H^+ ions are replaced by Na^+ ions. The speed of Na^+ ions is less than H^+ ions. Therefore conductance decreases when more and more of NaOH is added. When the strong acid has completely reacted we a have Na^+ and Cl^- ions and CH_3COOH. This point is the end point for strong acid noted as X in figure. If we add any more amount of NaOH the conductance increases. It is because the added NaOH reacts with the weak acid (CH_3COOH) and produces sodium acetate salt which totally ionizes to give Na^+ and CH_3COO^- ions.

$$CH_3COOH + Na^+ + OH^- \longrightarrow Na^+ + CH_3COO^- + H_2O$$

So during the addition of NaOH more and more of Na^+ and CH_3COO^- are produced and hence conductance increases. At the end point 'Y' the conductance is due to Na^+, Cl^- and CH_3COO^- ions only. The end point ˋY' gives the volume of alkali required by both acids.

Knowing X the volume, of alkali required by weak acid alone (Y-X) can be found. After the end point Y if we add any more amount of NaOH the conductance increases rapidly. It is because NaOH is a strong electrolyte and addition of it causes an increase of Na^+ and OH^- ions. The curve obtained in such a titration is shown in figure.



6. Precipitation titrations:

The titration of $AgNO_3$ against NaCl can be taken as an example. If we take $AgNO_3$ solution in the cell, it totally ionises as Ag^+ and NO_3^-

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

So it has high conductance value. If NaCl added now, the following reaction takes places.

$$Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$$

The less mobile Ag^+ ions are replaced by more mobile Na^+ ions. When more and more of NaCl is added more Na^+ is introduced and so the conductance increases regularly. At the end point we have Na^+ and NO_3 only. If we add any more amount of NaCl the conductance increases rapidly. It is because NaCl is a strong electrolyte and the addition of it causes an increases of Na^+ and Cl^- ions. The curve obtained in such a titration is similar to the curve as shown in figure 1.13. The break in the curve 'X' gives the end point.

HYDROLYSIS OF SALTS

Hydrogen ion or hydroxyl ion is formed directly from the add or base as a result of ionisation. But hydrogen ions and hydroxyl ions may be formed as a result of the reaction of an ion with water. The general type of *reaction in which the cation or anion of a salt interact with the solvent water to form either hydrogen ions or hydroxyl ions, is called salt hydrolysis.* Thus, the hydrolysis equilibrium represents **a** reverse reaction of the ionisation equilibrium.

From the point of view of salt hydrolysis, salts may be divided into four categories as below

(i) Salts of strong acids and strong bases - for example, sodium chloride, potassium sulphate. These salts do not undergo hydrolysis because, the conjugate base and acid are very weak to hydrolyse water. The solution will be. neutral.

(ii) Salts of weak acids and strong bases - for example, sodium acetate, potassium cyanide.

(iii) Salts of strong acids and weak bases - for example, ammonium chloride, magnesium sulphate.

(iv) Salts of weak acids and weak bases - for example, ammonium carbonate, ammonium acetate.

I. Hydrolysis of salt of Weak Acid and Strong Base*

If the salt of weak acid and strong base represented as NaA is dissolved in water, the anion of the salt A^- will react with die hydrogen ions of water to form almost unionised weak acid, HA

$$A^- + H_2O \rightleftharpoons OH^- + HA \quad \text{... (1)}$$

Applying the law of mass action to the above hydrolysis equilibrium,

$$K_h = \frac{[OH^-][HA]}{[A^-][H_2O]} \quad \text{... (2)}$$

Where, K_h is the hydrolysis constant of the salt.

The resulting solution will be basic, since an excess of hydroxyl ions are formed as a result of hydrolysis. This accounts for the well known fact that aqueous solutions of salts such as cyanides, acetates, borates and phosphates of alkali metals are basic.

We can calculate the extent to which hydrolysis occurs using a simple method. The ionisation equilibrium of the weak acid, HA may be written as

$$HA \rightleftharpoons H^+ + A^- \quad \text{...(3)}$$

The ionisation constant of the weak acid is given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{... (4)}$$

The ionisation equilibrium of water may be written as,

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{.... (5)}$$

Ionic product of water, $K_w = [H^+][OH^-]$ ... (6)

Dividing equation (6) by equation (4)

$$\frac{K_w}{K_a} = \frac{[H^+][OH^-][HA]}{[H^+][A^-]} \quad \text{... (7)}$$

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]} \quad \text{... (8)}$$

We know, $K_h = \frac{[OH^-][HA]}{[A^-][H_2O]}$

But the concentration of water remains practically a constant and omitting it in the above equation.

$$K_h = \frac{[OH^-][HA]}{[A^-]} \quad \text{... (9)}$$

Comparing equations (8) and (9)

$$K_h = \frac{K_w}{K_a} \quad \text{... (10)}$$

Degree of hydrolysis

***Definition** : It may be defined as the fraction of each mole of the salt which gets hydrolysed when dissolved in water.*

If h is the degree of hydrolysis and C is the concentration in • per litre of the salt solution, then

$$\begin{array}{lllll} A^- + H_2O & \rightleftharpoons & HA & + \; OH^- & \quad \ldots (1) \\ C(1-h) & & Ch & \;\; Ch & \end{array}$$

$$K_h = [HA]\,[OH^-]\,/\,[A^-] \quad \ldots (9)$$

$$K_h = (hC \times hC)/C\,(1-h) = h^2C\,/\,(1-h) \quad \ldots (11)$$

$$K_h \cong h^2C \quad \ldots (12)$$

$$\text{or, } h^2 = \frac{K_h}{C} \quad \ldots (13)$$

$$h = \sqrt{\frac{K_h}{C}} \quad \ldots (14)$$

$$\text{since, } K_h = \frac{K_w}{K_a} \quad \ldots (10)$$

$$h = \sqrt{\frac{K_w}{K_a C}} \quad \ldots (15)$$

From above discussions, it is clear that —

i) the hydrolysis constant, K_h is inversely proportional to **the** ionisation constant of the acid, K_a

ii) the degree of hydrolysis (h) of the salt of a weak acid **and** strong base is inversely proportional to the square root of the initial concentration, C.

Again if the acid HA is weak, it is difficult to remove a proton from the acid. But the anion of the acid, A^- (i.e.) its conjugate base can easily take up a proton from water or the anion undergoes hydrolysis readily. Acetic acid is a moderately weak acid, but Hydrocyanic acid is very weak acid. Hence, the cyanide ion is hydrolyzed to a greater extent than acetate ion.

To summarize, the reaction of the salt of a strong base and weak acid with water, produces a basic solution.

