IV – SEMESTER
STUDY MATERIAL

COURSE-4
INORGANIC, ORGANIC & PHYSICAL CHEMISTRY

PREPARED BY

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UNIT – I
ORGANO METALLIC COMPOUNDS

The compounds in which a metal atom is directly bonded to a carbon of hydrocarbon are organo metallic compounds.

Ex: CH_3Li, CH_3MgCl

CLASSIFICATION

OMC's are classified into simple and mixed OMC's

Simple OMC's

The OMC's in which metal atom is bonded with same alkyl group.

Ex: CH_3Li, $(C_2H_5)_2Mg$

These are further classified into symmetric and asymmetric OMC's

SYMMETRIC OMC'S

The OMC's in which metal is bonded to same alkyl groups.

Ex: CH_3Li, $(CH_3)_2Zn$

ASYMMETRIC OMC'S

The OMC's in which metal atom is bonded with different alkyl groups are called asymmetric OMC's.

Ex: $CH_3 – Mg – C_2H_5$

Mixed OMC's

These are formed by alkyl and other groups attached to the metal.

Ex: CH_3MgBr

COMPOUNDS ON THE BASIS OF BOND TYPE

Based on bond type OMC's are classified into four types

   a) Ionic OMC's
   b) Covalent OMC's
   c) Π-bonded OMC's
   d) Bridge bonded OMC's

Ionic OMC's

The OMC's of highly electro positive metals are ionic nture.

Ex: CH_3Li

Covalent OMC's

Lower electro positive and non-transition metals form covalent compounds.

Ex: $(CH_3)_2Zn$

Π-bonded OMC's

Transition metals form this type of compounds.

Ex: Ferrocene $(C_5H_5)_2 Fe$

Bridge bonded OMC's

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METAL CARBONYLS

Metal complexes containing CO molecules as ligands are called metal carbonyls.

GENERAL FORMULA

$M_x (CO)_y$

BONDING OF CARBONYLS

In CO there is a triple bond between carbon and oxygen. CO donates a pair of electrons to the transition metal atom to form a dative bond or coordinate covalent bond.

CLASSIFICATION

These are classified into three types

1. Mono nuclear carbonyls
   Ex: $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $V(CO)_6$
2. Bi nuclear carbonyls
   Ex: $Fe_2(CO)_9$, $Co_2(CO)_8$
3. Poly nuclear carbonyls
   Ex: $Fe_3(CO)_{12}$

Explain the following structures carbonyls

1. $Ni(CO)_4$
2. $Fe(CO)_5$
3. $Cr(CO)_6$
4. $Mn_2(CO)_{10}$

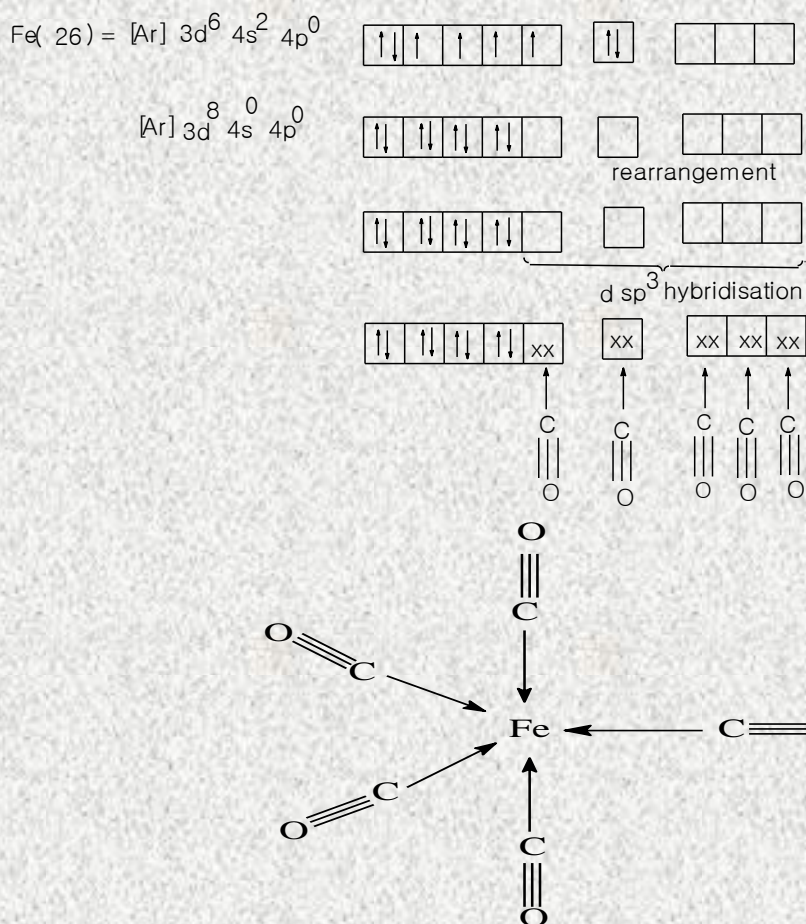## STRUCTURES OF METAL CARBONYLS

Ni (CO)$_4$

Outer most electronic configuration of Ni is $3d^8 4s^2$. The electrons in 4s orbital rearrange into 3d orbital. Now Ni undergoes sp^3 hybridisation. The hybrid orbitals are filled in by electron pairs donated by CO molecules. Hence the molecule is tetrahedral.
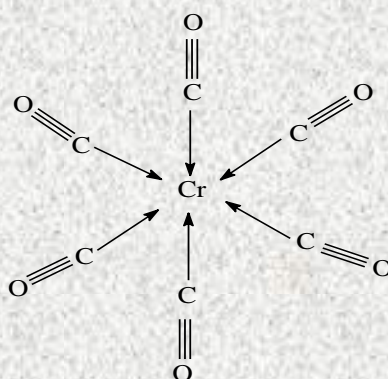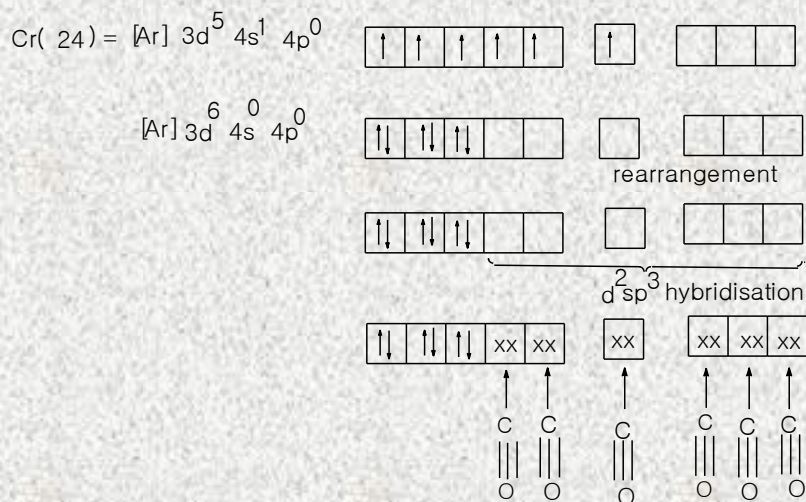
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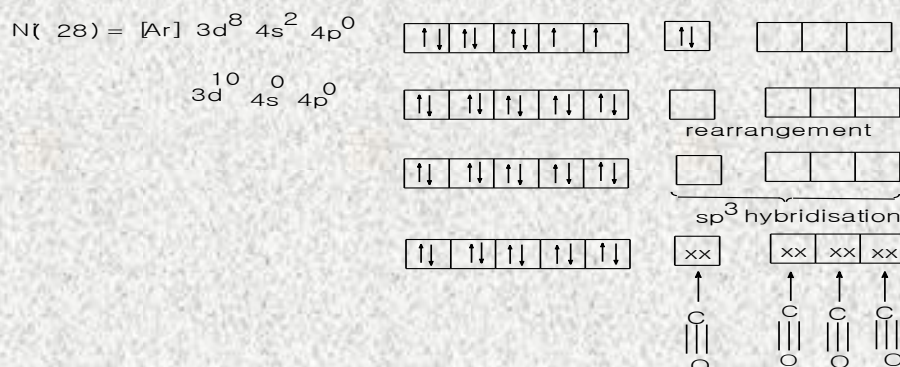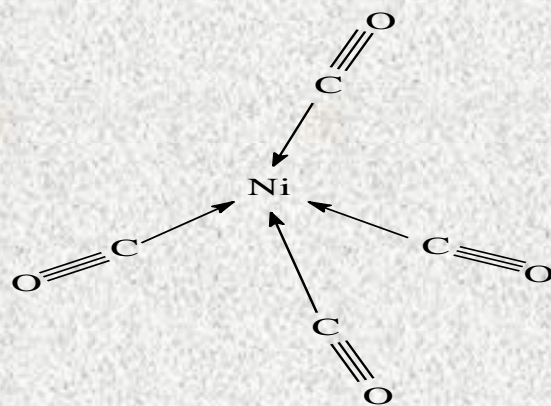
Fe (CO)₅

Outer most electronic configuration of Fe is $3d^6 4s^2$. The electrons in 4s orbital rearrange into 3d orbital. Now Fe undergoes sp^3d hybridisation. The hybrid orbitals are filled in by electron pairs donated by CO molecules. Hence the molecule is trigonal bi pyramid.
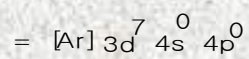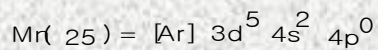
$Fe(26) = [Ar]\ 3d^6\ 4s^2\ 4p^0$

$[Ar]\ 3d^8\ 4s^0\ 4p^0$

rearrangement

$d\ sp^3$ hybridisation

Cr (CO)₆

Outer most Electronic configuration of Cr is $3d^5 4s^1 4p^0$. The electrons in 4s orbital rearrange into 3d orbital. Now Cr undergoes SP^3d^2 hybridisation. The hybrid orbitals are filled in electron pairs donated by CO molecules. Hence the molecule is regular octahedron.

$Cr(24) = [Ar] 3d^5 4s^1 4p^0$

$[Ar] 3d^6 4s^0 4p^0$

rearrangement

d^2sp^3 hybridisation

O
‖
C
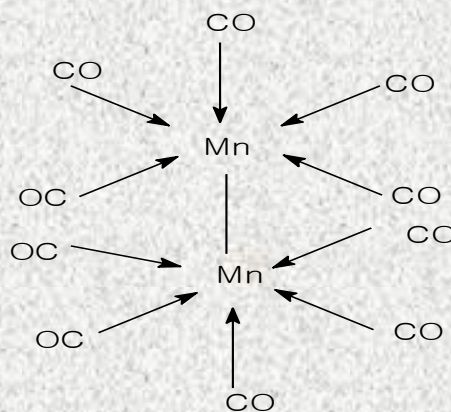O≡C   C≡O
      Cr
O≡C   C≡O
C
‖
O

Mn₂(CO)₁₀

Outer most electronic configuration of Mn is $3d^5 4s^2$. The electrons in 4s orbital rearrange into 3d orbital. Now Mn undergoes sp^3d^2 hybridisation. The hybrid orbitals are filled in electron pairs donated by CO molecules. Structure of Mn₂(CO)₁₀ consists of two Mn(CO)₅ units held together by metal metal bond between the two Mn atoms.

$Mr(25) =$ [Ar] $3d^5 4s^2 4p^0$

$=$ [Ar] $3d^7 4s^0 4p^0$

rearrangement

d^2sp^3 hybridisation

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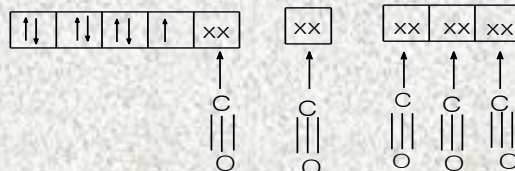
CARBOHYDRATES

Poly hydroxyl aldehydes, poly hydroxy ketones or any other compounds which on hydrolysis gives poly hydroxy carbonyl compounds are collectively called carbohydrates.
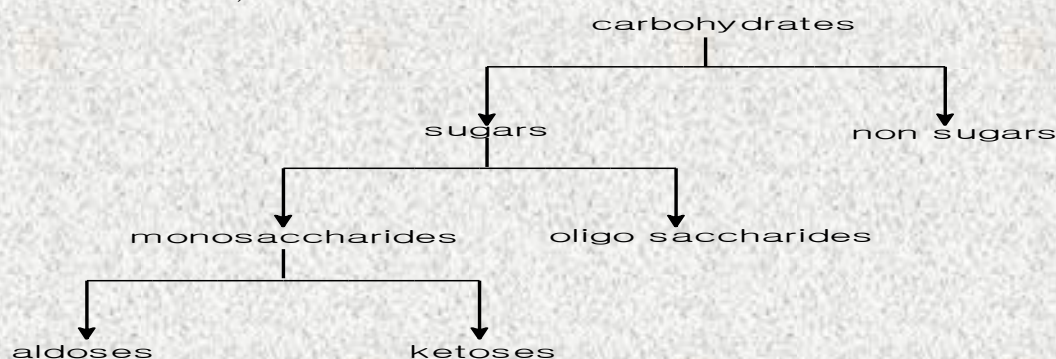
CLASSIFICATION

These are two types

1. Sugars
   a) Mono saccharides
   b) Oligo saccharides
2. Non sugars (polysaccharides)

MONO SACCHARIDES

These are poly hydroxyl aldehyde or ketones which cannot be hydrolysed further to simpler sugars.
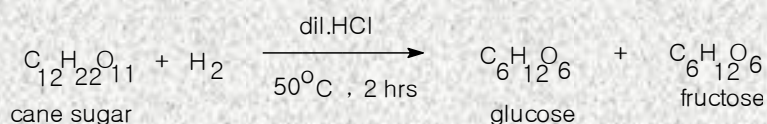
Ex: Aldo hexose, Keto hexose

STRAIGHT CHAIN STRUCTURE OF GLUCOSE
PREPARATION
FROM SUCROSE

It can be easily obtained in the laboratory by the hydrolysis of alcoholic solution of cane sugar with dil.HCl at 50^0C for about 2 hours.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2 \xrightarrow[50^oC \ , \ 2\,hrs]{dil.HCl} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

FROM STARCH

It is obtained by the hydrolysis of starch with hot, dilute mineral acids.
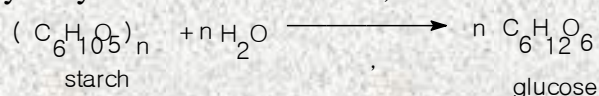
$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\hspace{2cm}} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

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CHEMICAL PROPERTIES

Structural formula of glucose is $CH_2OH.(CHOH)_4.CHO$

It indicates the presence of

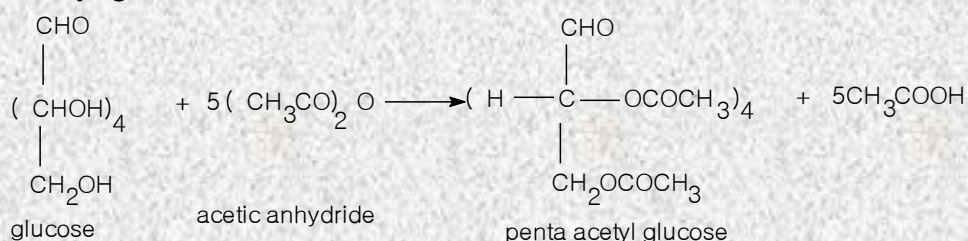   i)   One aldehyde group

    ii)   Four secondary alcoholic groups

    iii)   One primary alcoholic group

Hence glucose must give characteristic properties of aldehydes and alcohols.

Evidence for straight chain

ACETYLATION

Glucose reacts with acetic anhydride in the presence of anhydrous $ZnCl_2$ to form penta – acetyl glucose.

glucose   acetic anhydride   penta acetyl glucose

This reaction indicates the presence of 5 hydroxyl groups in glucose molecule.

1. **Formation of cyanohydrins (reaction with HCN)**

   Glucose reacts with HCN to form glucose cyanohydrins.

      glucose   glucose cyanohydrir
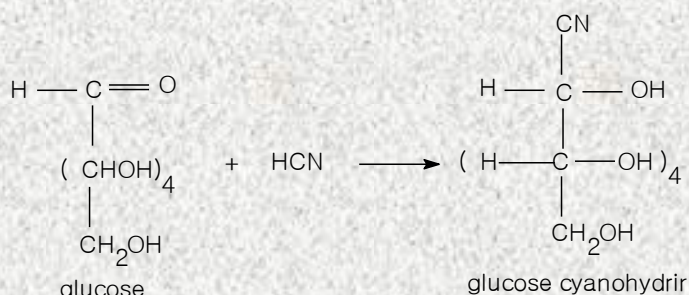
2. **Reduction**

   Reduction of glucose with concentrated hydroiodic acid and red phosphorus at 100^0C gives 2-iodohexane. Prolonged heating with conc. Hydroiodic acid and red phosphorus gives n-hexane.

$$CH_2OH.(CHOH)_4.CHO \xrightarrow[\text{P}]{\text{conc.HI}} CH_3.(CH_2)_3.CHI.CH_3$$

2-iodo hexane

$$CH_2OH.(CHOH)_4.CHO \xrightarrow[\text{with HI + P}]{\text{prolonged heating}} CH_3.(CH_2)_4 CH_3$$
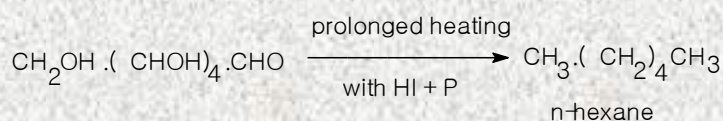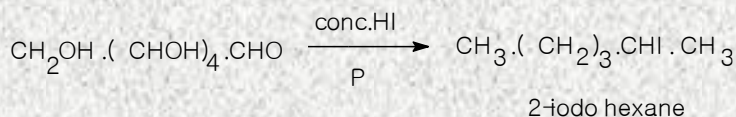
n-hexane

   Formation of n-hexane indicates the straight chain structure of glucose.

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*Glucose reduces Tollens reagent indicating that the carbonyl group is aldehydic in nature.