II. Hydrolysis of the salt of a Weak Base and a Strong Acid

If the base BOH (for example,NH_4OH) is weak, its conjugate acid B^+ (i.e., NH_4^+) will be appreciably strong and hence it will tend to react with the solvent water as below:

$$B^+ + H_2O \rightleftharpoons BOH + H^+ \qquad (1)$$

Thus an excess of hydrogen ion is left and the resulting solution is therefore acidic. The equilibrium constant for the above hydrolysis reaction may be written as,

$$K_h = \frac{[BOH][H^+]}{[B^+][H_2O]} \quad (2)$$

The ionisation constant of the weak base is given by,

$$BOH \rightleftharpoons B^+ + OH^- \quad (3)$$

The ionization constant of the weak base is given by,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad (4)$$

The ionic product of water, K_W is given by

The ionisation equilibrium of the base may be written as

$$K_w = [H^+][OH^-] \quad \dots (5)$$

Dividing equation (5) by equation (4)

$$\frac{K_w}{K_b} = \frac{[H^+][OH^-][BOH]}{[B^+][OH^-]} \quad \dots (6)$$

$$\frac{K_w}{K_b} = \frac{[H^+][BOH]}{[B^+]} \quad \dots (7)$$

The concentration of water remains practically a constant and hence omitting it in the equation (2) we have,

$$K_h = \frac{[H^+][BOH]}{[B^+]} \quad \dots (8)$$

Comparing equation (7) with (8) we have,

$$K_h = \frac{K_w}{K_b} \quad \dots (9)$$

Degree of hydrolysis, h:. If h is the degree of hydrolysis and C is the concentration in moles per litre of the salt solution, then

$$\begin{array}{llll} B^+ + H_2O & \rightleftharpoons BOH & + \; H^+ & \dots (1) \\ C(1-h) & \quad\; Ch & \quad Ch & \end{array}$$

$$K_h = \frac{[BOH][H^+]}{[B^+]} \quad \dots (8)$$

$$K_h = \frac{hC \times hC}{C(1-h)} = \frac{h^2C}{(1-h)} \quad \dots (9)$$

$$K_h = h^2C \quad \text{... (10)}$$

$$\text{or} \quad h^2 = K_h/C \quad \text{... (11)}$$

$$h = \sqrt{K_h/C} \quad \text{... (12)}$$

$$\text{since, } K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{\frac{K_w}{K_b\,C}} \quad \text{... (13)}$$

Thus, the hydrolysis constant, K_h *is* inversely proportional to the ionisation constant of the base, K_b.

The degree of hydrolysis *is* inversely proportional to the square root of the initial concentration, C.

The reaction of the salt of a weak base and strong acid with water produces an acidic solution.

III. Hydrolysis of the salt by a Weak Acid and Weak Base

In this case, since both the acid and base are weak, their conjugate pairs are strong and will appreciably interact with water. Such salts are therefore considerably hydrolysed in aqueous solution.

The hydrolysis equilibrium of the salt of a weak acid and weak base (BA) may be written as,

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA \quad \text{... (1)}$$

$$K_h = \frac{[BOH]\,[HA]}{[B^+]\,[A^-]\,[H_2O]} \quad \text{... (2)}$$

The ionisation constant of the acid, HA is given by,

$$HA \rightleftharpoons H^+ + A^- \quad \text{... (3)}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \quad \text{... (4)}$$

The ionisation constant of the base, BOH is given by

$$BOH \rightleftharpoons B^+ + OH^- \quad \text{... (5)}$$

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} \quad \text{... (6)}$$

The ionic product of water, $K_w = [H^+]\,[OH^-]$ ... (7)

Dividing the equation (7) by the product of equations (4) and (6) we have,

$$\frac{K_w}{K_a\ K_b} = \frac{[H^+][OH^-][BOH][HA]}{[H^+][A^-][OH^-][B^+]} \qquad \text{... (8)}$$

$$\frac{K_w}{K_a K_b} = \frac{[HA][BOH]}{[B^+][A^-]} \qquad \text{... (9)}$$

Omitting the concentration of water in equation (2)

$$K_h = \frac{[BOH]\ [HA]}{[B^+][A^-]} \qquad \text{... (10)}$$

Comparing the equation (9) with (10) we have

$$K_h = \frac{K_w}{K_a K_b} \qquad \text{... (11)}$$

Thus, the hydrolysis constant K_h of the salt of the weak acid and a weak base is inversely proportional to the ionisation constant of the acid and base.

If h is degree of hydrolysis and C is the concentration of the salt of the weak acid and a weak base in moles per litre.

$$\begin{array}{ccccccc} B^+ & + A^- & + H_2O & \rightleftharpoons & BOH & + HA & \text{... (12)} \\ C(1-h) & C(1-h) & & & Ch & Ch & \end{array}$$

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]}$$

$$K_h = \frac{Ch \times Ch}{C(1-h)\ C(1-h)} \qquad \text{... (13)}$$

$$K_h = \frac{h^2}{(1-h)^2} \qquad \text{... (14)}$$

$$K_h \cong h^2 \qquad \text{... (15)}$$

$$\text{or,} \quad h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}} \qquad \text{... (16)}$$

Thus, the degree of hydrolysis of the salt of a weak acid and weak base is independent of the initial concentration of the salt solution.

Note: The ultimate nature of these solution will depend upon the relative hydrolysis of the anion and cation.

(i) If both anion and cation react to the same extent with water, then the solution is neutral.

(ii) If the cation reacts to a larger extent with water than the anion, the solution is slightly acidic (Eg. ammonium acetate)

(iii) If the anion reacts to a larger extent with water than the cation, the solution is slightly basic (Eg. ammonium carbonate)

Buffer Solutions

The pH of pure water is 7. The addition of 1 ml of 1N HCl to a litre of pure water at 298 K changes the pH from 7 to about 4. Similarly, the addition of 1 ml. of 1 N NaOH to one litre of pure water raises the pH from 7 to about 10. On the other hand, if we add a little hydrochloric acid or sodium hydroxide to a solution of ammonium acetate, the pH of the solution does not alter to any appreciable amount. Such solutions are called Buffer solutions. **Thus, *a buffer solution is one, which can resist the change in its pH value on dilution or the addition of a solution of an acid or a base.*** The word buffer is derived from the German word *Puffer*.

The resistance to change in pH on the addition of acid or base is known as ***buffer action.***

The magnitude of buffer action of a given buffer solution is determined by its ***buffer capacity.***

Buffer solutions usually consist of a solution of a weak acid or a weak base in the presence of its salts. Some of the buffer solutions are —

1) Acetic acid arid sodium acetate.
2) Boric acid and borax.
3) Citric acid and sodium citrate.
4) Phthalic acid and potassium hydrogenphthalate.
5) Ammonium chloride and ammonium hydroxide.
6) Borax and sodium hydroxide.
7) Sodium carbonate and sodium bicarbonate.

Uses

The chief use of buffer solutions in the laboratory is for making solutions of known and constant pH. Such solutions cannot be made accurately by adding acids and alkalis to each other and these solutions cannot be easily preserved due to the sensitivity of the pH to dissolved gases like CO_2 or alkali from glass vessels. However, on the basis of Handerson's equations, it is possible to prepare buffer solutions of any pH between 1 and 13 by a suitable choice *of* substances and their judicial combination.

Many industries, like sugar, paper, textile, tanning, milk products rely on buffer solution Importance of buffer solution in the living systems

Buffer and *hydrogen* ion concentration assume primeplace in many reactions of biological. Any alteration in the pH value may lead to *pathological condition.* Few instances are given below:

1) The pH of normal *human blood* is 7.35 and remains constant. Carbonic acid and bicarbonate, or the electrolytes in the body acts as the buffer solution control the pH of the blood. For a diabetic person, the value of pH falls to 6.8.
2) The value of pH of gastric juice lies in the pH range 1.4to 2.0. The increase of pH causes vomiting and ulceration.
3) The activity and the efficiency of enzymes, the biocata-lysts, depend on the pH. The control of pH is very important for the digestive system because the efficiency of digestive enzyme is maximum only at a specific pH. Any deviation from the pH values hinder or even stop the action of the biocatalysts.

   For example, the enzyme pepsin is effective at pH 1.4 to 2 in the stomach.
4) Many biochemical reactions are to be carried out at constant pH in the laboratory.

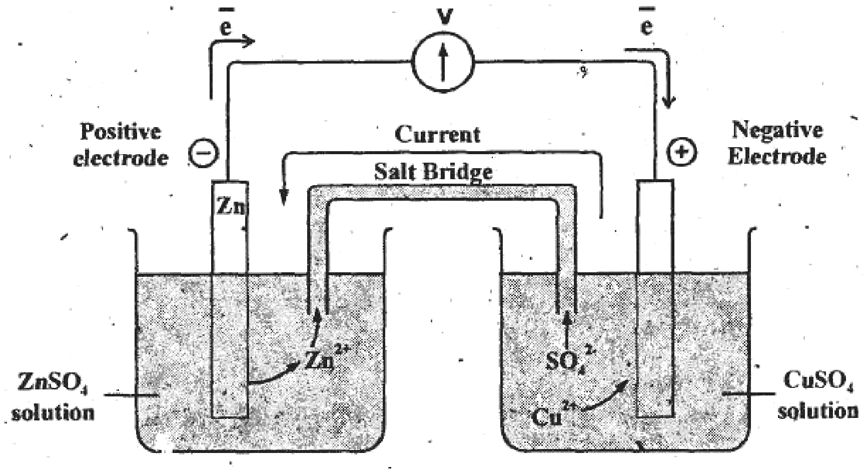
Galvanic cells

There are two types of cells namely Electrolytic cells and Galvanic cells. In an electrolytic cell *electrical emergy is consumed and a chemical change occurs.* In a galvanic cell *chemical* reaction occurs and electrical energy is produced.

The galvanic cell is a device used for the purpose of generating electrical' energy at the expense of chemical energy. It is also known as chemical cell or electrical cell.

A cell consists of two electrodes and a solution of an electrolyte. An electrode in contact with a sloution of an electrolyte is called a half cell.

A galvanic cell will consist of two such half cells. Daniel cell is an example of a galvanic cell The two half cells are Zn in contact with Zn^{2+} ion and Cu in contact with Cu^{2+}ions.



Galvanic Cell
Figure

At the zinc electrode electrons are produced by the following oxidation reaction.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

Such an electrode where electrons are pushed into the external circuit is called the anode. Oxidation takes place at the anode. The electrons so produced in the above step move through the external circuit. Then they enter the copper electrode where the following reduction takes place.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Such an electrode where electrons are pulled from the external circuit is called the cathode. Reduction takes place at the cathode.

Galvanic Cell	Electrolytic Cell
1. Electricity is produced	1. Electrolytes are decomposed
2. Chemical energy is converted into electrical energy	2 Electricity is used to decompose the electrolyte.
3. The positive electrode carries negative charge and the negative electrode carries positive charge	3. The positiv6 electrode is connected to the positive terminal of the battery and the negative electrode is connected to the negative terminal of the battery
4. Example **Daniel cell** Zinc rod is dipped in Zinc sulphate solution. Copper plate is dipped in copper sulphate solution and the salt bridge connects the two solutions.	4. Example **Copper electrolytic cell** The two electrodes are dipped in copper sulphate solution

Reversible and Irreversible Cells

A cell is said to be reversible if:

- i. the driving and the opposing forces differ very slightly from each other,
- ii. any change taking place in the cell can be reversed by applying a force infinitesimally greater than one acting on it.

If these conditions are not satisfied that cell is called an irreversible cell.

Examples: The cell consisting of a hydrogen electrode and a chlorine electrode dipping in HCl solution is an example for a reversible cell. The cell consisting of zinc and silver electrodes immersed in a solution of H_2SO_4 is an example for an irreversible cell.

Conventional representation of elcetro chemical cells

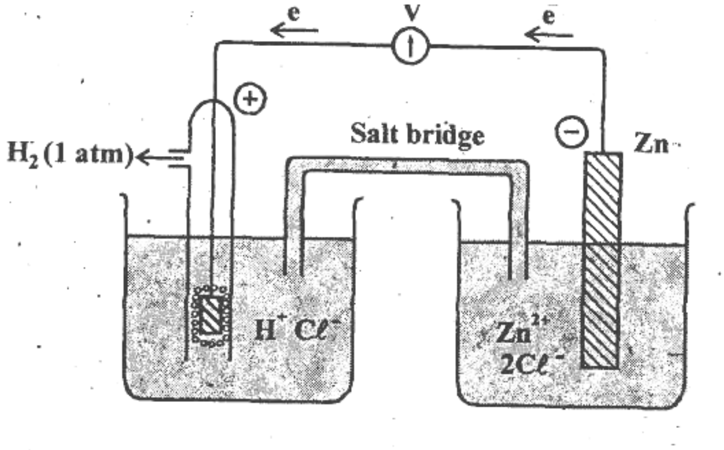
Electricity can flow from one point to another only when there is a potential difference between the two points. In a galvanic cell electricity flows because the two electrodes have different electrode potential. This difference of potential which causes the current to flow from an elctrode (which is at a lower potential) is called the e.m.f.(electro motive force).

An electrochemical cell has two electrodes. Let us imagine that the cell is placed before us. Let one electrode be on our right and the other on our left. The electromotive force of the cell is defined by

$$E_{Cell} = E^{o}_{Right} - E^{o}_{Left}$$

Explanation

Let our cell consists of a zinc-zinc ion electrode and a hydrogen electrode. The two electrodes are separated by a salt bridge. (A tube of agar-agar jelly saturated with KCl). This salt bridge separates the acid solution and the salt solution physically. But it provides electrical contact.



Figure

Zinc-zinc ion electrode is chosen as the RHS electrode Then the cell emf is

$$.E = E^{o}_{Zn^{2+},Zn} - E^{o}_{H^{+},H_2}$$

Symbol of the this cell is

$$Pt \mid H_2 \mid H^{+} \parallel Zn^{2+} \mid Zn$$

Here single vertical bar shows a phase boundary and the Double vertical bar shows a junction between the two electrode systems (half cell)

If we put the hydrogen electrode on the right hand side then the symbol will be

$$Zn \mid Zn^{2+} \parallel H^{+} \mid H_{2(g)} \mid Pt$$

The cell will be called the cell prime and emf of cell prime is

$$E^{o} = E_{H^{+},H_2} - E_{Zn^{2+},Zn} - E$$

The above notations are arbitrary, E may be either positive or negative. There is no difference which way we write the cell But we must not change the cell during a particular problem.

The cell reaction :

For the cell

$$Pt \mid H_2 \mid H^{+} \parallel Zn^{2+} \mid Zn \; ; \; E = E_{Zn^{2+},Zn} - E_{H^{+},H_2}$$

Both equilibria are written with the electrons on the reaction side.

Right electrode : $Zn^{2+}_{(aq)} + 2e^{-}(Zn) \rightleftharpoons Zn$ (1)

Left electrode : $2H^{+}_{(aq)} + 2e^{-}(Pt) \rightleftharpoons H_{2(g)}$ (2)

Subtfacting (1) from (2) i.e., right minus left

$$Zn^{2+}_{(aq)} + 2e^{-}\,(Zn) + H_{2\,(g)} \rightleftharpoons Zn + 2H^{+}_{(aq)} + 2e^{-}.(Pt)$$

This reaction gives the electrical and chemical changes which take placein the cell.

$$\text{i.e.,}\quad Zn^{2+}_{(aq)} + H_{2\,(g)} \rightleftharpoons Zn + 2H^{+}_{(aq)}$$

This chemical reaction which accompanies the electrical transformation is called the cell reaction.

EMF of a cell and its measurements

Electromotive force of **a cell** ***(EMF)***

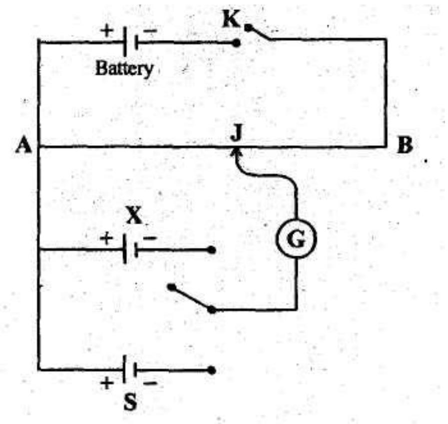
Electricity cannot flow from one point to another unless there is a potential difference between the two points. Hence the flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials.