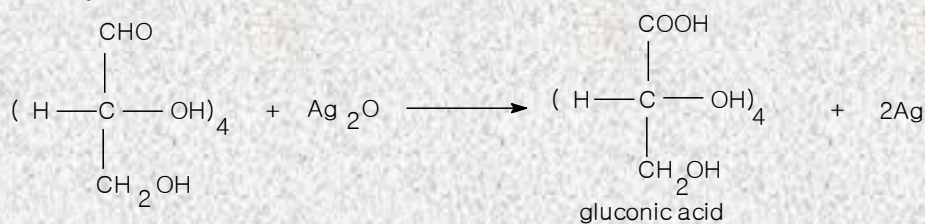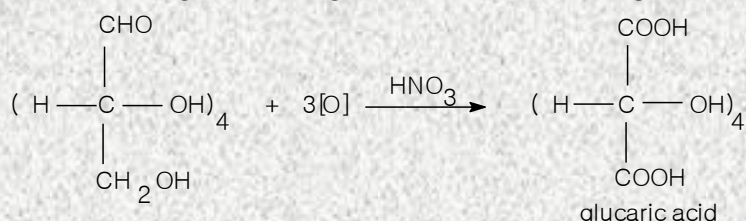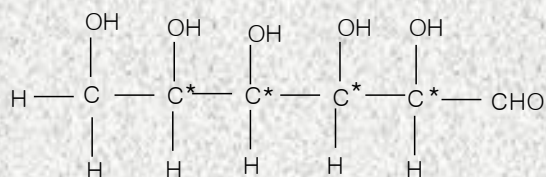$$(H\!-\!\underset{\underset{CH_2OH}{|}}{\overset{\overset{CHO}{|}}{C}}\!-\!OH)_4 \quad + \quad Ag_2O \quad \longrightarrow \quad (H\!-\!\underset{\underset{CH_2OH}{|}}{\overset{\overset{COOH}{|}}{C}}\!-\!OH)_4 \quad + \quad 2Ag$$

gluconic acid

3. **Oxidation**

Strong oxidizing agents like nitric acid oxidize both the groups (-CHO and –CH$_2$OH) of glucose to give the dibasic acid (glucaric acid or saccharic acid)

$$(H\!-\!\underset{\underset{CH_2OH}{|}}{\overset{\overset{CHO}{|}}{C}}\!-\!OH)_4 \quad + \quad 3[O] \quad \xrightarrow{HNO_3} \quad (H\!-\!\underset{\underset{COOH}{|}}{\overset{\overset{COOH}{|}}{C}}\!-\!OH)_4$$

glucaric acid

4. **Open chain structure**: On the basis of the above points glucose may be assigned following structure.

$$H\!-\!\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C^*}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C^*}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C^*}}\!-\!\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C^*}}\!-\!CHO$$

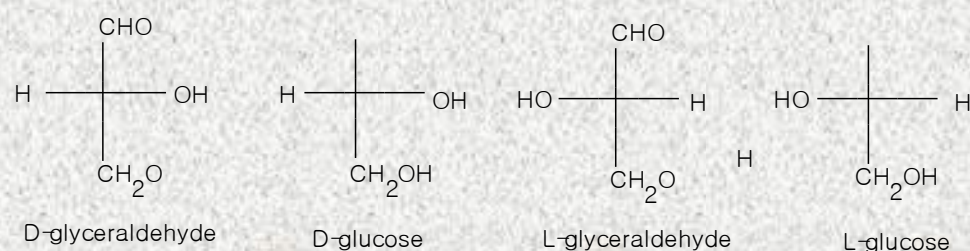5. **Configuration of glucose**

The above structure have four asymmetric carbon atoms, it can exist in $2^4 = 16$ optically active forms.

The configuration is written with CH$_2$OH at the bottom end. Then on the asymmetric carbon H is on the left hand side and OH is on the right hand side are written. –CHO group is written at top end. Carbohydrates with these configurations are called

D-carbohydrates or sugars. The sugars in whose configuration H is on the right hand side and –OH is on the left hand side are taken as L-sugars.

D-glyceraldehyde   D-glucose   L-glyceraldehyde   L-glucose

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6. **Objections to open chain structure of glucose**
    i)   Glucose does not form a bisulphate and aldehyde-ammonia compound.
    ii)   Glucose forms two isomeric penta acetates neither of which reacts with carbonyl reagents.
    iii)   Glucose shows mutarotation.
    iv)   Glucose reacts with methanol in presence of dry HCl gas to form two isomeric glucosides.

$$C_6H_{11}O_5\,O\boxed{H\ +\ OH}CH_3 \xrightarrow{\text{dil.HCl}} C_6H_{11}O_5.OCH_3 + H_2O$$

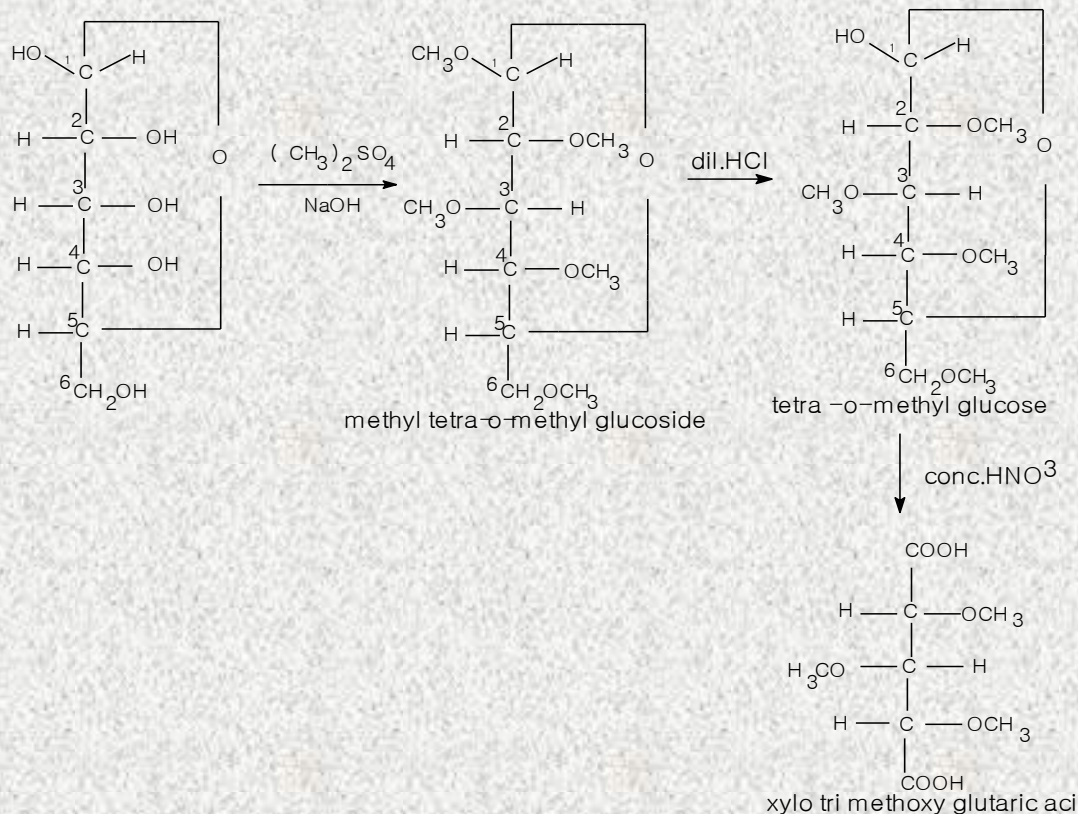   glucose   methanol   methyl glucosides

* The above reactions the carbonyl group in the glucose is not free. On the basis and stability of ϒ - lactones of the aldanoic acid, Tollen proposed a cyclic hemiacetal 5-membered ring between first and fourth carbon atom of D(+) -glucose.

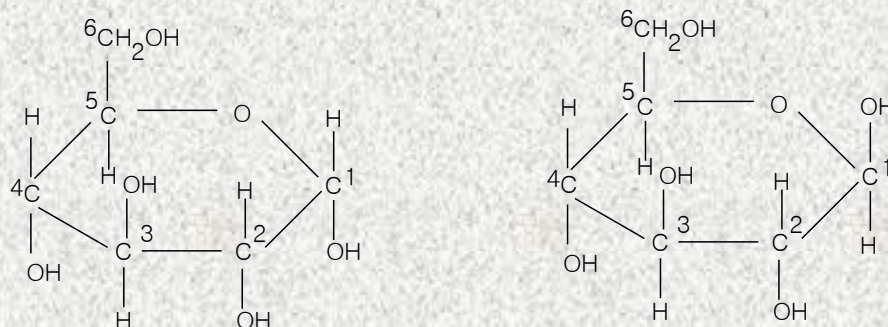Later Haworth proposed six membered rings between first and fifth carbon atoms.

open chain structure   5-membered   6-membered ring
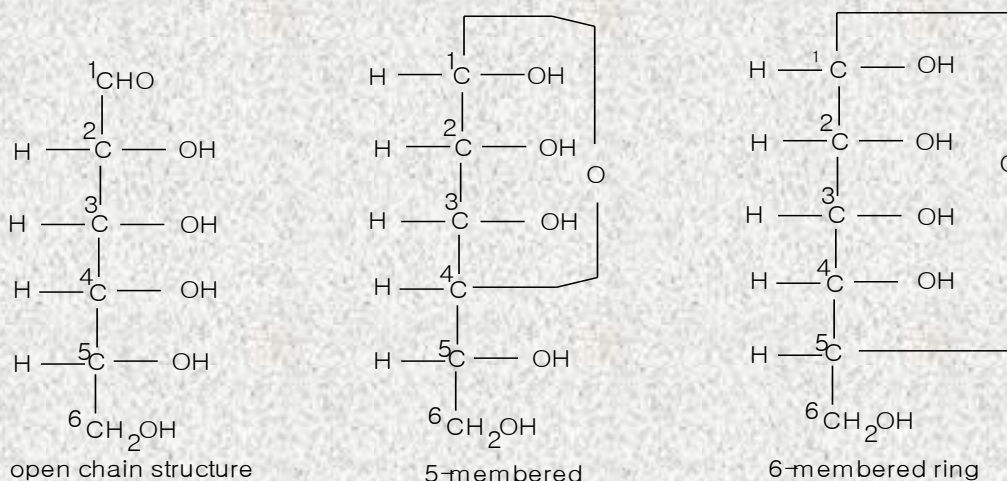
Proof for the ring size

The glucose is treated with a mixture of one mole alcohol and one moleHCl to form a mixture of α ,βmethyl glucosides. This mixture is separated and one glucoside is obtained. This is treated with dimethyl sulphate in presence of NaOH. Methyl-tetra-O-methyl glucoside is formed.this glucoside on treatment with HCl, the O-CH$_3$ present on acetyl carbon is converted into O-H. tetra-O-methyl glucose is obtained. Tetra-O-methyl glucose is oxidized with conc. HNO$_3$ to form Xylo tri methoxy glutaric acid.this is meso compound. The glucose gave finally six membered glutaric acid. This confirmed the pyranose ring structure.

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methyl tetra-o-methyl glucoside

tetra –o–methyl glucose

xylo tri methoxy glutaric aci
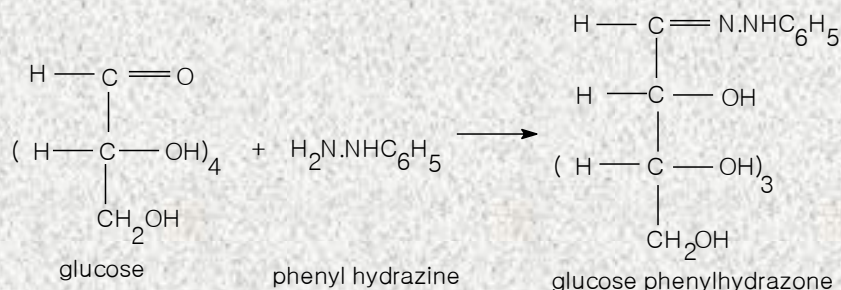
Different structures of glcose

MUTAROTATION

Glucose recrystallised from hot water melts at 146^0C. The specific rotation of the solution of this glucose is (+) 112.2^0. This value of this rotation gradually decreased with time and reached final constant value of (+) 52.7^0. The D-glucose crystals obtained on evaporating the glucose solution in water at 98^0C showed specific optical rotation of (+) 18.7^0 in aqueous solutions. This rotation value increased gradually with time and attained constant value of (+) 52.7^0. this means that the specific rotation of one solution at glucose in water gradually decreased and the specific rotation of another solution of glucose gradually increased with time but both reached finally a constant value. This type of change of specific rotation of glucose in solution with time is called mutarotation.

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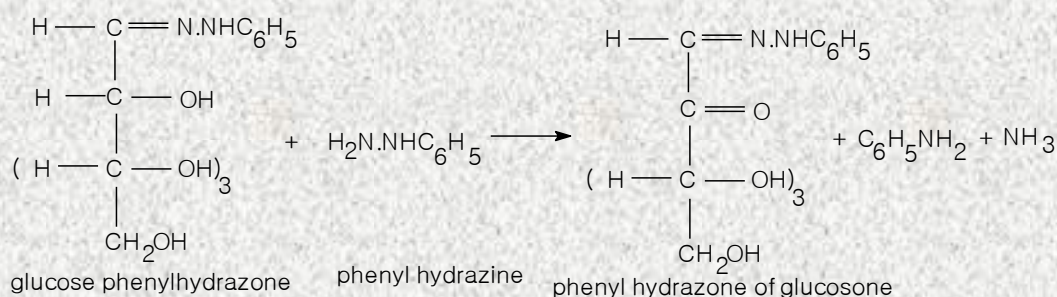*LECTURER IN CHEMISTRY*
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FORMATION OF OSAZONE

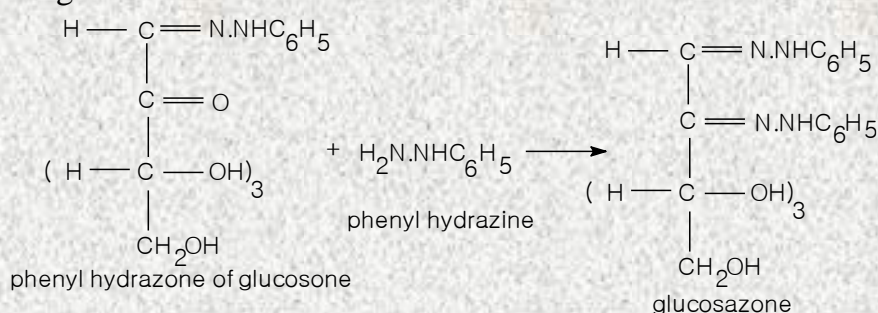Glucose reacts with excess (3molecules) of phenyl hydrazine to form glucosazone.

a) One molecule of phenyl hydrazine reacts with the aldehyde group of glucose to form glucose phenyl hydrazone.

$$H-C=O$$
$$(H-C-OH)_4$$
$$CH_2OH$$
glucose

$$+\ H_2N.NHC_6H_5$$
phenyl hydrazine

$$\longrightarrow$$

$$H-C=N.NHC_6H_5$$
$$H-C-OH$$
$$(H-C-OH)_3$$
$$CH_2OH$$
glucose phenylhydrazone

b) The second molecule of phenyl hydrazone oxidizes the secondary alcoholic group (-CHOH-) adjacent to the aldehyde group to a ketonic group and itself is reduced to aniline and ammonia.

$$H-C=N.NHC_6H_5$$
$$H-C-OH$$
$$(H-C-OH)_3$$
$$CH_2OH$$
glucose phenylhydrazone

$$+\ H_2N.NHC_6H_5$$
phenyl hydrazine

$$\longrightarrow$$

$$H-C=N.NHC_6H_5$$
$$C=O$$
$$(H-C-OH)_3$$
$$CH_2OH$$
phenyl hydrazone of glucosone

$$+\ C_6H_5NH_2\ +\ NH_3$$

c) The new keto group reacts with the third molecule of phenyl hydrazine to form glucosazone.

$$H-C=N.NHC_6H_5$$
$$C=O$$
$$(H-C-OH)_3$$
$$CH_2OH$$
phenyl hydrazone of glucosone

$$+\ H_2N.NHC_6H_5$$
phenyl hydrazine

$$\longrightarrow$$

$$H-C=N.NHC_6H_5$$
$$C=N.NHC_6H_5$$
$$(H-C-OH)_3$$
$$CH_2OH$$
glucosazone

INTER CONVERSIONS OF MONO SACCHARIDES

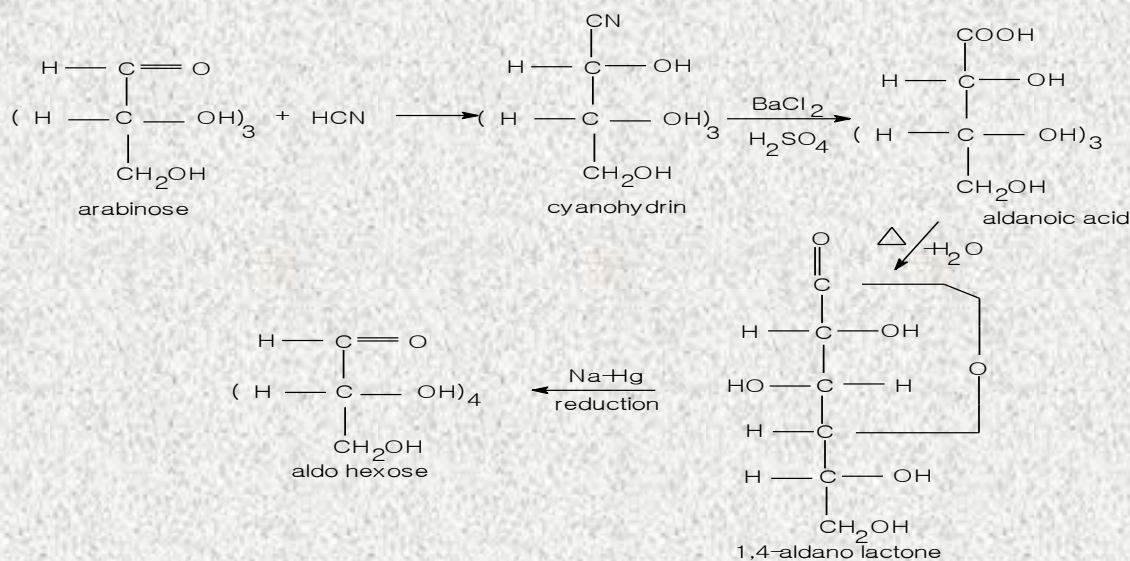1. **Kiliani's synthesis (aldo pentose to aldo hexose)**

   Ex: Arabinose to glucose

   i)   The aldopentose is treated with HCN additional carbon atom is introduced in the chain in the form of CN.

   ii) The cyanohydrins are hydrolysed with aqueous $Ba(OH)_2$ yielding a mixture of two aldanoic acid.

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iii)   Aldanoic acid is evaporated to dryness to give a mixture of two Υ-lactones.
iv)   The Υ-lactones are reduced in acetic medium to yield the corresponding aldose.

arabinose + HCN → cyanohydrin → (BaCl₂ / H₂SO₄) aldanoic acid → 1,4-aldano lactone → (Na+Hg reduction) aldo hexose

2. ALDOSE TO KETOSE

Ex: glucose to fructose

i)   Glucose is warmed with excess of phenyl hydrazine to form glucosazone.
ii)   Glucosazone is hydrolysed with conc.HCl to give glucosone.
iii)   Glucosone when reduced with zinc and acetic acid gives fructose.

glucose → (3H₂N.NHC₆H₅) glucosazone → (HCl hydrolysis) glucosone → (Zn / CH₃COOH) fructose

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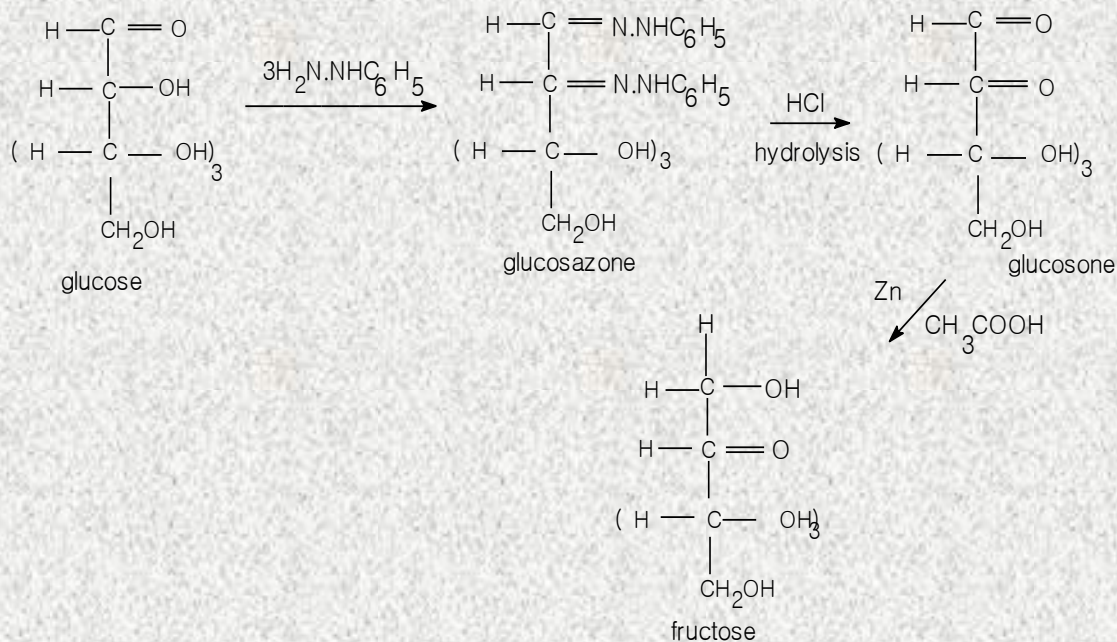
3. GLUCOSE TO ARABINOSE (RUFF'S METHOD)

i)   The aldose is oxidized with bromine water to the corresponding aldonic acid.

ii)   The calcium salt of the aldonic acid is oxidized by H_2O_2 in presence of ferrous salt as a catalyst [Fenton's reagent: $H_2O_2 + Fe^{+3}$] to the α-keto acid which is readily decarboxylated to the lower aldose.
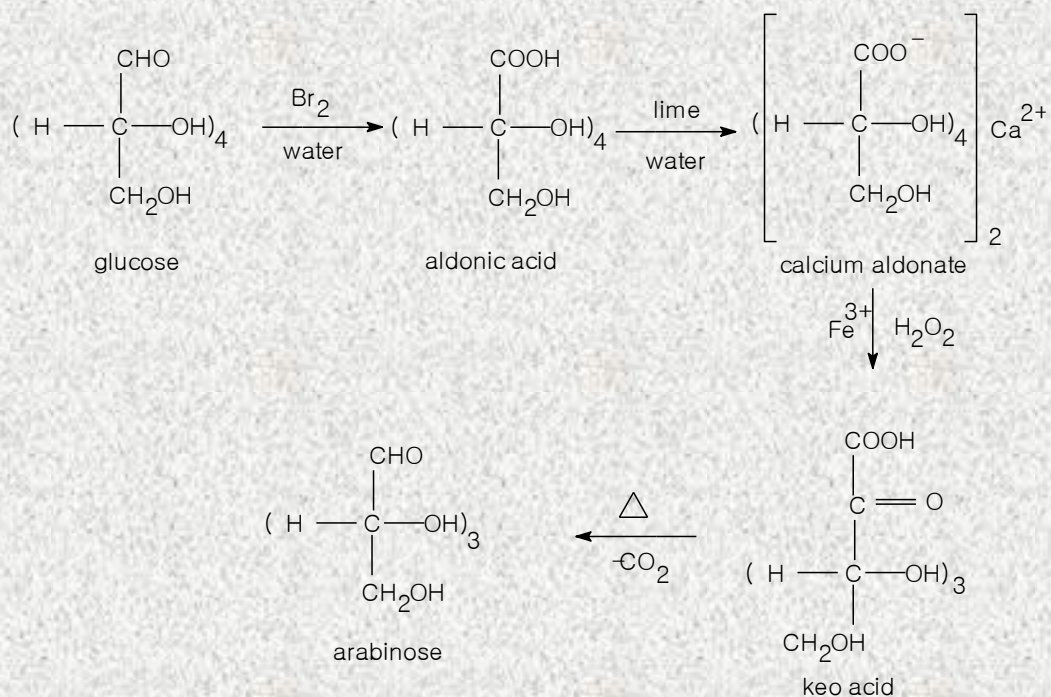
AMINO ACIDS

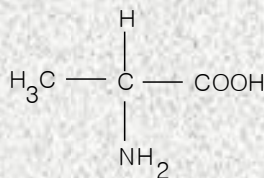Organic compounds containing both amino (- NH_2) and carboxyl group (-COOH) are known as amino acids.
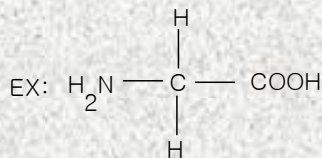
EX:

H$_2$N — C — COOH (with H above and H below)   glycine
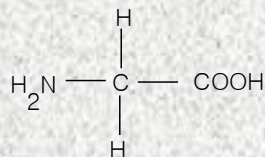
H$_3$C — C — COOH (with H above and NH_2 below)   alanine
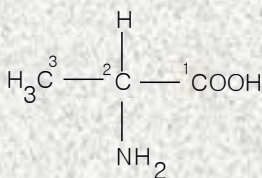
CLASSIFICATION

From the position of the amino group in the acid, amino acids are classified as α, β, ϒ – amino acids.

1. α-amino acids

The compounds in which the amino group and the carboxylic group are at the same carbon atom are α – amino acids or 2 – amino acids.

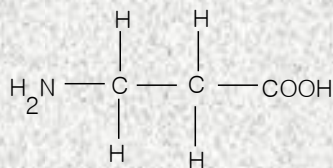EX: H$_2$N — C — COOH (with H above and H below)   glycine

H$_3$C^3 — ^{2}C — ^{1}COOH (with H above and NH_2 below)   alanine

2. β-amino acids

The compounds in which the amino group and the carboxylic groups are present on adjacent carbons are called β – amino acids.
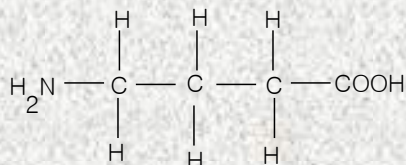
β – amino propionic acid

H$_2$N — C — C — COOH (each C with H above and H below)

3. ϒ- amino acids

The compounds in which there are two intermediate carbon atom between amino and carboxylic groups are called ϒ – amino acids.

ϒ- amino butyric acid

H$_2$N — C — C — C — COOH (each C with H above and H below)
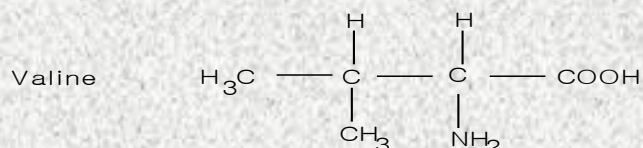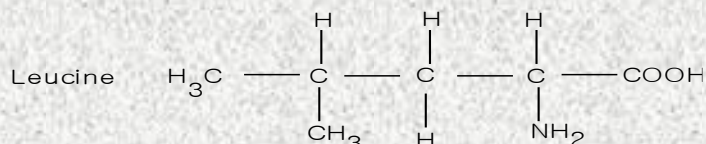
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4. Essential amino acids

The amino acids that cannot be synthesized by the body and must be supplied in the diet are called essential amino acids.

Ex: Valine, Leucine

Leucine
$$H_3C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}} - COOH$$

Valine
$$H_3C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}} - COOH$$

5. Non-essential amino acids

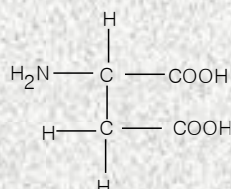The amino acids that can be synthesized by the body are called non essential amino acids.

Ex: Glycine, Alanine

α-amino acids are further classified into acidic, basic and neutral amino acids

1. Acidic amino acids

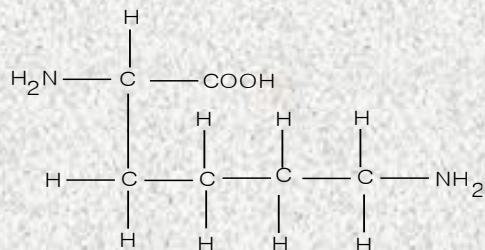These contain one amino and one or more carboxylic groups.

Ex: Aspartic acid

$$H_2N - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \;}{|}}{C}} - COOH$$
$$H - \overset{\overset{\displaystyle \;}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - COOH$$

2. Basic amino acids

These contain one carboxylic group and one or more amino groups.

Ex: Lysine

$$H_2N - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \;}{|}}{C}} - COOH$$
$$H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - NH_2$$
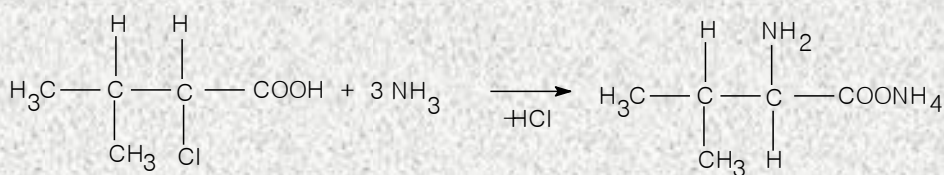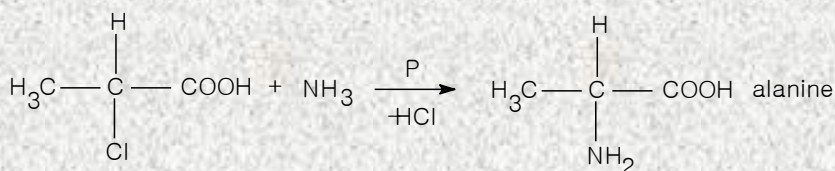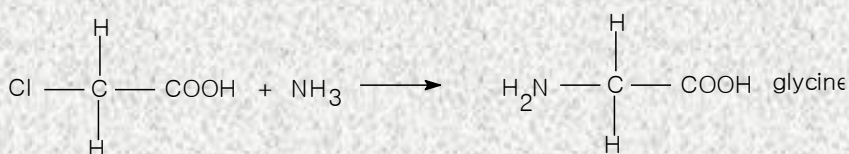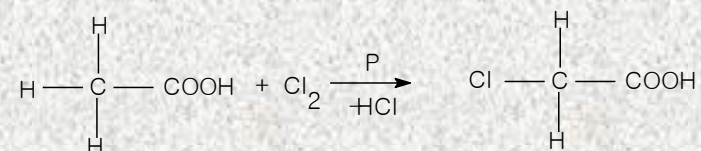
3. Neutral amino acids

If the number of amino groups and carboxylic groups are equal are called neutral amino acids.
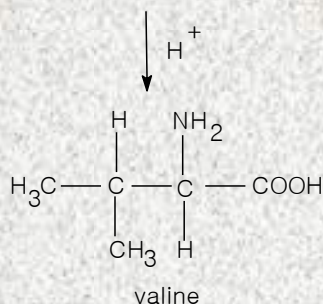
Ex: Glycine

SYNTHESIS OF α – AMINO ACIDS

1. Amination of α – halogen acids

In the presence of phosphorus carboxylic acids are reacted with chlorine or bromine α –halogenated acid are formed. These α – halo acid react with ammonia and give α – amino acids.
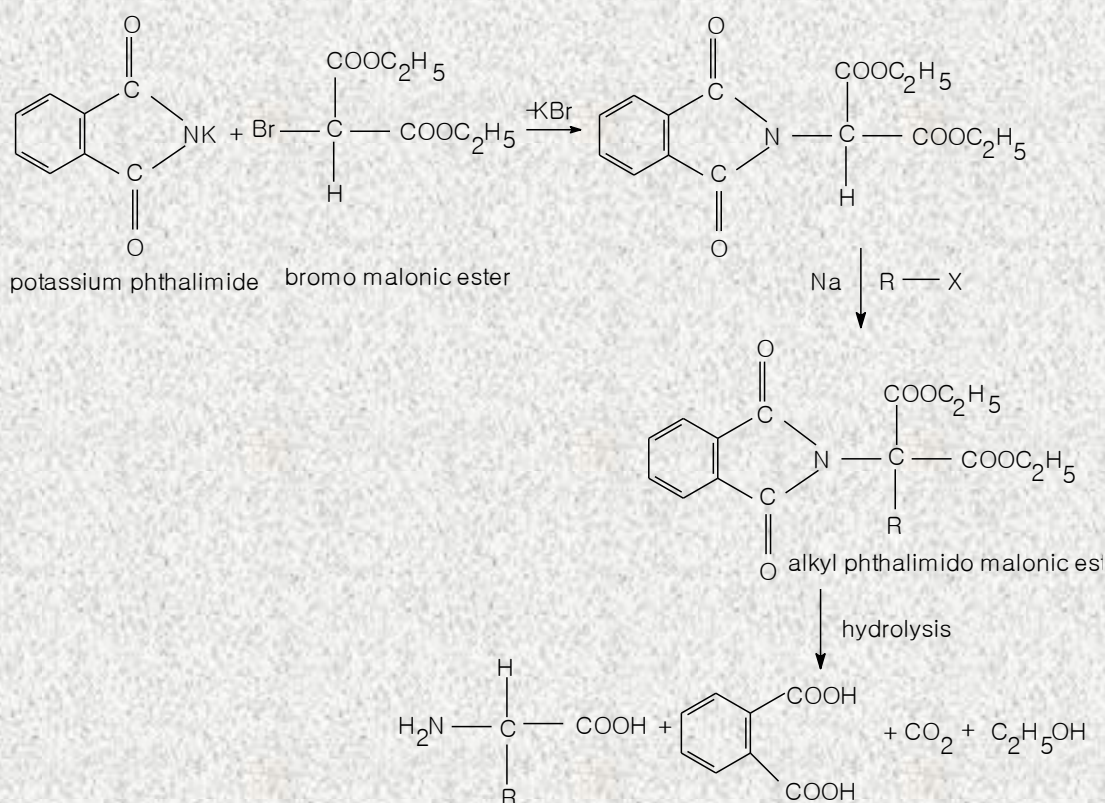

2-chloro-3-methyl butanoic acid

valine

2. Gabriel phthalimide synthesis

In this method an α – halo ester is treated with potassium phthalimide to form the corresponding substituted phthalimide. Which on hydrolysis gives phthalic acid and an amino acid.

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3. Malonic ester method

In this mehod malonic ester reacts with Na metal sodium malonic ester derivative is formed. This derivative reacts with alkyl halides alkyl malonic ester is formed which on hydrolysis gives alkyl amalonic acid. This acid reacts with bromine, bromine substituted carboxylic acid is formed. This reacts with ammonia α – amino acid is formed.

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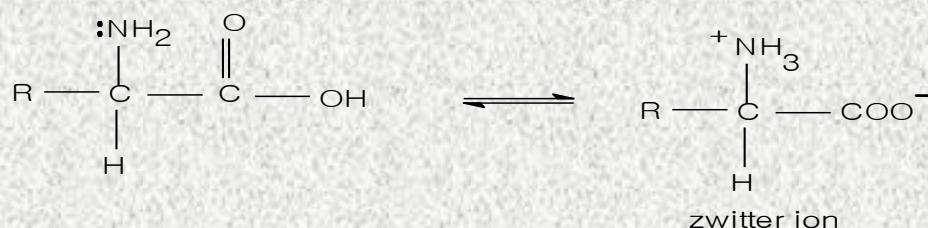*D.N.R.COLLEGE(A), BHIMAVARAM*
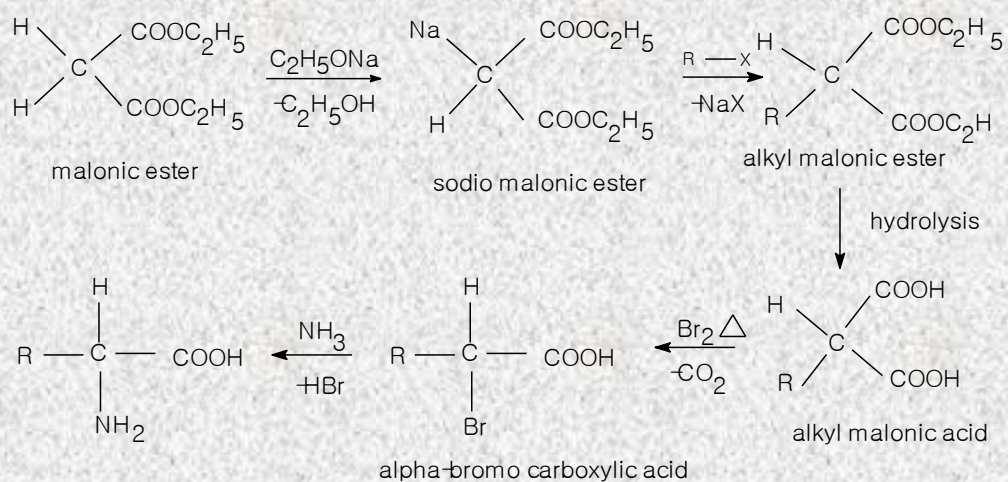
4. Strecker's method

In this method aldehydes are react with ammonium chloride and potassium cyanide gives amino cyanides. Which on hydrolysis gives α – amino acids.

$$R-CHO + NH_4Cl + KCN \longrightarrow R-\underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}}-NH_2$$

$$\downarrow HOH$$

$$R-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}-COOH$$
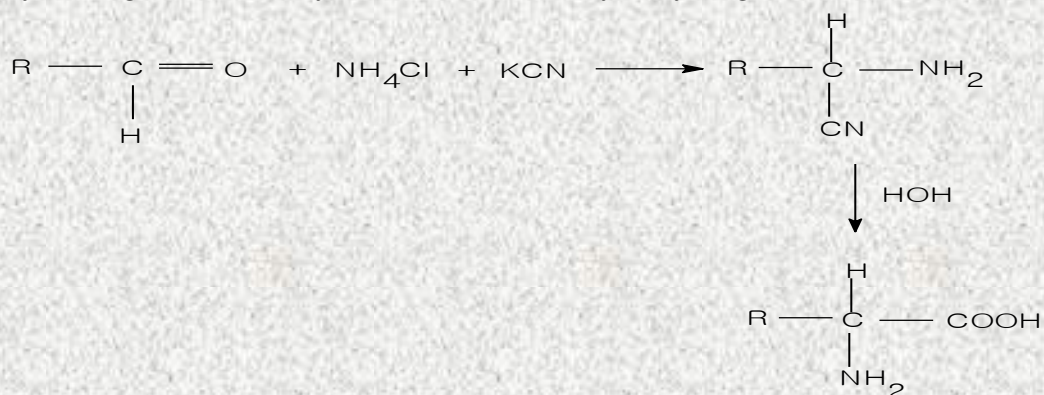
ZWITTER ION

In aqueous solution the acidic carboxylic group can lose a proton and the basic amino group can gain proton in a kind of internal acid – base reaction. The product of this internal reaction is called a dipolar ion or zwitter ion.
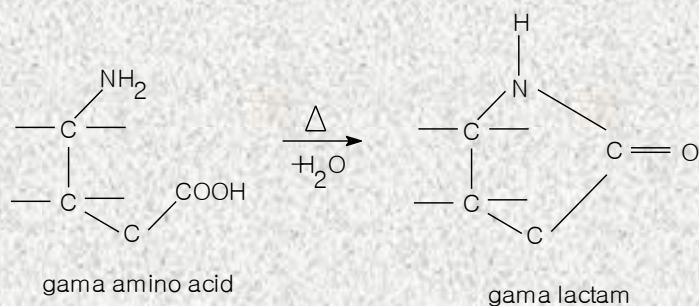
$$R-\underset{\underset{H}{|}}{\overset{\overset{:NH_2}{|}}{C}}-\overset{\overset{O}{||}}{C}-OH \rightleftharpoons R-\underset{\underset{H}{|}}{\overset{\overset{+NH_3}{|}}{C}}-COO^-$$

zwitter ion

Iso electric point

The P^H at which migration of amino acid does not occur towards any electrode is called iso electric point.