The difference of potential between the two electrodes which causes the flow of current from one electrode (of higher potential) to another electrode (of lower potential) is called the electromotive force (EMF) of the cell

Measurement of EMF

The e.m.f. of a cell can be measured by connecting the two electrodes tothe two terminals of a voltmeter. The potential difference is then read directlyfrom the instrument. This method surfers from two defects. 1) As some currentis drawn from the cell during the process of measurement itselfj chemical reactionoccurs to some extent.This alters the concentration of the electrolyte. 2) Withflow of current, a part of the e.m.f. is used up in overcoming the internal resistanceof the cell. Hence the potential difference, as read from the voltmeter, will not bethe correct e.m.f. of the cell. ■

The correct measurement of e.m.f. is done using a potentiometer using Poggendorff's compensation principle. Connection are given as shown in the following diagram, (Figure). It consists of a uniform wire AB of high resistance.



A storage battery of constant e.m.f. which should be larger than the e.m.f. of the cell to be measured is connected at the ends of A and B of the potentiometerwire. The cell X whosed e.m.f. is to'be determined is included in the circuit by connecting the positive pole at the same point A at which the positive of the battery is connected. A galvanometer and sliding contact J are connected as shown in the diagram in the galvanometer. The position of J is noted. The e.m.f. of the cell (E_x) is proportional to the distance AJ.

That is $E_x \alpha AJ$

The cell X is now replaced by a standard cell S, whose e.m.f. is known. The position of the sliding contact is readjusted till there is null deflection in the galvanometer. The position J is noted.

$$\text{Now } E_S \ \alpha \ AJ'$$

$$\text{Therefore} \quad \frac{E_X}{E_S} = \frac{AJ}{AJ'}$$

Or $$E_X = \frac{AJ}{AJ'} \times E_S$$

Knowing E_s, E_x can be calculated.

Computation of the cell *EMF*

To calculate the cell emf for any combination of electrodes, the same procedure is to be followed

$$\text{i.e., } E = E_{\text{Right}} - E_{\text{Left}}$$

But Nernst equation for each half cell emf is to be used. Taking the cell

$$Pt \mid Sn^{2+}, Sn^{4+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$$

RHS half cell equation

$$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+} \qquad (3)$$

LHS half cell equation

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+} \qquad (4)$$

cell equation is RHS half cell equation - LHS half cell equation i.e.; (3) — (4)

$$2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+} \qquad (5)$$

$$\text{The cell emf } E_{Cell} = E_{Fe^{3+}, Fe^{2+}} - E_{Sn^{4+}, Sn^{2+}} \qquad (6)$$

Nernst equation for the half cell reactions are

$$E_{Fe^{3+}, Fe^{2+}} = E^o_{Fe^{3+}, Fe^{2+}} - \frac{RT}{2F} \ln \frac{a^2_{Fe^{2+}}}{a^2_{Fe^{3+}}} \qquad (7)$$

and

$$E_{Sn^{4+}, Sn^{2+}} = E^o_{Sn^{4+}, Sn^{2+}} - \frac{RT}{2F} \ln \frac{a^2_{Sn^{2+}}}{a^2_{Sn^{4+}}} \qquad (8)$$

Substituting (6) and (7) in (8)

$$E_{Cell} = E^o_{Fe^{3+}, Fe^{2+}} - E^o_{Sn^{4+}, Sn^{2+}} - \frac{RT}{2F} \ln \frac{a^2_{Fe^{2+}}}{a^2_{Fe^{3+}}} + \frac{RT}{2F} \ln \frac{a^2_{Sn^{2+}}}{a^2_{Sn^{4+}}} \qquad (9)$$

$$\therefore \ E_{Cell} = E^o_{Fe^{3+}, Fe^{2+}} - E^o_{Sn^{4+}, Sn^{2+}} - \frac{RT}{2F} \ln \frac{a^2_{Fe^{2+}} \, a^2_{Sn^{4+}}}{a^2_{Fe^{3+}} \, a^2_{Sn^{2+}}} \qquad (10)$$

[The same result can be obtained by simply seeing the cell reaction].

Standard Electrode potentials, Sign conventions

Standard Electrode Potential

The potential developed at an electrode in contact with I M Solution of its own ions at 298 K is arbitrarily chosen as the standard electrode potential of the element.

Sign Conventions

We know each well consists of two electrodes. At one electrode oxidation takes place, i.e electrons are evolved. At the other electrode reduction takes place, i.e electrons are consumed. Each electrode is regarded as a half - cell.

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution, is called the electrode potential. If the tendency is to lose electrode it is called reduction potential.

Thus oxidations potential is the reverse of reduction potential. Thus if the. oxidations potential of an electrode is 2.2 volts, then its reduction potential is 2.2 volts and vice versa.

It is not possible to determine experimentally the potential of a single electrode, (i.e of a half-cell) It is only difference of potential between two electrodes that we can measure by combining them to give a complete cell. By arbitrarily fixing the potential of one electrode as zero. We can assign numerical values to the potentials of the various other electrode. So the potential of a reversible hydrogen electrode in which the gas at the one atmosphere pressure is bubbled through a solution of Ht ions of units activity has been fixed as zero. This electrode is known as Standard Hydrogen Electrode (SHE) All other single electrode potentials are referred to as potentials on the hydrogen scale.

To find the electrode potential 1 say a Zn^{2+} electrode. We have to combine it with SHE. The cell will be

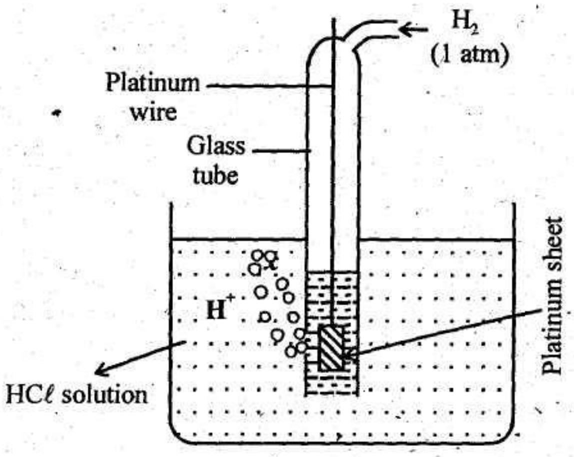
$Zn |Zn^{2+}|| H^{+}(c = 1), H_2$ (latm) | Pt

The ems of the cell is determined potent metrically. The potential of the cell gives the electrode potential of the Zn / Zn^{2+} electrode since the potential of the SHE has been taken as zero.

Standard Electrode

1. Standard hydrogen electrode

If purified hydrogen gas is passed over a platinum electrode



Hydrogen Eelctrode

which is in contact with HCl sloution. It is called the hydrogen electrode.

If we pass purified hydrogen gas at one *atmosphere pressure* through the glass tube over the platium electrode which is in contact with 1N HCl, then the system is known as the Standard Hydrogen Electrode (SHE) or the Normal Hydrogen Electrode (NHE).