Lactams from ϒ and δ – amino acids

ϒ and δ – amino acids are heated, loss water to form carboxylic and amino groups in the same molecule and cyclic amides are fored. The cyclic amides are called lactams.
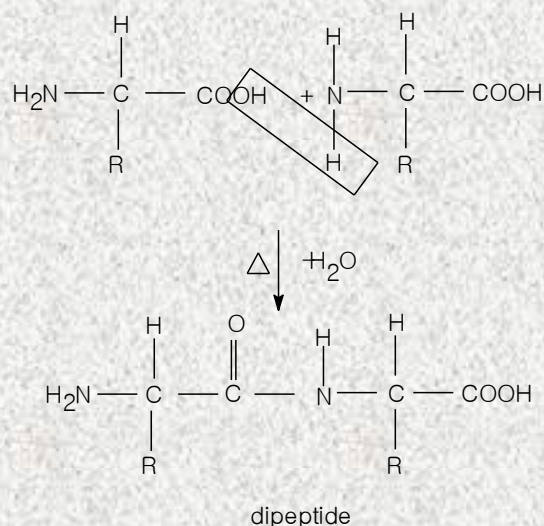
gama amino acid   gama lactam

PEPTIDES

If two amino acids are mixed together and heated, one water molecule is lossed from them and an amide link is formed. This amide link is called peptide bond.
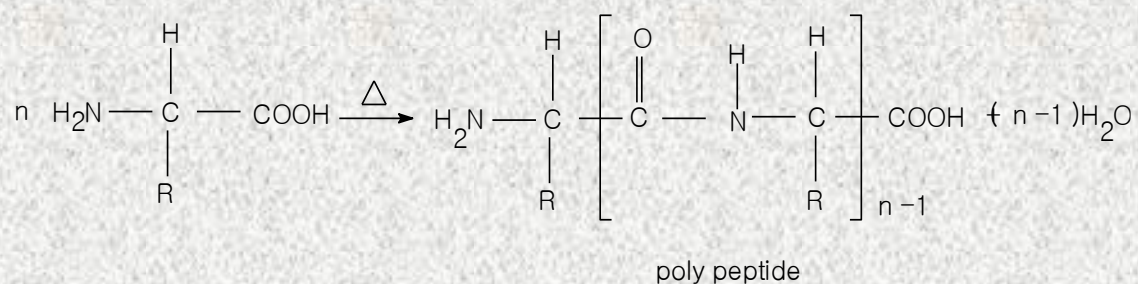
The compound formed from two amino acids are called dipeptide.

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dipeptide

Poly peptides

The peptides with molecular weights ranging from 10,000 are called poly peptides. The polypeptides with molecular weights higher than this are generally called proteins.

poly peptide

The amino acid containing carbon or the end with – COOH group is called " C" end or C – terminal, and the one with – NH$_2$ group is called – N terminal acid.

Primary structure of protein

The representation of serial order of the amino acids in the protein is called the primary structure of the protein. This starts with N – terminal acid and ends with C – terminal.

N-terminal   C-termina

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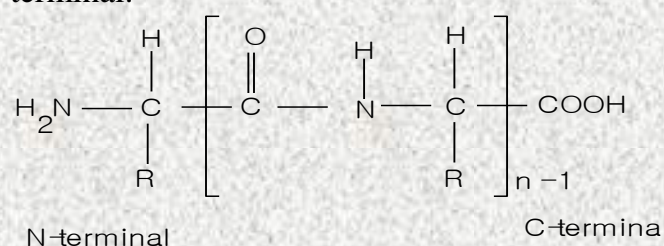
To identify N – terminal amino acid

2,4-dinitro fluoro benzene(DNFB) is introduced as the reagent by Sanger.

In N – terminal amino acid, the free – NH_2 group reacts with this reagent and forms DNFB derivative.

2,4-di nitro fluoro benxene
Sanger reagent
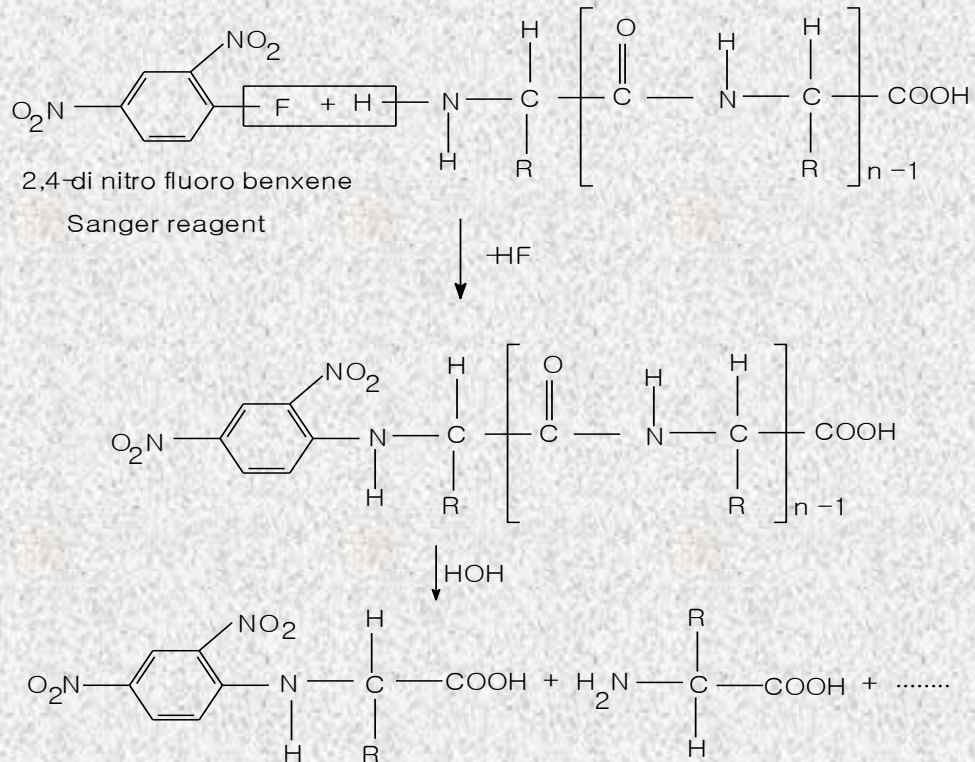
HETEROCYCLIC COMPOUNDS

Cyclic compounds which contain one or more atoms of other elements along with carbon atoms are called hetero cyclic compounds. Non carbon in the ring is called hetero atom.

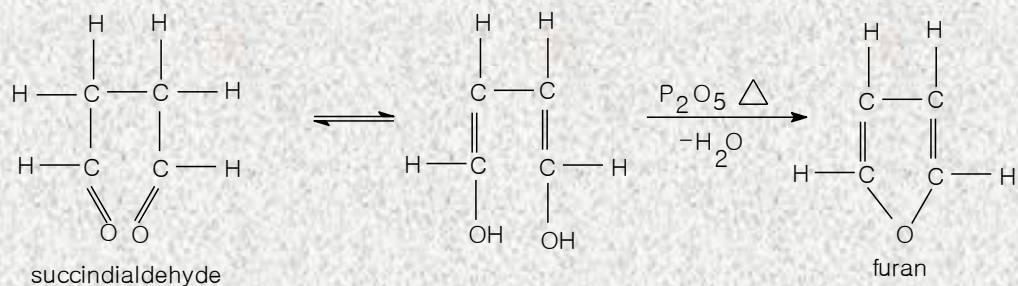CLASSIFICATION

Depending upon the size of the hetero cyclic rings these are generally classified into three types.
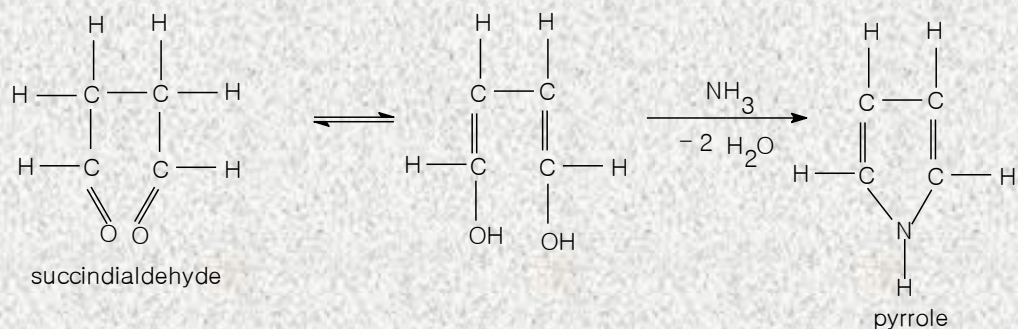
1. Five membered hetero cyclic compounds
   Ex: Furan, Thiophene, pyrrole
2. Six membered hetero cyclic compounds
   Ex: pyridine, piperidine
3. Condensed hetero cyclic compounds
   Ex: Indole, benzofuran,quinoline, carbazole

- Recently hetero cyclic compounds have been divided into two classes.
  i)   Hetero paraffins
         Ex: Tetra hydrofuran(THF), piperidine
  ii)   Hetero aromatics
         Ex: furan (oxaole) thiophene (thiole) pyrrole(azole)

Preparation of Furan, Pyrrole and Thiophene from dicarbonyl compounds (Paul – Knorr synthesis)

i)   Dicarbonyl compounds on heating with P_2O_5 undergo dehydration and furan derivatives are formed.

succindialdehyde   furan

ii)   Dicarbonyl compounds on heating with NH_3, pyrrole derivatives are formed.

succindialdehyde   pyrrole

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iii) Dicarbonyl compounds on heating with P_2S_5, thiophene derivatives are formed.

succindialdehyde   thiophene
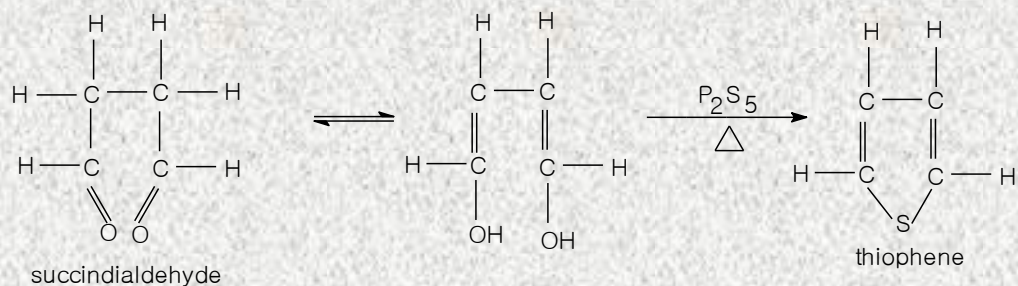
Preparation of furan from Mucic acid

Mucic acid gives furoic acid on dry distillation, the latter acid is then decarboxylated at its b.p. to furan.

mucic acid   furoic acid   furan
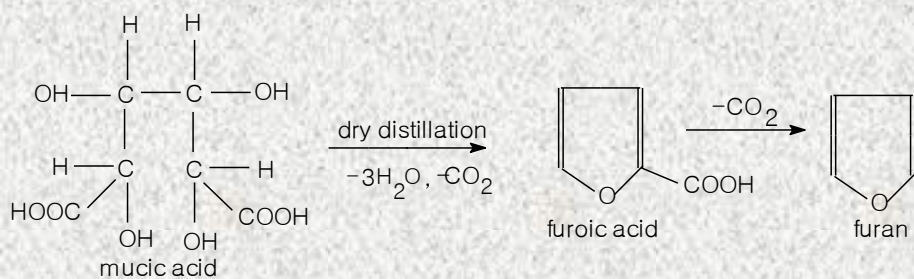
Preparation of thiophene

By passing acetylene and hydrogen sulphide over alumina at 400^0C.
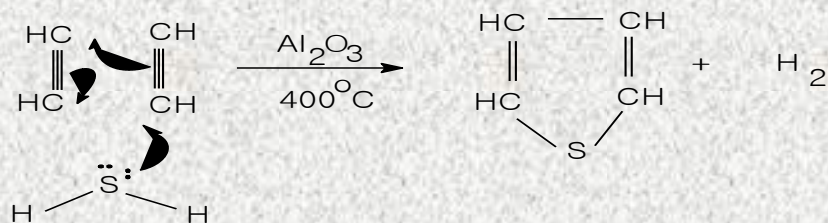
Preparation of Pyrrole

By passing a mixture of furan, ammonia and steam over hot alumina.

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Chemical properties of furan

1. **Catalytic reduction**

   When furan is treated with hydrogen gas in the presence of Ni,Pt or Pd tetra hydro furan is formed.
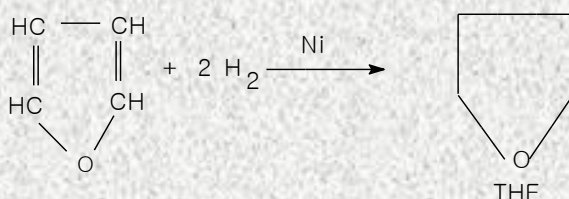
2. **Reaction with maleic anhydride(Diels alder reaction)**

adduct
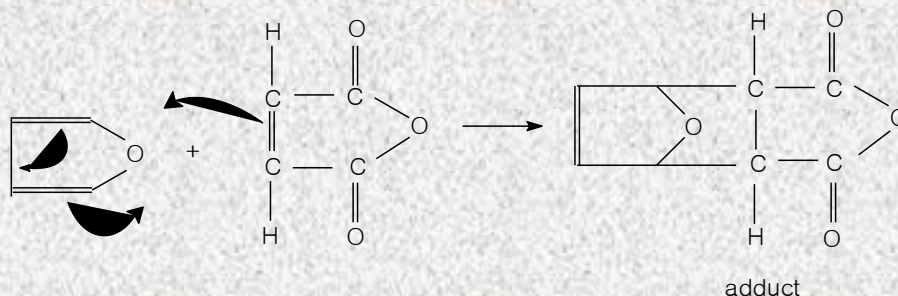
ELECTROPHILIC SUBSTITUTION REACTION IN PYRROLE,FURAN AND THIOPHENE

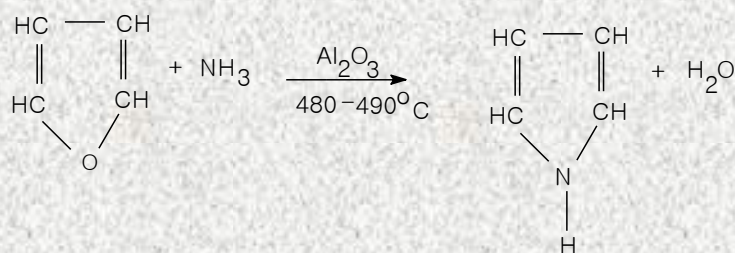These compounds undergo electrophilic substitution reactions more readily than benzene. Because they are resembles benzene derivatives such as amines and phenols. The high reactivity of these compounds towards these substitution reactions is due to greater electron density at the carbon atom of these compounds. In these compounds this substitution reactions takes place at 2 or 5 positions.

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more stable cations

$-H^+$

2-substituted product
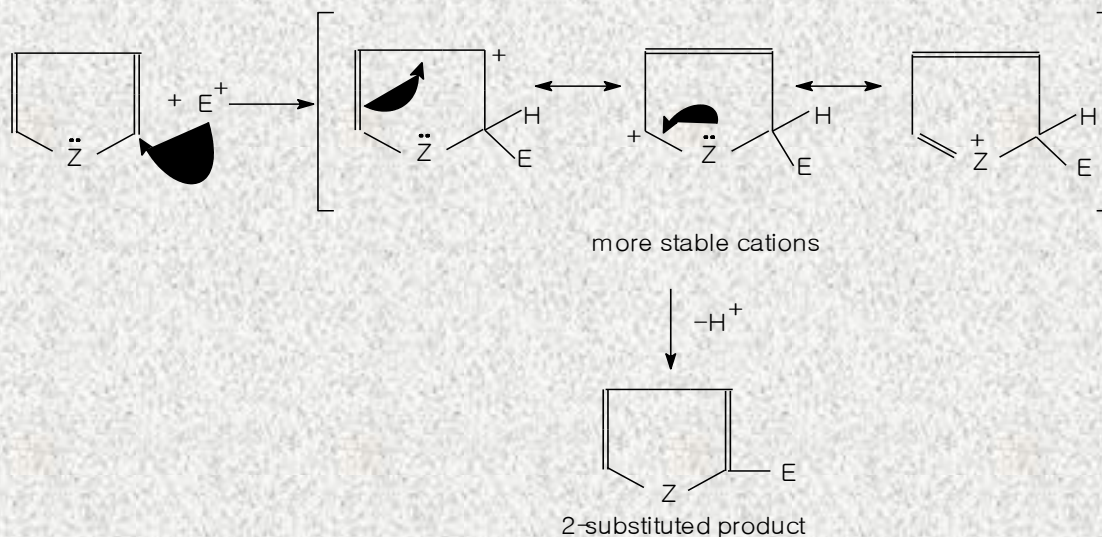
Nitration

When furan is treated with HNO_3 in acetic anhydride 2 – nitro furan is formed.