Symbol: $H^+|H_{2(g)}|Pt$

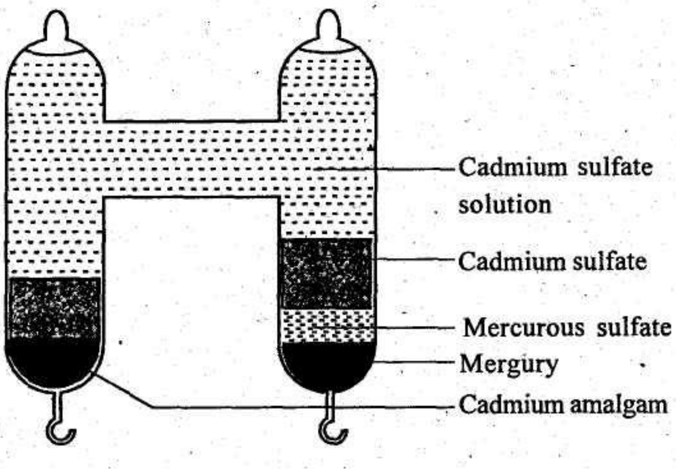
At the electrode surface the following equilibrium exists.

$$H^+ + e^- \rightleftharpoons ½ H_{2(g)}$$

By convention, the potential of SHE is taken as zero.

2. Weston standard cell

A standard cell is that which is capable of giving constant and reproducible E.M.F. independent of the temperature changes. The cell most commonly used as almost universal standard for potentiometric work is Weston standard cell shown in figure.



It consists of an H - shaped glass vessel with a platinum wire sealed through the bottom of each limb. One limb contains a layer of pure mercury (1 cm. deep) which is covered with a paste of sparingly soluble salt, ' mercurous sulphate (paste made with saturated solution of cadmium sulphate), which constitutes the anode. The other limb constituting the cathode, contains 12.5% cadmium amalgam covered with layer of cadmium sulphate crystals ($3CdSO_4.8H_2O$). The electrolyte is a saturated solution of cadmium sulphate. It may be represented as

Cd in Hg | $3CdSO_4.8H_2O$ (saturated solution) ; $Hg_2SO_4(s)$ | Hg.

The cell has a definite E.M.F. given by

$E_t = 1.018300-4.06xl0-^{6}(t-20)-9.5xl0-^{7}(t-20)^{2}-lxl0-^{8}(t-20)^{3}$,So that the value is 1.0813 volts at 20°C. The temperature coefficient i.e., change of E.M.F. with change of temperature of the Western cell is negligibly small.

Reference Electrodes

A reference electrode is necessary to determine the emf of an electrode, i.e., single electrode potentials.

We know that a cell is made of two half cells i.e., two electrodes. We always use a reference electrode as one of these electrodes. We derermine the E_{cell} knowing the values of E_{cell} and $E_{reference\ electrode}$. We can calculate the E of the other electrode.

A good reference electrode must be

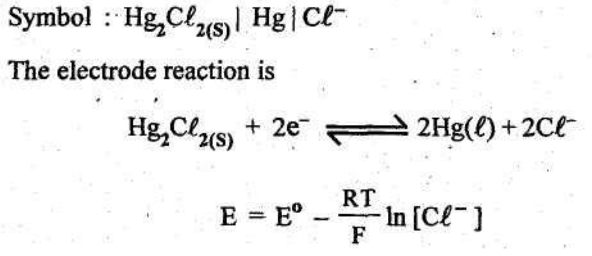
(i) reproducible (ii) easy to set up (iii) capable of being used for a long time and (iv) it should not require a salt bridge.

The standard hydrogen electrode, is used as a reference electrode for single electrode potential. But it is difficult to setup SHE because maintaining the activity of H^+ ions at unity and keeping the pressure of the H_2 at 1 atm, is difficult. To overcome these difficulties some other electrodes called secondary reference electrodes are used.

One such secondary reference electrode is calomel electrode.

Calomel Electrode:

This is a metal - insoluble salt - anion electrode.



Symbol : $Hg_2C\ell_{2(S)}$ | Hg | $C\ell^-$

The electrode reaction is

$$Hg_2C\ell_{2(S)} + 2e^- \rightleftharpoons 2Hg(\ell) + 2C\ell^-$$

$$E = E^o - \frac{RT}{F} \ln [C\ell^-]$$

The potential of calomel electrodes depend on the concentration of the KCl solution used in them.

The following table gives the standard values of various calomel electrodes.

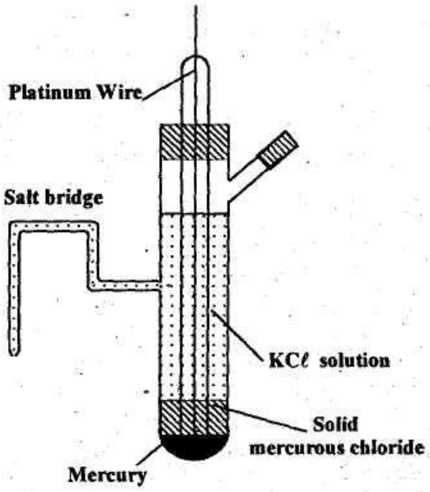
Table

Name	Solution	E volts
Saturated calomel electrode	Saturated KCl	+0.242
Normal calomel electrode	1N (or 1 M) KCl	+0280
Decinormal calomel electrode	0.1N(or0.1M)KCl	+0.334

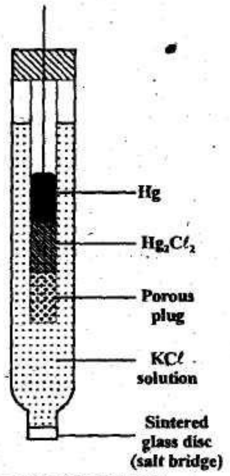
Usually saturated calomel electrode is used as a reference electrode because it could be very easily prepared.

Description

The calomel electrode consists of mercury, solid mercurous chloride and solution of KCl.



Calomel Electrode.



A dipping calomel electrode

Pure mercury is placed at the bottom of a glass tube. A paste of mercurous chloride (calomel) is placed over mercury. A solution of KCl is introduced abovethe paste. The concentration of KCl is either saturated, normal or decinormal as the case may be. This electrode is reversible with respect to the chlorideion. When dipping calomal electrode is used salt bridge is not necessary.