2 –nitro furan

.

2-nitro pyrrole
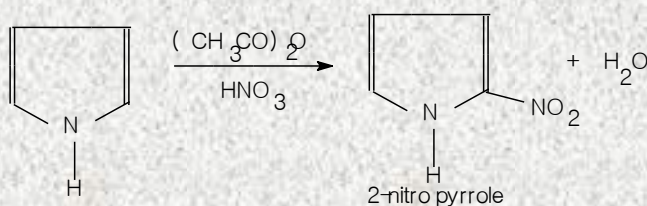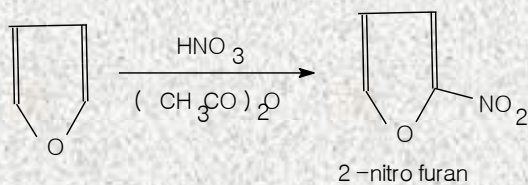
Sulphonation

when furan is treated with SO_3 in pyridine furan 2 – sulphonic acid is formed.

furan 2 –sulphonic acid

pyrrole 2–sulphonic acid
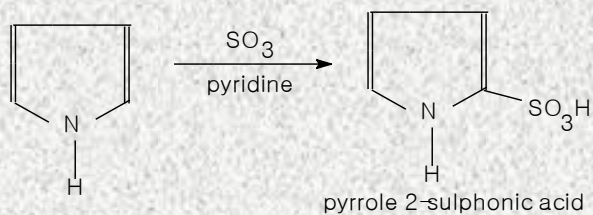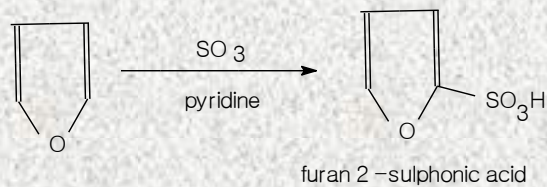
Friedel – Craft's acylation

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2-acetyl furan

2-acetyl pyrrole
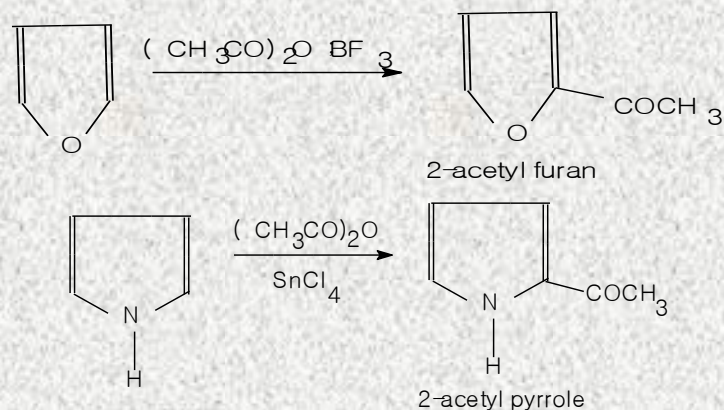
Preparation of pyridine (C_5H_5N)

By passing a mixture of acetylene and hydrogen cyanide through a red hot tube.
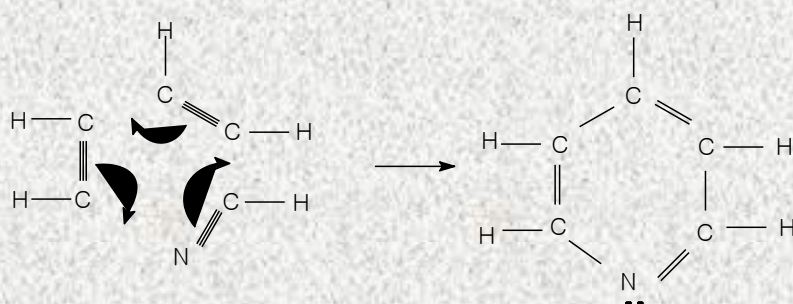
- ### Reaction with sodamide (Chichibabin reaction)

  Pyridine reacts with sodamide in liquid ammonia at about 100^0C to form 2 – amino pyridine.

2-amino pyridine
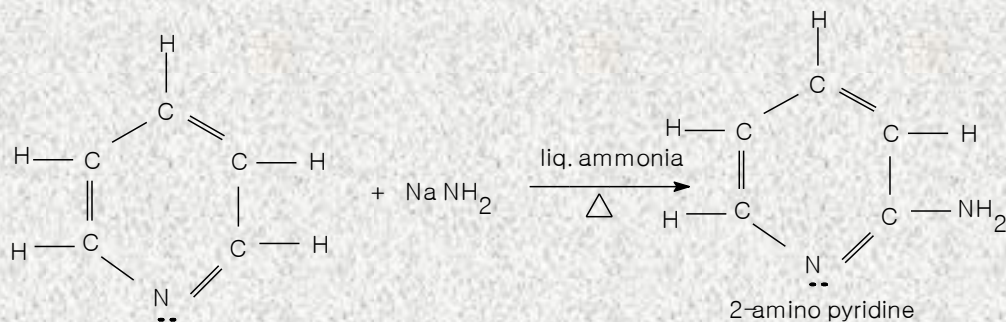
- ### Basicity of pyridine

  it behaves like a base and it reacts with acids to form stable salts. Because the lone pair of electrons on nitrogen atom in pyridine are in SP^2 hybridisation. They are not involve in the formation of delocalized $\prod$ molecular orbital. They are readily available for the formation of a new N – H bond with proton. It is stronger base thanpyrrole or aniline.

- ### Aromaticity of Pyridine

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In the pyridine 5carbon atoms and one nitrogen atom are in SP^2 hybridisation. These SP^2 hybrid orbitals overlap with S orbital of hydrogen atom to form C – H σbond. All the σbonds in pyridine lie in the same plane. In pyridine ring each carbon atom is having an unhybridised P – orbital and they are at right angles to the plane of the σ bonds. The later overlapping of these P – orbital produces a delocalized ∏ molecular orbital containing six electrons. Pyridine obeys Huckel's rule so pyridine shows aromaticity.
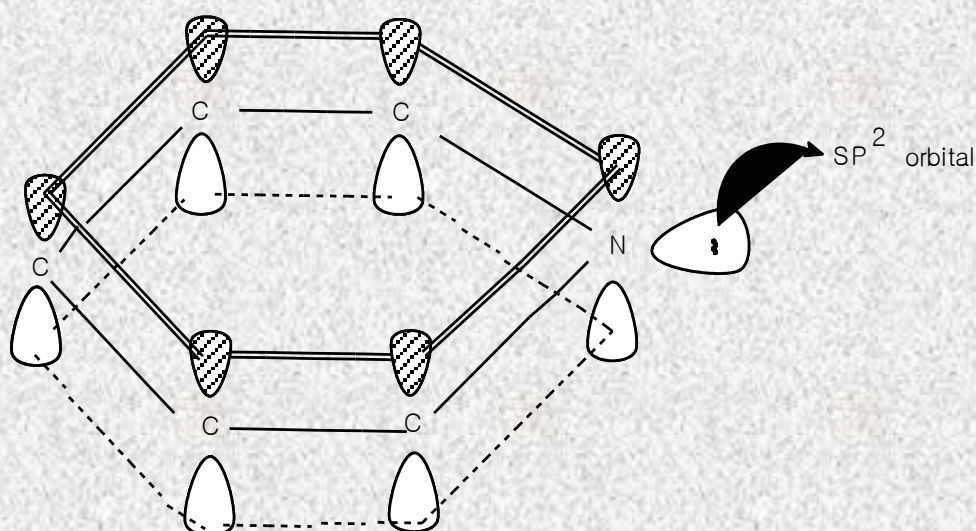
Relative reactivity of pyrrole, furan and thiophene
- Like benzene they exhibit aromatic character and are resonance stabilized.
- Thiophene the least reactive among the three hetero cyclic compounds.
- The decreasing order of their reactivity is below
  Pyrrole > furan > thiophene > benzene
- Pyrrole is so reactive towards electrophilic substitution reactions that its reactivity is comparable to that of aniline and phenol for instance it undergoes Kolbe Schmidt, Reimer Tiemann reaction.
- Reason: one of the contributing structures of 2 – substituted intermediate carbocation, III is particularly more stable because in III every atom has an octet of electrons and nitrogen accomadates the positive charge more easily than O (furan) and S (thiophene)[among these three elements nitrogen is the least electro negative]
- Furan is less reactive than pyrrole because oxygen accomdates a positive charge less readily than nitrogen. Thiophene is less reactive than furan because the +M effect of S is smaller than that of O.

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`NITROGEN COMPOUNDS

In hydrocarbons if one of the hydrogen is replaced by $-NO_2$ (nitro) functional group, the compound is called nitro hydro carbons.

$$R - H \longrightarrow R - NO_2$$
alkane   nitro alkane

General formula

$R - NO_2$
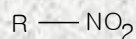
If R =alkyl nitro alkanes

If R=aryl   aromatic nitro hydro carbons

Classification

Depending on the nature of carbon which the $-NO_2$ group attached the nitro alkanes are classified into 1^0, 2^0, 3^0.
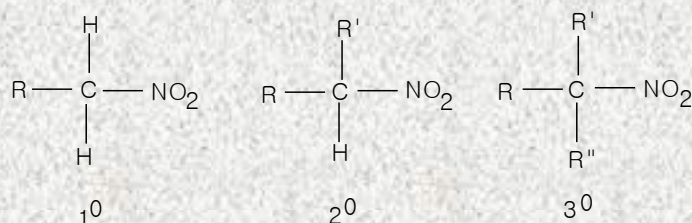
Preparation

1. **Direct nitration of paraphins (alkanes)**

   If alkanes are nitrated at high temperatures nitro alkanes are formed.
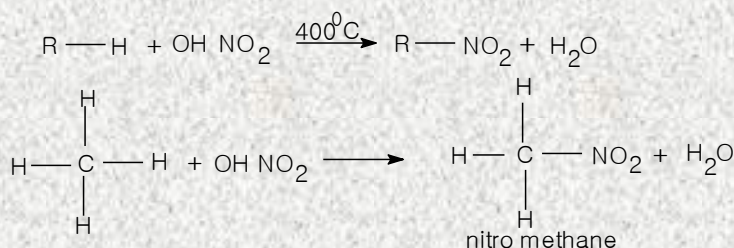
Chemical properties

1. Primary, secondary nitro alkanes are readily halogenated in presence of alkalies. Halogen atom enters the α-position.

   chloropicrin(nitro chloroform)
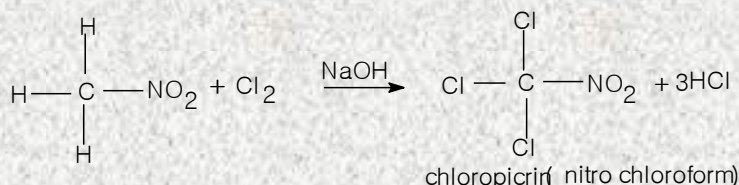
   Chloropicrin is a lachrymatory substance and is also used as soil sterilizing agent.

2. Action of nitrous acid

a) Primary nitroalkanes react with nitrous acid to form nitrolic acid which dissolves in sodium hydroxide gives red solution.

$$CH_3-CH_2-NO_2 + O{=}NOH \longrightarrow H_3C-\overset{\overset{\displaystyle NOH}{\|}}{C}-NO_2 + H_2O$$
nitrolic acid

$$H_3C-\overset{\overset{\displaystyle NOH}{\|}}{C}-NO_2 + NaOH \longrightarrow H_3C-\overset{\overset{\displaystyle NONa}{\|}}{C}-NO_2$$
nitrolic acid ..... sodium nitrolate(red)
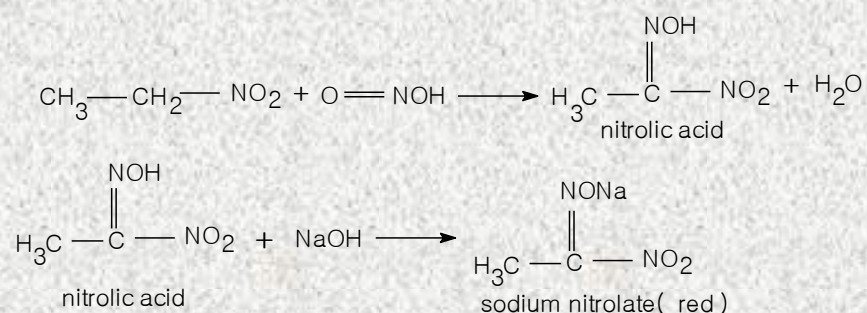
b) Secondary nitro alkanes react with nitrous to give colourless crystalline pseudo nitroles which give blue colour with NaOH solution.

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-NO_2 + O{=}NOH \xrightarrow{NaOH} R-\overset{\overset{\displaystyle N{=}O}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-NO_2 + H_2O$$
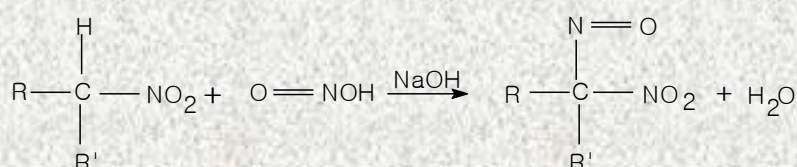
c) Tertiary nitro alkanes do not react with nitrous acid because they do not contain α-hydrogen.

Tautomerism of nitro alkanes

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-N\overset{\diagup O}{\diagdown O} \longleftrightarrow R-\overset{\overset{\displaystyle H}{|}}{C}{=}N\overset{\diagup O-H}{\diagdown O}$$
iso form ..... aci form
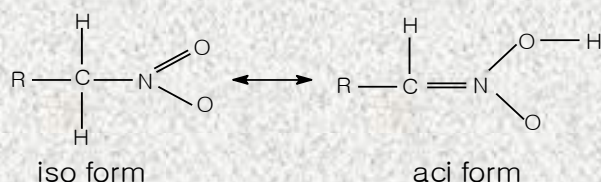
3. Nef reaction

Sodium salts of primary and secondary nitro alkanes give aldehydes and ketones respectively, on acidification with 50% H_2SO_4 at room temperature. (aci form of 1^0, 2^0 nitro alkane salts are hydrolysed with H_2SO_4 give aldehyde and ketone)

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$$R - C \underset{H}{\overset{H}{|}} - N \overset{\nwarrow O}{\underset{O}{\diagup}} \longleftrightarrow R - C \overset{H}{=} N \overset{O-H}{\underset{O}{\diagdown}} \xrightarrow{NaOH} \left[R - C \overset{H}{=} N \overset{O}{\underset{O}{\diagdown}} \right]^{-} Na^{+}$$

$$\downarrow H_2SO_4$$

$$R - \underset{H}{\overset{}{C}} = O + 1/2\ N_2O + NaHSO_4 + H_2O$$
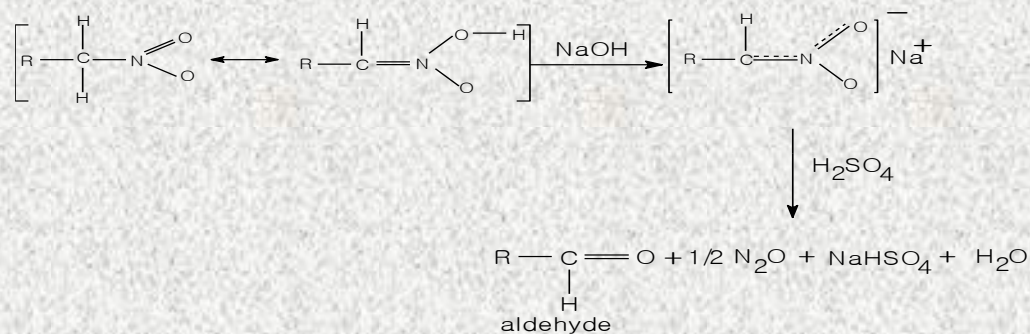
aldehyde

4. Mannich reaction

Condensation reaction occurs between formaldehyde , compounds having α-hydrogens and ammonia are called Mannich reaction.

$$R - \underset{H}{\overset{H}{C}} - NO_2 + HCHO + NH_3 \xrightarrow{HCl} R - \underset{H}{\overset{NO_2}{C}} - \underset{H}{\overset{H}{C}} - NH_2 + H_2O$$

mannich base
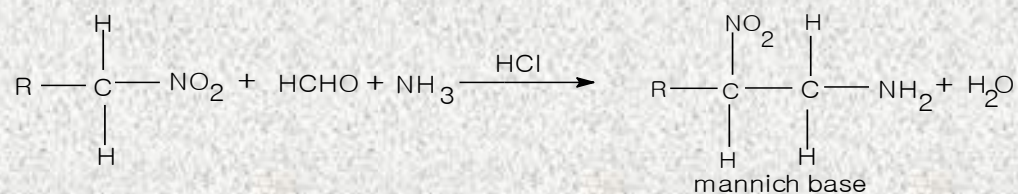
5. Michael addition

The addition reactions that take place between the compounds containing olefinic double bond in presence of bases are called Michael reaction.

$$R - \underset{H}{\overset{H}{C}} - NO_2 + (CH_3)_2 = CH - \underset{O}{\overset{O}{C}} - CH_3$$

unsaturated ketone

$$\downarrow NaOH\ sol.$$

$$(CH_3)_2 - \underset{\underset{H}{\overset{|}{R - C - NO_2}}}{\overset{|}{C}} - CH_2 - \underset{O}{\overset{}{C}} - CH_3$$
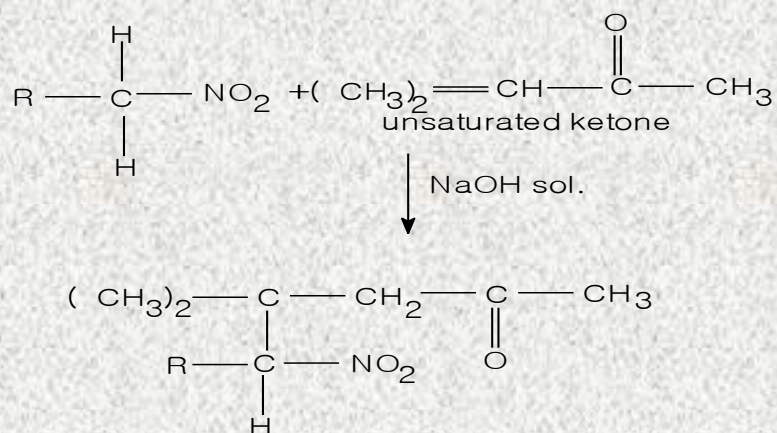
AMINES

Amines are the derivatives of ammonia. These are formed when one, two or three hydrogens of ammonia molecule are substituted by alkyl or aryl groups are called amines. If one hydrogen is replaced, the amine is called primary amine, if two or three hydrogens are replaced in order, the amines formed are called secondary, tertiary amines respectively.