The other secondary standard electrodes are

1. Quinhydrone electrode
2. Glass electrode

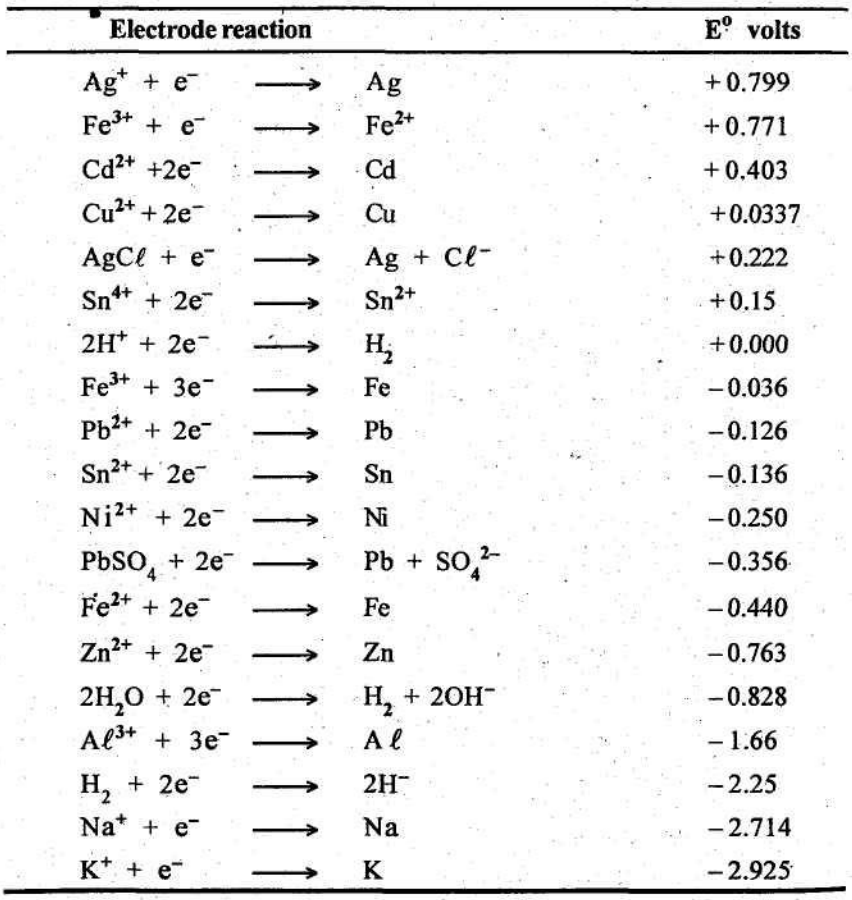
Electro chemical series

The potential of an electrode, at a given temperature, depend upon the concentration of the ions in the surrounding solution. If the concentration of the ion is unity and the temperature is 25°C, the potential of the electrode is termed as the standard electrode potential, E°. The standard electrode potentials (reaction) of a number of electrodes are given is table 3. The values of standard potentials arranged in the decreasing order is called the electro chemical series.

Table

Electro chemical series

Standard electrode potentials(Reduction) at 25°C



Electrode reaction			E° volts
$Ag^+ + e^-$	$\longrightarrow$	Ag	+0.799
$Fe^{3+} + e^-$	$\longrightarrow$	Fe^{2+}	+0.771
$Cd^{2+} + 2e^-$	$\longrightarrow$	Cd	+0.403
$Cu^{2+} + 2e^-$	$\longrightarrow$	Cu	+0.0337
$AgC\ell + e^-$	$\longrightarrow$	$Ag + C\ell^-$	+0.222
$Sn^{4+} + 2e^-$	$\longrightarrow$	Sn^{2+}	+0.15
$2H^+ + 2e^-$	$\longrightarrow$	H_2	+0.000
$Fe^{3+} + 3e^-$	$\longrightarrow$	Fe	−0.036
$Pb^{2+} + 2e^-$	$\longrightarrow$	Pb	−0.126
$Sn^{2+} + 2e^-$	$\longrightarrow$	Sn	−0.136
$Ni^{2+} + 2e^-$	$\longrightarrow$	Ni	−0.250
$PbSO_4 + 2e^-$	$\longrightarrow$	$Pb + SO_4^{2-}$	−0.356
$Fe^{2+} + 2e^-$	$\longrightarrow$	Fe	−0.440
$Zn^{2+} + 2e^-$	$\longrightarrow$	Zn	−0.763
$2H_2O + 2e^-$	$\longrightarrow$	$H_2 + 2OH^-$	−0.828
$A\ell^{3+} + 3e^-$	$\longrightarrow$	$A\ell$	−1.66
$H_2 + 2e^-$	$\longrightarrow$	$2H^-$	−2.25
$Na^+ + e^-$	$\longrightarrow$	Na	−2.714
$K^+ + e^-$	$\longrightarrow$	K	−2.925

Significance of electro chemical series :

i) Determination of feasibility of a reaction:

The half cell potential is a measure of the tendency of a reaction to occur.

E.g., From the table : [a] $Zn^{2+} + 2e^- = Zn$; the $E^o_{zn^{2+}, zn}$ is −0.763 V.

This potential is with reference to the SHE. This means that the cell reaction is non spontaneous. That is Zn^{24+} ions can not be reduced by hydrogen at 1 atm. pressure by oxidising itself to H^+ ions at unit activity because E° value is negative.

$$\text{b) } Ag^+ + e^- = Ag\text{ ; the } E^o_{Ag^+, Ag} \text{ is } + 0.799\text{ V}$$

This means that the cell reaction is spontaneous. That is Ag^+ ions can bereduced by hydrogen at 1 atm. pressure by oxidising itself to H^+ ions at unitactivity because E° is positive.

In general, the compounds of metals with high negative standard potentials are not reduced by hydrogen. In fact they reduce H^+ ions to hydrogen. [i.e., they liberate hydrogen from acids] E.g., Zn, K, Na, Mg etc.

Nobel metals, e.g., Cu, Ag etc., have high positive standard potential values. Their compounds are easily reduced by hydrogen. They do hot liberate hydrogen from acids.

ii) Determination of solubility product

From Nernst equation we know that E of a metal depends on activity of the metal ion is solution.

$$\text{E.g., } E_{Ag^+, Ag} = E^o_{Ag^+, Ag} - 0.05915 \log \frac{1}{a_{Ag^+}}$$

assuming $a_{Ag+} = [Ag^+]$, if we decrease $[Ag^+]$ E_{Ag+} + also decreases. Thus reagents which precipitate Ag^+ lower E value. E.g., Addition of NaCl decreases $[Ag^+]$ in solution and hence $E_{Ag+\,,\,Ag}$ also decreases.

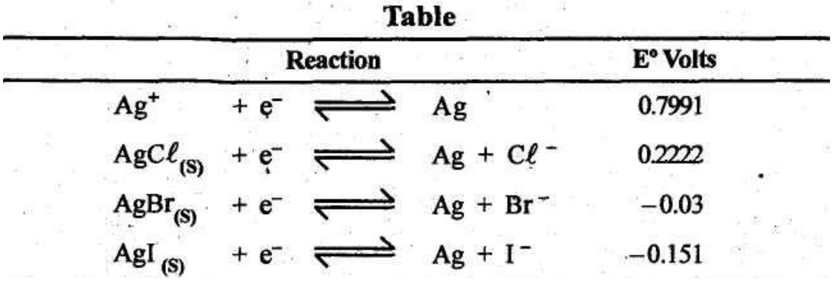
This principle is used it the determination of the solubility product of sparingly soluble salts such as AgCl.

$$E^o_{AgC\ell,\ Ag\ ,\ C\ell^-} = E^o_{Ag^+, Ag} + 0.05915 \log K_{sp}$$

Thus if we can measure $E^0_{AgCl,\ Ag\ Cl^-}$ and $E_{Ag+\ ,\ Ag}$ we can calculate K_{sp} of AgCl, where K_{sp} is the solubility product of AgCl.

iii) Comparison of solubilities of substances :

From E° values for the same metal in various compounds we can find which is soluble.



Table

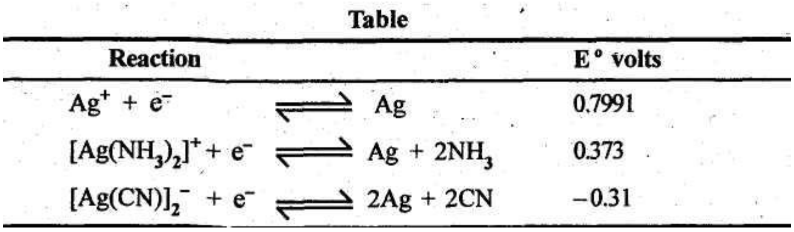
Reaction	E° Volts
$Ag^+ + e^- \rightleftharpoons Ag$	0.7991
$AgC\ell_{(S)} + e^- \rightleftharpoons Ag + C\ell^-$	0.2222
$AgBr_{(S)} + e^- \rightleftharpoons Ag + Br^-$	−0.03
$AgI_{(S)} + e^- \rightleftharpoons Ag + I^-$	−0.151

a) From the above table $E^0_{Ag,\ I,\ ^-\ AgI^-}$ is found to have a negative potential. This means that silver will dissolve in HI and liberate hydrogen and, therefore, this reaction takes place first. Later, reaction stops because a layer of insoluble Agl is formed on the Ag surface and prevent it from attack by HI

b) $E^0_{AgCl^+\,,\ Ag\ Cl^-}$ is less then $E^0_{Ag,Br,\ Ag,\ Br^-}$ which is less than $E^0_{AgCl,\ Ag\ Cl^-}$ This means that the solubility increases in that order i.e., Agl is less soluble than AgBr or AgCl.

iv) Effect of complexing on E°

Substances which from soluble complexes with metal ions also lower the electrods potential.