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D.N.R.COLLEGE(A), BHIMAVARAM

ammonia → primary → secondary → tertiary
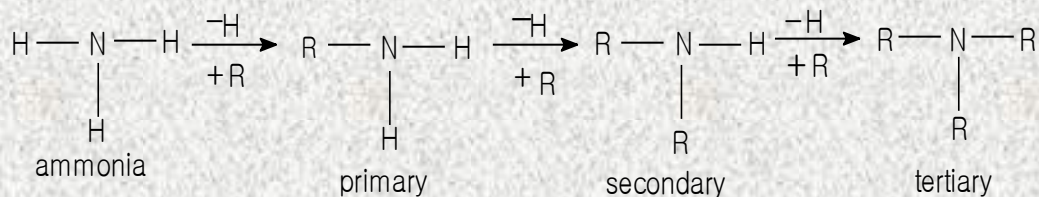
Preparation of amines

1. **Ammonolysis of alkyl halides(Hofmann method)**

   Aqueous or alcoholic solution of ammonia and alkyl halide is heated in a sealed tube at 100^0C.

   $$C_2H_5I + HNH_2 \longrightarrow C_2H_5NH_2 + HI$$

   $$C_2H_5I + H_2NC_2H_5 \longrightarrow C_2H_5NHC_2H_5 + HI$$

   $$C_2H_5I + NH(C_2H_5)_2 \longrightarrow (C_2H_5)_3N + HI$$

   $$C_2H_5I + (C_2H_5)_3N \longrightarrow (C_2H_5)_4N^+I^-$$
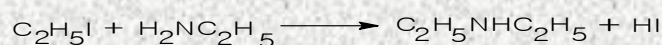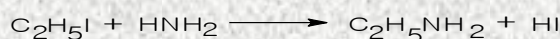
2. **Gabriel's synthesis**

   The method of preparation of primary amines using potassium phthalimide is called Gabriel's synthesis.

   Phthalimide is first of all treated with KOH to form potassium phthalimide. Which on heating with alkyl halides gives N – alkyl phthalimide. The later is hydrolysed with 20% HCl under pressure to give primary amine.
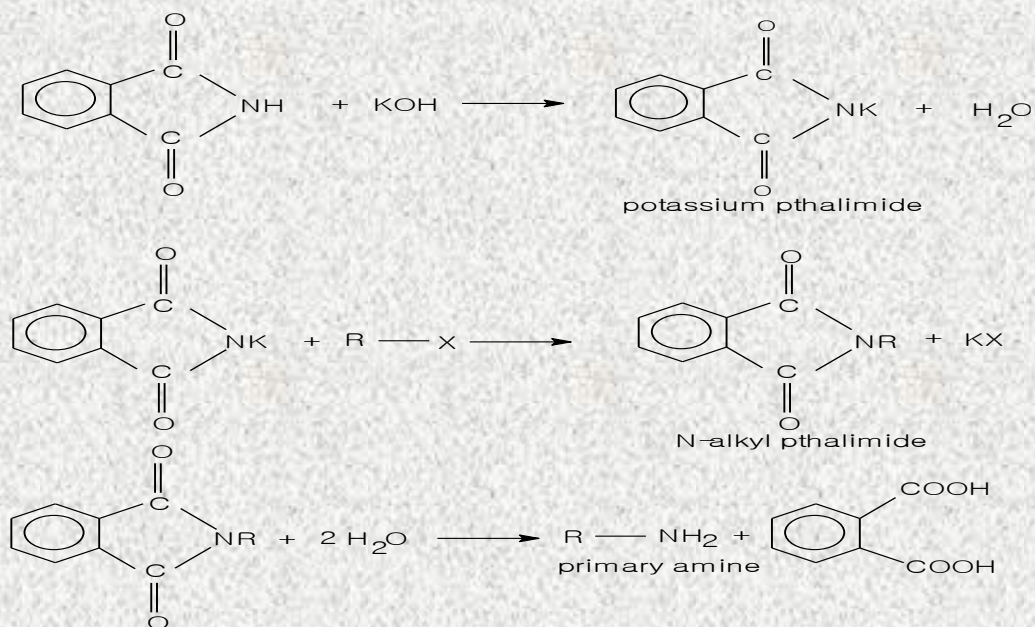
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3. Hoffmann's bromamide reaction (mechanism)

When amides are treated with a mixture of halogens (Br_2) and alkali, primary amines are formed. This reaction is called Hoffmann bromide or degradation or rearrangement.

$$CH_3CONH_2 + Br_2 + 4\ KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2\ H_2O$$

Mechanism

$$CH_3CONH_2 + Br_2 + KOH \longrightarrow \underset{\text{acetobromamide}}{CH_3CONHBr} + KBr + H_2O$$
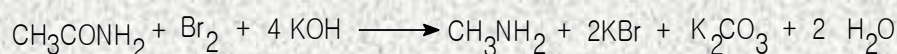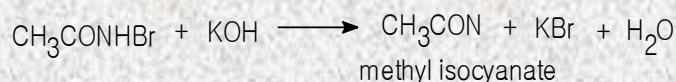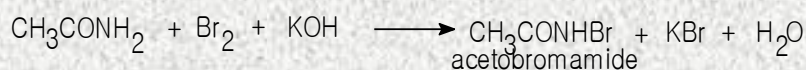
$$CH_3CONHBr + KOH \longrightarrow \underset{\text{methyl isocyanate}}{CH_3CON} + KBr + H_2O$$

$$CH_3NCO + 2KOH \longrightarrow \underset{\text{methyl amine}}{CH_3NH_2} + K_2CO_3$$

4. Reduction of amides

Amides on reduction with $LiAlH_4$ we get amines.

$$\underset{\text{acetamide}}{CH_3CONH_2} + 4(\ H\ ) \xrightarrow{LiAlH_4} \underset{\text{ethyl amine}}{CH_3CH_2NH_2} + H_2O$$
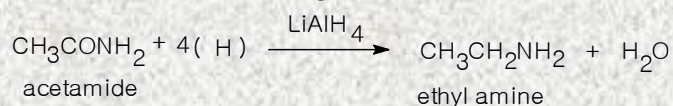
5. Schmidt reaction

The addition reaction between the carboxylic acids or carbonyl compounds and hydrazoic acid is called Schmidt reaction.

$$RCOOH + \underset{\text{hydrazoic acid}}{HN_3} \xrightarrow{H^+} R - N = C = O \xrightarrow{H_2O} \underset{\text{primary amine}}{R - NH_2} + N_2 + CO_2$$
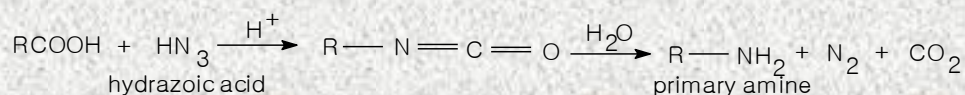
Basicity of amines

1. Basicity of amines depends upon the tendency of donation of the lone pair of electrons on nitrogen.
2. Methyl amine is stronger base than NH_3. Because the alkyl group is electron releasing group. It increases the electron density around nitrogen.
3. Tertiary amine having more number of alkyl groups it is less basic than secondary amine. Due to steric hinderance of three alkyl groups. That means the path of electron is blocked.
4. In aromatic amines the lone pair of electrons on nitrogen are attached by the ring due to resonance. Then nitrogen cannot donate electrons easily. Hence aromatic amines are less basic than aliphatic amines.

CHEMICAL PROPERTIES

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1. Alkylation

Amines react with alkyl halides to form quarternary ammonium salts as the final product.

$$(CH_3)_4NI$$
tetramethyl amm.iodide
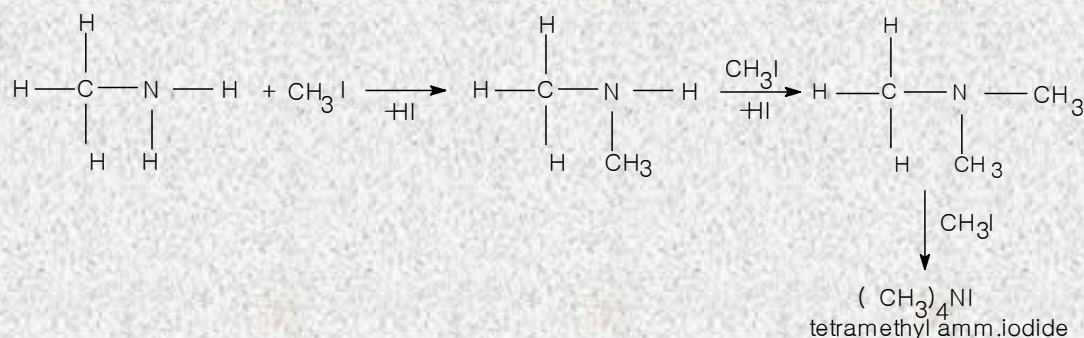
2. Acylation (Reaction with acetyl chloride)

Primary and secondary amines react with acid chlorides and acid anhydrides to form acyl derivatives or substituted amides.

acetyl methyl amine
(methyl acetamide)

$$(CH_3)_2NCOCH_3$$
dimethyl acetamide
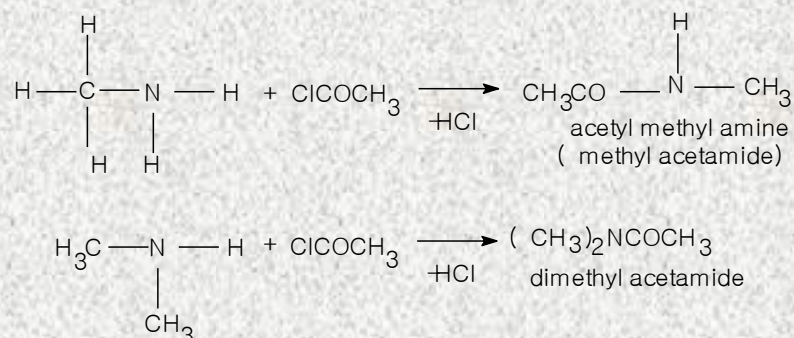
3. Carbyl amine reaction (iso cyanide test)

primary amines when heated with chloroform and alcoholic caustic potash give isocyanides(carbyl amine) having unpleasant smell.

$$C_6H_5NH_2 + 3 CHCl_3 + 3KOH \xrightarrow{\triangle} C_6H_5NC + 3KCl + 3H_2O$$
phenyl isocyanide
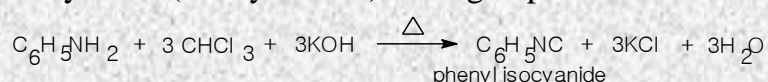
4. HINSBERG METHOD

The mixture of amines is treated with benzene sulphonyl chloride (Hinsberg's reagent) and shaken with alkali (KOH)solution when the three amines behave in different ways.

i) Primary amine forms n-alkyl benxene sulphonamide which dissolves in alkali to form potassium salt of mono alkyl sulphonamide.

n-alkylbenzene sulphonamide

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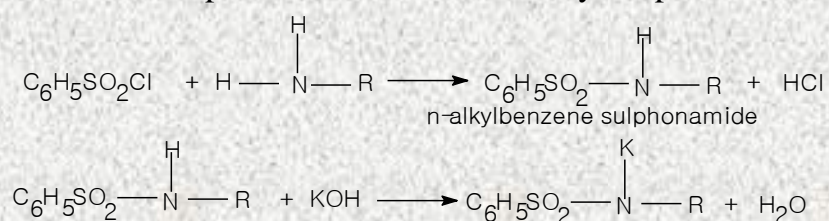
ii) Secondary amine forms di alkyl benxene sulphonamide which does not form salt with alkali and hence remains insoluble in alkali solution.

$$C_6H_5SO_2Cl \ + \ H-\underset{\underset{R}{|}}{N}-R \ \longrightarrow \ C_6H_5SO_2-\underset{\underset{R}{|}}{N}-R \ + \ HCl$$

dialkyl benzene sulphonamide

$$\downarrow KOH$$

no reaction
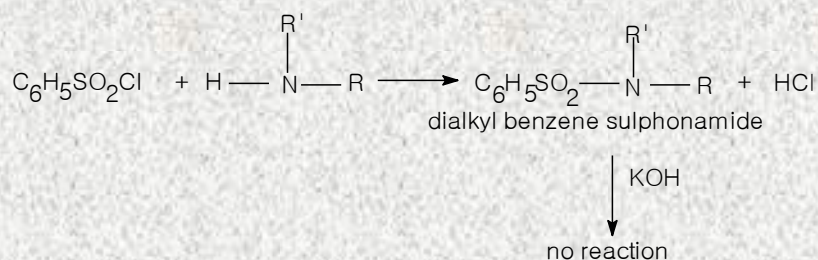
iii) Tertiary amine does not react with the Hinsberg's reagent.

The above alkali solution of the amines is extracted with ether when tertiary amine and dialkyl benzene sulphonamide go to ethereal layer while potassium monoalkyl benzene sulphonamide remains in the water layer. The two layers then separated.

Recovery of primary amine (treatment of aqueous layer)

The aqueous layer containing potassium mono alkyl benzene sulphonamide is acidified with dil. HCl when mono alkyl benzene sulphonamide is formed. The later is heated with conc. HCl to form primary amine hydrochloride which is distilled with caustic soda to regenerate primary amine as distillate.

$$C_6H_5SO_2-\underset{\underset{K}{|}}{N}-R \ + \ HCl \ \longrightarrow \ C_6H_5SO_2-\underset{\underset{H}{|}}{N}-R \ + \ KCl$$

mono alkyl benzene sulphonamide

$$C_6H_5SO_2-\underset{\underset{H}{|}}{N}-R \ + \ H_2O \ \xrightarrow{conc.HCl} \ C_6H_5SO_2OH \ + \ RNH_2 \ HCl$$

benzene sulphonic acid   primary amine hydrochloric

$$RNH_2 \ HCl \ + \ NaOH \ \longrightarrow \ RNH_2 \ + \ NaCl \ + \ H_2O$$

1^O amine
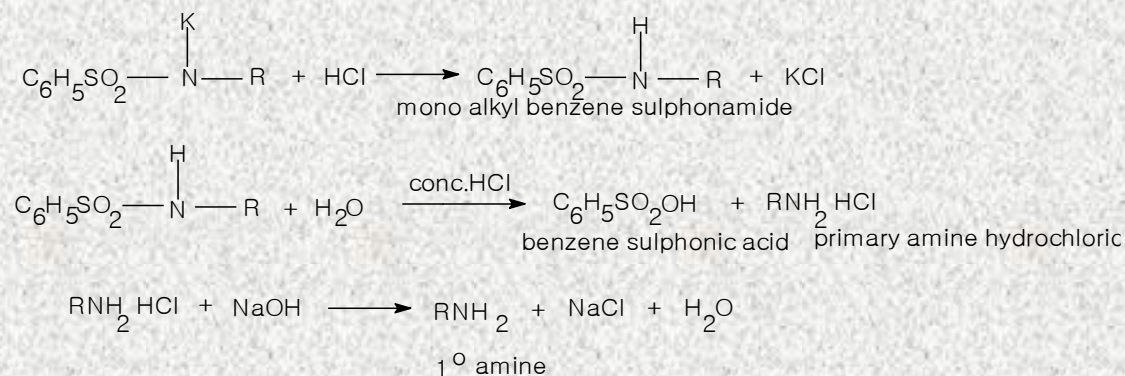
Recovery of secondary and tertiary amines (treatment of ethereal layer)

The ethereal layer is fractionally distilled, when ether and tertiary amine distil over in quick succession leaving behind solid dialkyl benzene sulphonamide as residue. The later is hydrolysed by boiling with conc. HCl to form secondary amine hydrochloride which is then distilled with caustic soda to get free amine.

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$$C_6H_5SO_2 - \underset{\underset{R'}{|}}{N} - R \ + \ 3^o \ amine \ \xrightarrow{distillation} \ \begin{array}{l} 3^o amine \ + \ ether \\[4pt] C_6H_5SO_2 - \underset{\underset{R'}{|}}{N} - R \end{array}$$

$$C_6H_5SO_2 - \underset{\underset{R'}{|}}{N} - R \ + \ H_2O \ \xrightarrow{conc.HCl} \ \underset{\text{benzene sulphonic acid}}{C_6H_5SO_2OH} \ + \ \underset{\text{secondary amine hydrochlorid}}{R \ R'N \ H \ HCl}$$

$$RR'NHHCl \ + \ NaOH \ \longrightarrow \ \underset{\underset{\underset{2^o \ amine}{R'}}{|}}{R - N - H} \ + \ NaCl \ + \ H_2O$$
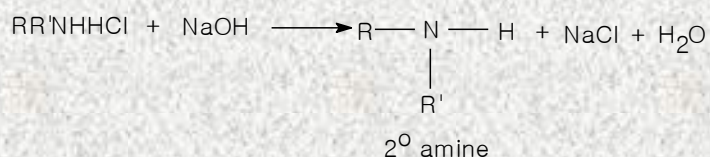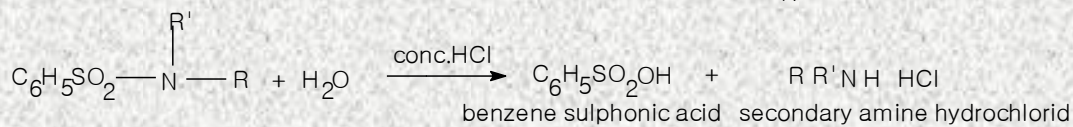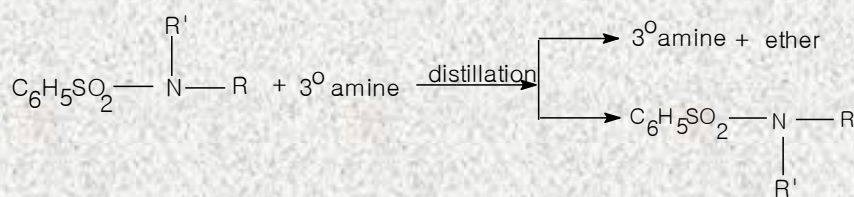
5. Reaction with nitrus acid (HNO₂)

Nitrus acid is unstable substance. This is prepared by adding HCl to nitrate salt (NaNO₂ + HCl).

$$NaNO_2 \ + \ HCl \ \longrightarrow \ NaCl \ + \ HNO_2$$

Primary amine (except methyl amine) form primary alocohols with nitrus acid.

$$\underset{\text{ethyl amine}}{C_2H_5NH_2} \ + \ HONO \ \longrightarrow \ \underset{\text{ethyl alcohol}}{C_2H_5OH} \ + \ N_2 \ + \ H_2O$$
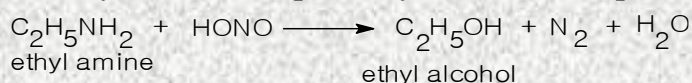
Secondary amines react with nitrus acid to form N – Nitrosoamines.

$$(CH_3)_2NH \ + \ HONO \ \longrightarrow \ \underset{\text{N-nitrosodimethyl amine}}{(CH_3)_2N - N = O} \ + \ H_2O$$
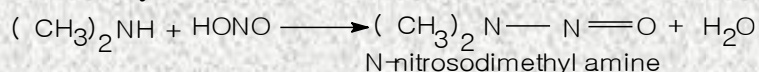
Tertiay amine give water soluble salts.

$$(CH_3)_3N \ + \ HONO \ \longrightarrow \ \underset{\text{nitrite}}{(CH_3)_3N \ HNO_2}$$
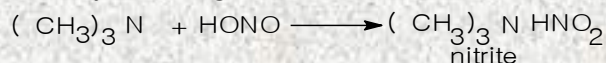
This differential reaction can be used to distinguish primary, secondary and tertiary amines.

ELECTROPHILIC SUBSTITUTION REACTIONS OF AROMATIC AMINES

1. Bromination

Bromination of aniline directly gives 2,4,6-tri bromoaniline.
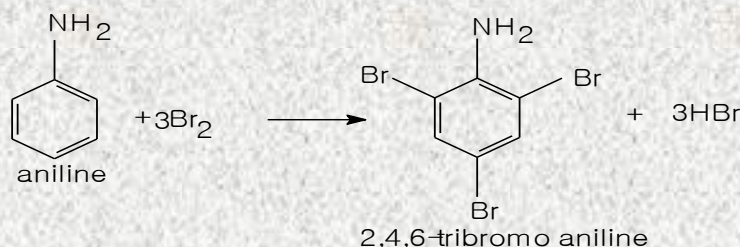
2. Nitration

Direct nitration of aniline faces two complications. So to prevent the two complications the amino group is protected by acetylation to give acetanilide which is nitrated and finally hydrolysed to o – and p – nitro anilines.
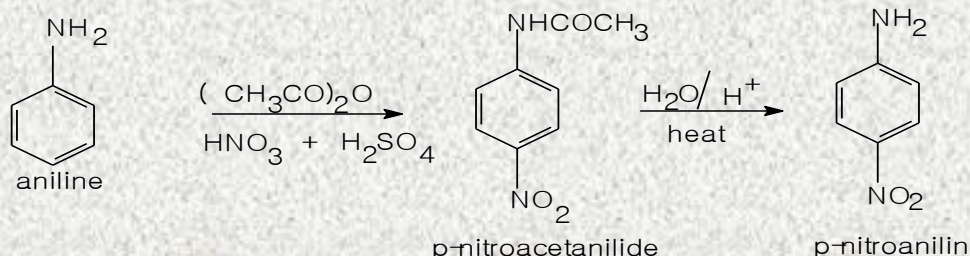
3. Oxidation of aryl and 3º amines

Aniline is oxidized with sodium dichromate and sulphuric acid gives p – benzoquinone.
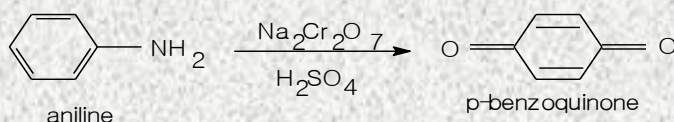
4. Diazotization (reaction with nitrous acid):

Primary aromatic amine is dissolved in conc. HCl and cooled to 5 – 10ºC.In another vessel a saturated solution of $NaNO_2$ is prepared and cooled. To acidify primary amine solution this cooled nitrite solution is added. Now diazonium chloride solution is formed. This reaction is known as diazotization.
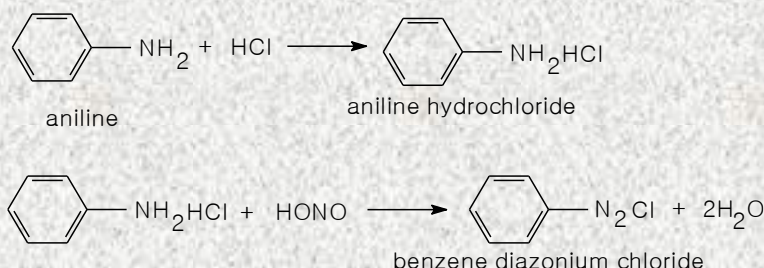
CYANIDES AND ISO CYANIDES

Compounds containing – CN group are called cyanides, compounds containing – NC group are called isocyanides. These are isomeric forms.

Preparation of cyanides

1. From alkyl halides

Alkyl halides on reaction with alkali cyanides give cyanides.

$$R-X \ + \ KCN \longrightarrow R-CN \ + \ KX$$

$$Ex: \ C_2H_5Br \ + \ KCN \longrightarrow C_2H_5CN \ + \ KBr$$
ethyl cyanide

2. From amides

When amides are heated with strong dehydrating agents like P_2O_5, amides are dehydrated to give cyanides.

$$R \longrightarrow CONH_2 \xrightarrow[\triangle]{P_2O_5} R \longrightarrow CN + H_2O$$

Ex: $C_6H_5CONH_2 \xrightarrow[\triangle]{P_2O_5} C_6H_5CN + H_2O$
benzamide   phenyl isocyanide
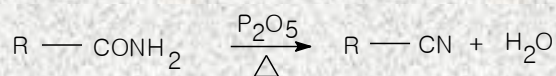
3. From aldoximes

Aldoximes are dehydrated with acetic anhydride or thionyl chloride gives nitriles.

$$RCHO + H_2NOH \longrightarrow RCH = NOH + H_2O$$
aldoxime

$$RCH = NOH \xrightarrow[\triangle \, (CH_3CO_2)O]{P_2O_5 \text{ or}} R \longrightarrow CN + H_2O$$
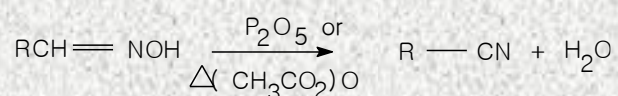
Preparation of isocyanides

1. From alkyl halides

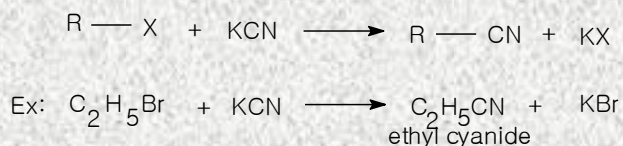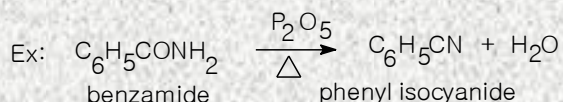Alkyl halides on heating with silver cyanide (AgCN) gives isocyanides.

$$R \longrightarrow X + AgCN \longrightarrow R \longrightarrow N \equiv C + AgX$$

Ex: $CH_3Cl + AgCN \longrightarrow CH_3NC + AgCl$
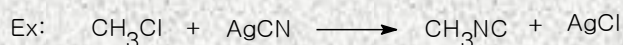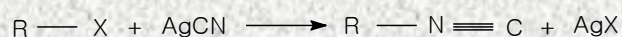
2. From amines

Primary amines are heated with chloroform and alkali solution gives isocyanides. This reaction is used to identify primary amine.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\triangle} C_6H_5NC + 3KCl + 3H_2O$$
aniline   phenyl isocyanide
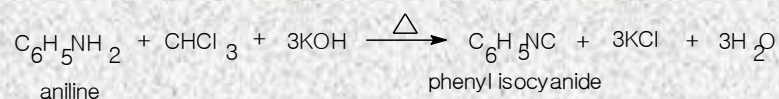
Properties of cyanides and isocyanides

1. Hydrolysis

When cyanides are heated in presence of acids or bases carboxylic acids are formed.

Isocyanides gives amines and formic acid under the same condition.

$$R \longrightarrow CN \xrightarrow[NaOH \, \triangle]{H_3O^+ \text{ or}} R \longrightarrow COOH + NH_3$$

$$R \longrightarrow NC \xrightarrow[NaOH \, \triangle]{H_3O^+ \text{ or}} R \longrightarrow NH_2 + HCOOH$$

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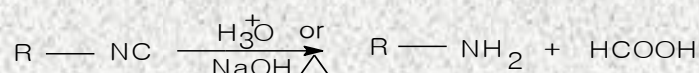
2. Reduction

Nitriles on chemical or catalytic reduction give primary amines.

$$R - CN + 4(H) \xrightarrow{\text{LiAlH}_4} RCH_2NH_2$$

PHOTO CHEMISTRY

Photo chemical reactions

The reactions that occur in presence of light due to absorption of light are called photo chemical reactions.

➢ Some reactions occur in presence of light
➢ Some reactions occur both in presence and absence of light
➢ Some reactions occur in absence of light are called thermo chemical reactions.

Difference between thermal and photo chemical reactions

Thermo chemical reactions	Photo chemical reactions
➢ The chemical reactions take place in the absence of light (or) under the influence of heat energy are called thermo chemical reactions. ➢ In this reaction the activation energy Is made available through the collision between reacting molecules.	➢ The chemical reactions occur in presence of light are called photo chemical reactions. ➢ For Photo chemical reactions to occur the reactants shall absorb light.

LAWS OF PHOTO CHEMISTRY

Grotthus – Draper law

The light radiation that is absorbed by the reacting system alone can bring forth the photochemical reactions. $I\infty = Io - It$

I∞ = intensity of light absorbed
Io= intensity of light that enters the medium
It= Intensity of transmitted light

Stark – Einstein's law of photo chemical equivalence
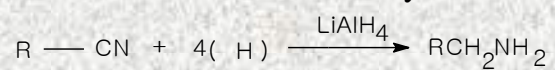
In photo chemical reactions one molecule of the reactant absorbs are quantum (hυ) of light.

If the frequency of light absorbed is υ, the quantum is given by hυ.

The energy absorbed by one mole

$$E= \frac{Nh\vartheta}{4.184 \; x \; 10^7} \qquad N=6.023 \; x \; 10^{23}$$

$$H= 6.625 \; x \; 10^{-27}$$

$$C= 3 \; x \; 10^{10}$$

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"The energy absorbed by one mole of the reactant molecules is called Einstein"

Quantum yield (φ):

Ratio between molecules consumed in the reaction and number of quanta of light.

OR

The ratio between number of moles absorbed and number of Einstein.

As per Einstein law this is always equal to one.

Ferri oxalate actinometry

- For the determination of φ of a photo chemical reaction knowledge of incident light flux Io is needed.
- Number of quanta falling on the molecule in one unit time Io

$$\Phi = \frac{\frac{-dc}{dt}}{Io \times fraction\ of\ light\ absorbed}$$

Io is calculated if φ and rate are known. Ioను φ, .

- One of the methods is based on the standardization of light source chemically using a standard photo chemical reaction, preferably redox reaction. This method is known as Actinometry.
- Most widely used are is the utilization of ferri oxalate reduction. This is therefore is known as ferri oxalate actinometry.
- Photo decomposition of potassium ferri oxalate was developed into an actinometer by Parker and Hatchard..
- This covers wave length range between 250 nm to 577 nm.
- Irradiation of ferrioxalate solution results in the reduction of Fe^{+3} to Fe^{+2}. Which is estimated colorometrically by using ortho phenonthroline as complexing agent.

The absorbance at 510 nm is compared with a standard solution.

.

- Recommended standard solution used for wave length upto 400 nm contains 0.006M potassium ferri oxalate in 0.1 N H_2SO_4.
- For longer wave lengths 0.15 M solution is used instead of 0.006M solution.
- Quantum yield varies between 1.2 (λ254 – λ365 nm) to (1. 1 at higher wave lengths)

$$2Fe(C_2O_4)_3 \longrightarrow 2Fe(C_2O_4)_2 + (C_2O_4) + CO_2$$

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Photo chemical reactions between H_2 and Cl_2

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$\text{mechanism} \quad Cl_2 + h\nu \xrightarrow{K_1} 2\ Cl$$

$$Cl + H_2 \xrightarrow{K_2} HCl + H$$

$$H + Cl_2 \xrightarrow{K_3} HCl + Cl$$

$$Cl\ (\text{at the walls of container}) \xrightarrow{K_4} 1/2\ Cl_2$$
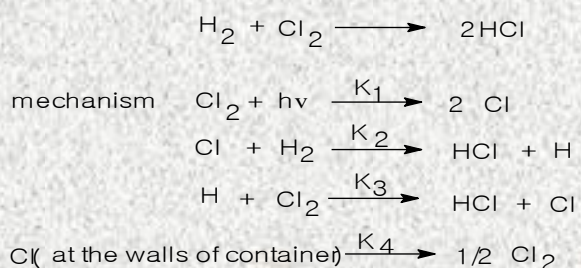
On the basis of above mechanism, the rate equation for the reaction is derived

$V = \dfrac{d[HCl]}{dt}$

$= K_2\ [Cl][H_2] + K_3\ [H][Cl_2]$

But [Cl] is written as follows

$\dfrac{d[Cl]}{dt} = K_1\ I_a - K_2[Cl][H_2] + K_3[H][Cl_2] - K_4[Cl] = 0$

Similarly

$\dfrac{d[H]}{dt} = K_2\ [Cl][H_2] - K_3[H][Cl_2] = 0$

Rate of formation – Rate of disappearance =0
$K_1\ I_a - K_4[Cl] = 0$

$[Cl] = K1\ \dfrac{Ia}{K4}$

$[H] = \dfrac{K1\ K2\ Ia\ [H2]}{K4} + \dfrac{K1\ K2\ Ia\ [H2]}{K4}$

$\quad = \dfrac{2K1\ K2\ Ia\ [H2]}{K4}$

$= \dfrac{2\ K1\ K2}{K4}\ Ia\ [H_2]$

$\quad = K\ I_a\ [H_2]$

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Photo chemical reactions between H_2 and Br_2

$$H_2 + Br_2 \longrightarrow 2\ HBr$$

mechanism

$$Br_2 + h\nu \xrightarrow{K_1} 2\ Br$$

$$Br + H_2 \xrightarrow{K_2} HBr + H$$

$$H + Br_2 \xrightarrow{K_3} HBr + Br$$

$$H + HBr \xrightarrow{K_4} H_2 + Br$$
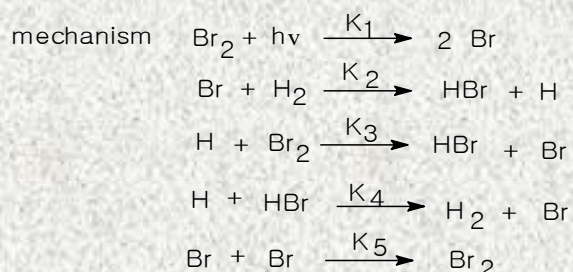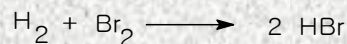
$$Br + Br \xrightarrow{K_5} Br_2$$

$V = \dfrac{d[HBr]}{dt} = K_2[Br][H_2] + K_3[H][Br_2] - K_4[H][HBr]$

$\dfrac{d[H]}{dt} = K_2[H_2][Br] - K_3[H][Br_2] - K_4[H][HBr]$

$\dfrac{d[Br]}{dt} = K_1\ Ia - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - K_5[Br]^2 = 0$

$\qquad K_1\ Ia - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - K_5[Br]^2 = 0$

$\qquad K_1\ Ia + K_3[H][Br_2] + K_4[H][HBr] = K_2[Br][H_2] + K_5[Br]^2$

From above two equations

$K_1\ Ia = K_5\ [Br]^2 = 0$

$[Br] = \sqrt{\dfrac{K1\ Ia}{K5}}$

Similarly

$[H] = \dfrac{K2\ [H2]\sqrt{\dfrac{K1\ Ia}{K5}}}{K3[Br2] + K4[HBr]}$

$\dfrac{d[HBr]}{dt} = \dfrac{2K2\ \sqrt{\dfrac{K1}{K5}}}{1 + \dfrac{K4\ [HBr]}{K5\ [Br2]}}\ X\ \dfrac{[H2][Br2]}{1}$

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Jablonski diagram

One molecule after absorbing light radiation, it is excited and it may be subjected to various physical processes.

- In the ground state, in many molecules many electrons are paired up. The total spin state of the electrons in molecule is given by$(2S +1)$, depending on the value of this
  $(2S +1)$, there will be spin multiplicity.
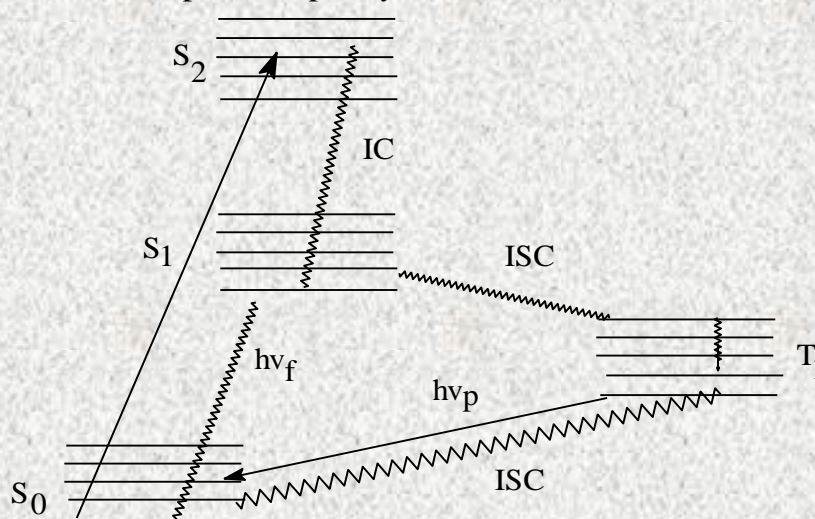
Ex: 1.
For an electron pair
The value of $(2S +1)$ is$(2 \times 0 + 1)1$. Hence electron paired state is called singlet state. This is shown by S

(Ex: 2. If the electrons are not paired (un paired) the value of $2S + 1= 3$
        Hence unpaired electron state is called triplet state. This is shown by T.

A molecule in the ground state as well as in the excited state can be in the singlet state($S0$ or Sn). The excited singlet states depend on the value of n (n=1,2,3…). The singlet states are called excited singlet states.
In a similar way in the excited state there may be triplet states these are called T_1, T_2……T
The energy of singlet state (S) is higher than the energy of the corresponding triplet state(T).

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- If a molecule absorbs light radiation, the molecule goes from S_0 to S_1, $S2$, S_3,…..For every singlet state, there may be corresponding triplet state.
- Excited molecule (A*) may reach ground state in different ways. Thus transfer may be from
  $S_3 - S_0$, $S_3 - S_1$, $S_3 - S_2$
- An excited molecule reaches from higher energy state to lower energy state without change in multiplicity; the transformation is called internal conversion.
- If the transformation from higher energy state to lower energy state with the change in multiplicity is called interstate crossing (ISC)
- The energy difference between the excited state molecule and the lower energy state molecule is distributed with in molecule itself in the form of heat.