Table

Reaction	E° volts
$Ag^+ + e^- \rightleftharpoons Ag$	0.7991
$[Ag(NH_3)_2]^+ + e^- \rightleftharpoons Ag + 2NH_3$	0.373
$[Ag(CN)]_2^- + e^- \rightleftharpoons 2Ag + 2CN$	−0.31

v) To find the nobility of metals

Whether a metal is noble or active depends on it environments. From Tables 4 and 5 it is clear that Ag is a noble metal since it does not give hydrogen with HCl. In the presence of iodide, sulphide and cyanide ions it is an active metal since it liberates H_2 from HI.

vi) Effect of alloying (Amalgamation)

If the activity of the reduced member is decreased by some method the potential of the electrode increases. If the reduced member is a metal its activity is decreased by alloying it with another metal (usually Hg). That is why in some cases amalgam electrode are used instead of pure metals. Here the reactivity of the metal is decreased by adding Hg and there by converting it into an amalgam.

Electroplating

Electroplating is the art of depositing one metal over another metal with the help of electric current.

The primary reaction in electroplating is the deposition of metal from ions in solutions. The concentration of these ions in solution can be maintained in the following two ways —

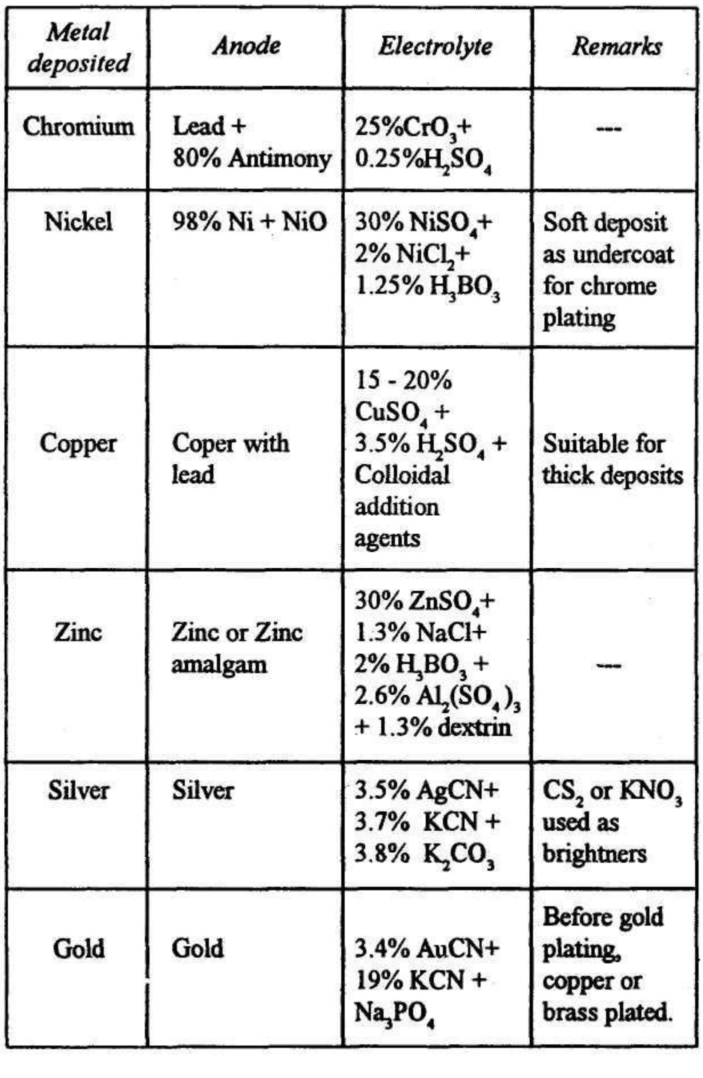
(i) by the addition of soluble salt of the metal

(ii) by the use of continuously dissolving anode of the metal.

The deposited metal must possess some superior properties. The iron articles are coated with tin, zinc, chromium, nickel etc. to prevent rusting and thus increases their life. Baser metals are coated with gold and silver to enhance their beauty. Since electroplating is used both for decoration and protection of the base metal from corrosion, it is important to secure a coating which is adherent, coherent, continuous and uniform.

Procedure: Electroplating is carried out in a tank which is made of iron, concrete, soap stone, stoneware, cement, wood etc. For small scale work, it may consist of glass, enamelled iron etc. It may be lined inside with a suitable material like rubber, lead or asphalt. The plates are hung in this tank from rods horizontally and its top is known as *bus-bars* which are insulated from the tank by using hard rubber.

A number of tank are generally worked out at the same time and these may be set up in series or in parallel. The article to be electroplated is made cathode and the anode consists of the metal to be deposited or of some insoluble substance (as in chrome plating, where lead is used as anode) Some features of electroplating are summarised in the following table.



Metal deposited	*Anode*	*Electrolyte*	*Remarks*
Chromium	Lead + 80% Antimony	25%CrO_3+ 0.25%H_2SO_4	---
Nickel	98% Ni + NiO	30% $NiSO_4$+ 2% $NiCl_2$+ 1.25% H_3BO_3	Soft deposit as undercoat for chrome plating
Copper	Coper with lead	15 - 20% $CuSO_4$ + 3.5% H_2SO_4 + Colloidal addition agents	Suitable for thick deposits
Zinc	Zinc or Zinc amalgam	30% $ZnSO_4$+ 1.3% NaCl+ 2% H_3BO_3 + 2.6% $Al_2(SO_4)_3$ + 1.3% dextrin	---
Silver	Silver	3.5% AgCN+ 3.7% KCN + 3.8% K_2CO_3	CS_2 or KNO_3 used as brightners
Gold	Gold	3.4% AuCN+ 19% KCN + Na_3PO_4	Before gold plating, copper or brass plated.

Determination of pH

The pH of a solution can be conveniently measured from emf measurements. In principle the activity of hydrogen ions in a solution can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions. The electrode is dipped in the solution of unknown pH. The other electrode is a reference electrode such as standard hydrogen electrode or quinhydrone electrode or glass electrode or standard calomel electrode. The liquid junction potential can be eliminated either by using a salt bridge or by dipping the reference electrode directly into the solution.

1. Determination of pH using hydrogen electrode

A cell of the type

$$\text{Pt} \mid H_2(1\,\text{atm}) \mid H^+_{(aH^+)} \parallel H^+_{(a=1)} \mid H_2, (1\,\text{atm}) \mid \text{Pt}$$

is set up.

The net cell reaction is $H^+_{(a=1)} = H^+_{(aH^+)}$

The emf of the cell is given by

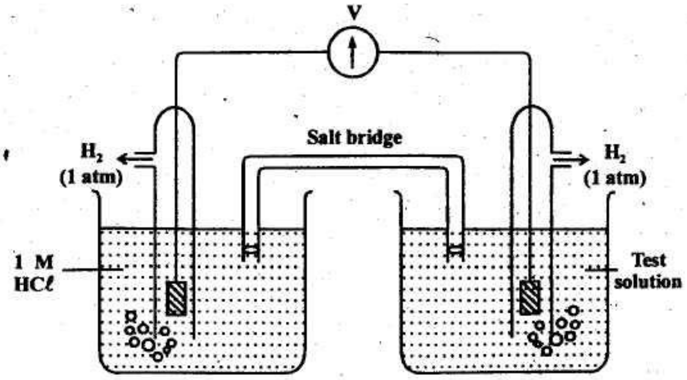
$$E = \frac{-RT}{F} \ \ln a_{H^+} = \frac{2.303RT}{F} \ \log_{10} a_{H^+}$$

By definition $pH = -\log_{10} a_{H^+}$

Now the above equation becomes

$$E = \frac{2.303RT}{F} \ pH = 0.0591\ pH$$

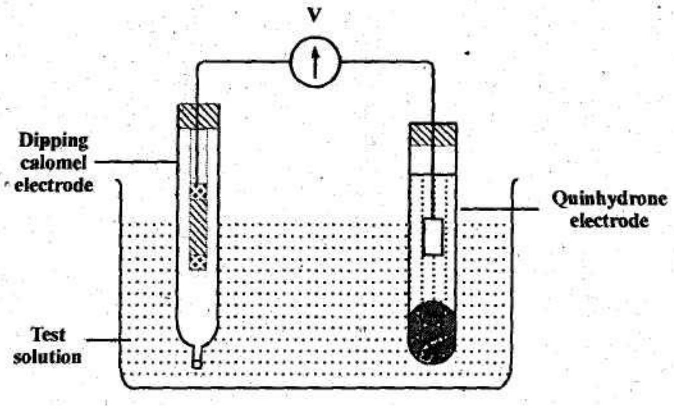
$$\therefore \ pH = \frac{E}{0.0591}$$



Thus the pH can be determined using hydrogen electrode.

2. Determination of pH using quinhydrone electrode :

Quinhydrone electrode is another commonly employed electrode for pH measurements. Quinhydrone is **a** 1:1 molecular compound of quinone (Q) and hydroquinone (H.Q).



Pt | Solution of unknown pH || SCE
(saturated with quinhydrone)

To measure the pH of an unknown solution it is saturated with quinhydrone and an insert electrode of Pt is dipped in solution. The electrode is then combined with a reference electrode such as an SCE (Standard Calmocal Electrode) to form the cell

The reaction at LHS

$$H_2Q = 2H^+ + Q + 2e^-$$

The potential E_L

$$E_L = E^o_L + \frac{RT}{F} \ \mathrm{in} \ a_{H^+}$$

(Since the concentration of H_2Q and Q are equal

$$-\frac{RT}{F} \ln \frac{a_{H_2Q}}{a_Q} \text{ will become zero)}$$

The $E^o{}_L$ of quinhydrone electrode is +0.699 V at 298 K.

$$\text{Now } E_L = +0.699 + \frac{RT}{F} \ \mathrm{In} \ a_{H^+}$$

$$= 0.699 + \frac{RT\,2.303}{F} \log_{10} a_{H^+}$$

$$= -0.699 - \frac{RT}{F} 2.303 \ \text{pH}$$

The cell emf EMF $E = E_R - E_L = E_{Ref} - E_L$.

Reference electrode is SCE. The emf of EMF $E_{Ref} = 0.2415$

$$\text{Now } E = 0.2415 - \left(0.699 - \frac{RT}{F} 2.303\, pH\right)$$

$$= 0.2415 - 0.699 + 0.0591\, pH$$

$$= -0.4575 + 0.0591\, pH$$

$$E + 0.4575 = 0.0591\, pH\, ; \quad \frac{E + 0.4575}{0.0591} = pH$$

$$\therefore pH = \frac{E + 0.4575}{0.0591}$$

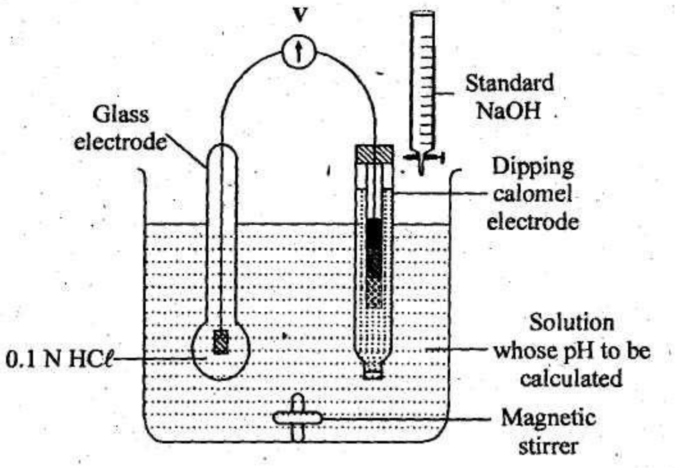
If the pH of the solution is greater than 7, the electrode acts as cathode then the cell becomes

SCE || unknown soln. | Pt

$$\text{Now } pH = \frac{0.4575 - E}{0.0591}$$

3. Determination of pH using glass electrode :

Glass electrode is universally employed electrode for pH measurement. The glass electrode is made of low melting and high conductivity glass. It consists of a thin glass bulb filled with 0.1 N HCl and a Ag wire coated with AgCl immersed in it. The bulb is then placed in the solution of unknown pH and is combined with a reference electrode yielding the cell.



Ag | AgCℓ | 0.1N HCℓ | Glass | Solution pH = x || SCE

$$E = E_R - E_L = E_{ref} - E_G = E_{ref} - E^o{}_G - 0.0591\, pH$$

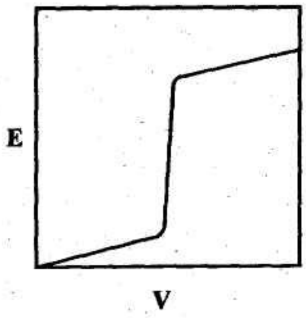
$$\left(E_G = E^o{}_G - \frac{RT}{2F} \ln a_{H^+} = E^o{}_G + 0.0591\, pH\right)$$

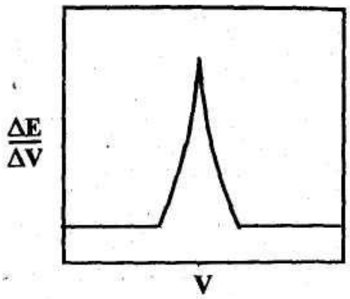
So from the above equation knowing the cell emf and the emf of the reference electrode the pH of the unknown solution can be determined.

4. Determination of pK_a of acids by Potentiometric methods;

The pK_a of acids can be determined by potentiometric titration method. The potentiometric titration is based upon the fact that near the end point there is a sudden change in emf of hydrogen or any standard electrode.

The acid under consideration is kept in a beaker. A standard hydrogen electrode is dipped in the acid solution. A standard Calomel electrode is connected by means of a salt bridge. A standard solution of the alkali is added from the burette and after each addition the emf is measured by means of a potentiometer. The values of emf are plotted against the volume of alkali as shown in the figure. The sharp point of inflexion represents the equivalence (end) point.





To find out the sharp end point another graph is drawn with $\Delta E / \Delta V$ against V, the volume of alkali added (Figure). The peak of the curve shows the sharp end point. From Henderson equation

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

At the half neutralisation point (50% of neutralisation)

the concentration of acid = the concentration of salt.

Then

$$pH = pK_a$$

The half neutralisation point is found from the graph. The pH value is calculated from emf measurements. Then from the equation

pK-pH

NOTES

NOTES