Fluorescence

The absorption of light and the emission of light occur almost simultaneously is called fluorescence.
Fluorescence is exhibited by substances in the dilute solutions.
Ex: molecules with rigid structures exhibit this phenomenon.

Phosphorescence
A substance absorbs light and emits it for some time even after the external light is cut off is called phosphorescence.

THERMODYNAMICS

Mutual relationship between the heat energy and mechanical energy and also to explain the laws relating the mutual changes between these two energies is called thermodynamics.

System

A small part of the universe chosen for thermodynamic study is called system.

Surroundings

The remaining part of the universe in contact with the system is known as surroundings.

Universe= system + surroundings

Systems are classified as follows:

1. **Open system**

    A system which can exchange both matter and energy with its surroundings is an open system.

2. **Closed system**

    A system which can exchange energy but not matter with its surroundings is called closed system.

3. **Isolated system**

    A system in which neither matter nor energy is exchanged with the surroundings.

4. **Homogeneous system**

    A system containing only one phase is called a homogeneous system.

    Ex: Mixture of gases, solutions.

5. **Heterogeneous system**

    A system containing two or more phases is called heterogeneous system.

Types of thermodynamic properties

These are divided into two types

a) **Intensive property**

    The property which is independent of the mass and size of the system is known as intensitive property.

    Ex: Tmperature, pressure,density, boilingpoint, melting point.

b) **Extensive property**

    Property of a system which depends upon mass and size of the system is known as extensive property.

    Ex: mass, volume, energy, enthalpy, entropy

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Thermodynamic processes

   a) **Isothermal process**

     A thermodynamic process in which the temperature of the system remains constant called isothermal process.

     So dT= 0

   b) **Adiabatic process**

     If the system does not exchanges energy with surroundings is called adiabatic process. dQ= 0

   c) **Isobaric process**:

     A process is carried out at constant pressure is called an isobaric process. dP=0

   d) **Isochoric process**: A process is carried out at constant volume is called an isobaric process. dV=0

FIRST LAW OF THERMODYNAMICS

Energy may be converted from one form into another; it cannot be created or destroyed. Whenever a quantity of one kind of energy disappears an exactly equivalent amount of other kind must be produced.

$Q=\Delta E+W$

INTERNL ENERGY

Energy stored in the substance at constant temperature and pressure is called internal energy.

$\Delta E=Q-W$

ENTHALPY

The amount of heat exchanged by a system with it surroundings at constant pressure and temperature.

$H=E+PV$

$\Delta H=H_{products}-H_{reactants}$

HEAT CAPACITY

The amount of heat required to raise temperature of a substance by $1^{0}C$.

Molar heat capacity of gas at constant volume Cv

The amount of heat required to raise the temperature of one mole a gas by $1^{0}C$ at constant volume is called molar heat capacity of a gas at constant volume.

$Q_{v}=C_{v}\Delta T$

The amount of heat required to raise the temperaturefrom T_1 to T_2

$Q_{v}=C_{v}(T_{2}-T_{1})$

At constant volume $Q_{v}=\Delta E$ (from first law of thermodynamics W=Pdv, dv=0)

$\Delta E=C_{v}\Delta T$

$C_{v}=\frac{\Delta E}{\Delta T}$

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$$C_v = \frac{dE}{dT}$$

Similarly

$$Q_p = C_p \Delta T$$
$$Q_p = C_p (T_2 - T_1)$$
$$Q_p = \Delta H$$
$$\Delta H = C_p \Delta T$$
$$C_p = \frac{\Delta H}{\Delta T} \quad \text{or} \quad C_p = \frac{dH}{dT}$$

Relation between C_p and C_v

As per the definition of enthalpy H=E+PV

Differentiated w.r.t. temperature we have

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT}$$

The equation for one mole of gas is PV=RT

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(RT)}{dT}$$

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

As per definition

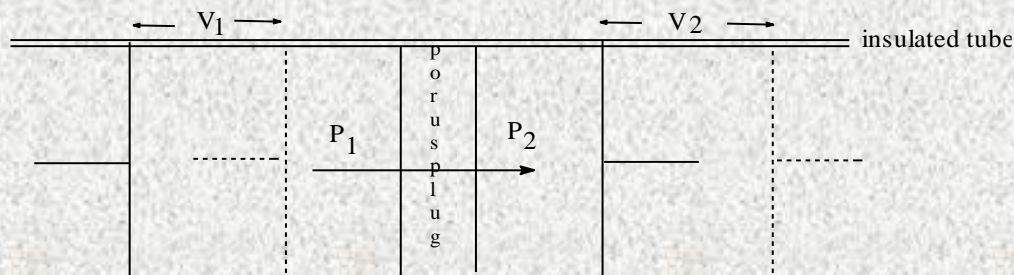$$C_p = \frac{dH}{dT}, \quad C_v = \frac{dE}{dT}$$
$$C_p - C_v = R$$

$$\frac{C_p}{C_v} = \gamma$$

JOULE THOMSON EFFECT

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as Joule Thomson effect.

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W= $-P_1V_1$

W= P_2V_2

According to first law of thermodynamics

Q=ΔE + W

ΔE= $-$ W

$E_2 - E_1 = -$ a $(P_2 V_2 - P_1V_1)$

$E_2 + P_2 V_2 = E_1 + P_1 V_1$

$H_2 = H_1$

$H_2 - H_1 = 0$

ΔH=0

Joule Thomson coefficient (μ $_{JT}$)

The change in the number of degrees of temperature produced by one atmospheric pressure, when the gas expands under conditions of constant enthalpy.

$μ_{JT}$ is positive gas is cooled

μ $_{JT}$ is negative gas is warmed up

μ $_{JT}$ is zero is called inversion temperature.

.

Derive expression for maximum work done in isothermal reversible expansion.

The processes that take place at constant temperature are called isothermal process.

Let an ideal gas taken in a cylinder fitted with piston. The cylinder is placed in a thermostat.

Let the initial volume be V_1 and the pressure inside and outside is P (i.e. piston is in equilibrium state). Now the external pressure is reduced by a very small amount say dP and then the piston moves upwards through a distance, say dl. Let the increase in volume be dV.

Then the work done by this step is

$dW_{rev}=$ (P – dP) dV

   = PdV – dP dV   (dP and dV are very small

= PdV   (For expansion, work is negative)

dW$_{rev}$ = $-$ PdV --- 1

The final volume of V_2 reached through a number of such small steps by decreasing pressure by dP at each step.

Now the total work done by the gas during expansion from V_1 to V_2 can be derived by integration of the equation.

$dW_{rev}=\int_{v1}^{v2} PdV$

For n moles of an ideal gas PV=nRT

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$$P = \frac{nRT}{V}$$

$$= nRT \int_{v1}^{v2} \frac{dV}{V}$$

$$= nRT \ln \frac{V2}{V1}$$

$$dW_{rev} = 2.303 \; nRT \log \frac{V2}{V1}$$

Derive expression for maximum work done in adiabatic reversible expansion.

In this process no heat enters or leaves the system at any stage.

So q=0

Let one mole of the gas taken in a vessel at a pressure P, occupies the volume V.

According to first law of thermodynamics

Q=ΔE + W

ΔE= $-$ W

Expansion work done by the gas is $-$ W= PdV

dE= $-$ PdV

C_vdT = dE

= $-$ PdV---- 1

Relationship between temperature and volume.

For an ideal gas

PV=RT

$$P = \frac{RT}{V} \; --- 2$$

Substituting the value of P in equationa, we get

$$C_v dT = - \frac{RT}{V} dV$$

$$Cv \frac{dT}{T} = - R \frac{dV}{V} \; ----- 3$$

Integrating equation c between the limits T_1, T_2 and V_1, V_2

$$Cv \int_{T1}^{T2} \frac{dT}{T} = - R \int_{V1}^{V2} \frac{dV}{V}$$

$$Cv \ln \frac{T2}{T1} = -R \ln \frac{V2}{V1}$$

$$Cv \ln \frac{T2}{T1} = R \ln \frac{V1}{V2}$$

$$Cv \ln \frac{T2}{T1} = (Cp - Cv) \ln \frac{V1}{V2}$$

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$$\ln\frac{T2}{T1} = \frac{Cp-Cv}{Cv}\ln\frac{V1}{V2}\frac{Cp}{Cv} = \Upsilon$$

$$\ln\frac{T2}{T1} = (\Upsilon - 1)\ln\frac{V1}{V2}$$

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{\Upsilon-1}$$

Taking antilogarithm of both sides, we get

$$\frac{T_2}{T_1} = = \left(\frac{V_1}{V_2}\right)^{\Upsilon-1}$$

$$T_1 V_1^{\Upsilon-1} = T_2 V_2^{\Upsilon-1}$$

$$T V^{\Upsilon-1} = \text{Constant}$$

Relationship between pressure and volume
According to ideal gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

$$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\Upsilon-1}$$

$$(P_1V_1)^{\Upsilon} = (P_2V_2)^{\Upsilon}$$

$$PV^{\Upsilon} = \text{Constant.}$$

Work done in an adiabatic reversible expansion of an ideal gas
For an adiabatic process, we have derived that $PV^{\Upsilon} = \text{Constant}$ --- 1
Differentiating the above equation 1 we get
$$\Upsilon P V^{\Upsilon-1} dV + V^{\Upsilon} dP = 0 \text{ --- 2}$$
Dividing throughout equation 2by $V^{\Upsilon-1}$, we get
$$\Upsilon P dV + VdP = 0$$

$$VdP = -\Upsilon P dV \text{ --- 3}$$
For n moles of an ideal gas PV=nRT --- 4

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PdV + V dP = nRdT

VdP= nRdT – PdV --- 5
Equating equations 3 and 5

$- \Upsilon\, P\, dV = nRdT - PdV$

$PdV - \Upsilon\, P\, dV = nRdT$

$(1 - \Upsilon)\, PdV = nRdT$

$PdV = \dfrac{nRdT}{1-\Upsilon}$

Work done $W = \int_{V1}^{V2} PdV$

$$= \int_{T1}^{T2} \frac{nRdT}{1-\Upsilon}$$

$$= \frac{nR}{1-\Upsilon} \int_{T1}^{T2} dT$$

$$W = \frac{nR\,(T2-T1)}{1-\Upsilon}$$

SECOND LAW OF THERMODYNAMICS
1. Heat cannot pass from a colder body to warmer body.
2. Entropy increases in every natural process.
3. It is impossible to convert heat into work without transfer of heat from higher temperature to lower temperature.
4. Heat cannot be completely converted into work without leaving permanent changes in the systems involved or their surroundings.

Conversion of heat into work

$$Q \longrightarrow W$$

According to first law of thermodynamics
Q= ΔE + W
For an isothermal process ΔE=0
Q=W
So heat can be converted to work.
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State functions

Properties of the systems which depend on the initial and the final state of the system but are independent of the path of the system are state functions.

Ex: Pressure, Temperature, Volume, mass

Heat engines

The machines which takeup heat and convert it into work are called Heat engines.

- Heat engine works at two temperatures. High temperature one is called Reservoir, The low temperature one is called Sink.
- Carnot proposed that the maximum efficiency of the machine is obtained in a cyclic process. This is called Carnot's cycle.

Explain Carnot's cycle and write Carnot's theorem.

One mole of gas is used as the working substance.

- The gas is enclosed in a cylinder fitted with a piston. The gas undergoes expansion and compression reversibly in this cylinder.
- In this process a reservoir or source(T_2) and a sink isT_1, both isothermal and adiabatic process can occur in this ccylinder.
- There are four stages in Carnot's cycle.
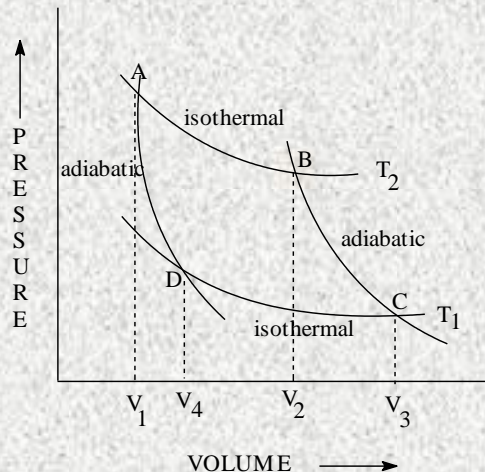
Stage 1: Isothermal reversible expansion

The gas cylinder is kept at T_2 and the gas is expanded reversibly and isothermally. The gas absorbs heat Q_2. The volume of gas changes from V_1 to V_2.

Step 1 is isothermal ($\Delta E=0$)

According to the first law of thermodynamics $\Delta E= Q - W$

$W_1=Q_2$

$W_1= RT_2 \ln \dfrac{V2}{V1}$ ---- 1

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Stage 2:Adiabatic reversible expansion

The cylinder is removed from the source and it is surrounded insulating material. So heat cannot go out from the cylinder or heat cannot enter the cylinder from the surroundings. So gas expands adiabatically and reversibly from V_2 to V_3. In this expansion the temperature decreases to T_1. At this stage the work is done under adiabatic condition.

$W_2 = -\Delta E$

$= -C_v(T_1 - T_2)$ --- 2

Stage 3: Isothermal reversible compression

The cylinder is removed from the insulating material and placed in the thermostat. The gas is compressed isothermally the volume decreases from V_3 to V_4

$W_3 = -Q_1$

$W_3 = RT_1 \ln \dfrac{V4}{V3}$ --- 3

Stage 4: Adiabatic compression

The cylinder is now removed from the sink and placed again in the insulating material. The gas is compressed adiabatically and reversibly from volume V_4 to V_1. Temperature rise from T_1 to T_2.

$W_4 = -\Delta E$

$= -C_v(T_2 - T_1)$ ---- 4

The total work done in the cycle $W = W_1 + W_2 + W_3 + W_4$

$= RT_2 \ln \dfrac{V2}{V1} - C_v(T_1 - T_2) + RT_1 \ln \dfrac{V4}{V3} - C_v(T_2 - T_1)$

$= RT_2 \ln \dfrac{V2}{V1} + RT_1 \ln \dfrac{V4}{V3}$

For adiabatic process

$\left(\dfrac{V_3}{V_2}\right)^{\Upsilon - 1} = \dfrac{T_2}{T_1}$

From above equations $\dfrac{V4}{V3} = \dfrac{V1}{V2}$

$W = RT_2 \ln \dfrac{V2}{V1} + RT_1 \ln \dfrac{V1}{V2}$

$W = RT_2 \ln \dfrac{V2}{V1} - RT_1 \ln \dfrac{V2}{V1}$

$= R(T_2 - T_1) \ln \dfrac{V2}{V1}$

In this cyclic process the gas absorbed Q_2 calories heat

$\therefore$ Total work $= R(T_2 - T_1) \ln \dfrac{V2}{V1}$

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The efficiency of cyclic process $= \dfrac{W}{Q2}$

But $Q_2 = W_1$

$$= RT_2 \ln \dfrac{V2}{V1}$$

$$\dfrac{W}{Q2} = \dfrac{R(T2-T1)\ln\dfrac{V2}{V1}}{RT2 \ln\dfrac{V2}{V1}}$$

$$\dfrac{W}{Q2} = \dfrac{T2-T1}{T2}$$

So the efficiency depends only on the temperature. It does not depend on the working substance.

Efficiency

The ratio of the net work done to the heat absorbed during one complete cyclic process.
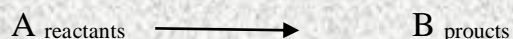
$$\Phi = \dfrac{Net\ work\ done}{Absorbed\ heat}$$

$$= 1 - \dfrac{T1}{T2}$$

$$\Phi\% = \left(1 - \dfrac{T1}{T2}\right) \times 100$$

Variation of heat of reaction with temperature (Kirchoff's Equation)

When the reaction is carried out at constant pressure

$$A_{\text{reactants}} \longrightarrow B_{\text{proucts}}$$

Suppose H_A and H_B are the heat contents (enthalpies) of the reactants and products

$\Delta H = H_B - H_A$

Differentiating w.r.t. temperature at constant pressure we get

$$\dfrac{d(\Delta H)}{dT} = \dfrac{dHB}{dT} - \dfrac{dHA}{dT} \quad \text{--- 1}$$

But according to the definition of heat capacity at constant pressure

$$Cp = \dfrac{dH}{dT} \quad \text{---- 2}$$

From equation 1 and 2 we get $\dfrac{d(\Delta H)}{dT} = Cp\ B - Cp\ A$

$Cp_{(B)}$ and $Cp_{(A)}$ are the mean molar heat capacities of the products and reactants respectively

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$$\frac{d(\Delta H)}{dT} = \Delta Cp$$

$d(\Delta H) = (\Delta Cp)\Delta T$ ---- 3

Integrating we get

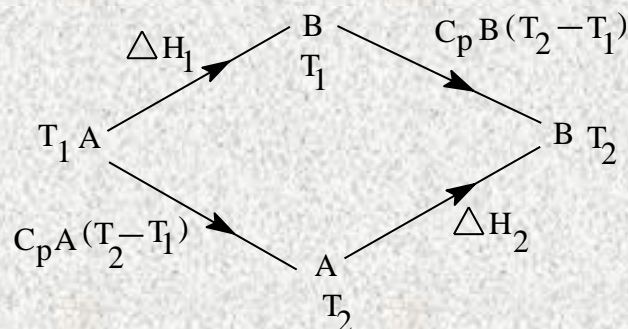$$\int_{\Delta H1}^{\Delta H2} d(\Delta H) = \int_{T1}^{T2} \Delta Cp . \Delta T$$

$\Delta H_2 - \Delta H_1 = (\Delta Cp)(T_2 - T_1)$

$$\frac{\Delta H2 - \Delta H1}{T2 - T1} = \Delta Cp$$

$$\Delta Cp = \sum Cp(prouct) - \sum Cp(reactant)$$

OR

$A_{reatants} - B_{products}$

Path 1: The reaction is carried out at T_1.

The reactant (A) T_1 is changed into the product (B) at T_1. The enthalpy change in the process is ΔH_1.

The product (B) at T_1 is changed to B at T_2.

The enthalpy change $\Delta H_1 + Cp\ B\ (T_2 - T_1)$ ---- a

Total enthalpy change = $\Delta H_1 + Cp\ B\ (T_2 - T_1)$

Path 2: The temperature of the reactant (A) is changed from T_1 to T_2.

The enthalpy change in the process is ΔH_2.

The reactant A at T_2 is changed to the product B at T_2.

The enthalpy change $\Delta H_2 + Cp\ A\ (T_2 - T_1)$ ----- b

From the first law of thermodynamic the enthalpy change must be the same

$\Delta H_1 + Cp\ B(T_2 - T_1) = \Delta H_2 + Cp\ A\ (T_2 - T_1)$

$Cp\ B(T_2 - T_1) - Cp\ A\ (T_2 - T_1) = \Delta H_2 - \Delta H_1$

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$T_2 - T_1(\ Cp \ B \ - \ Cp \ A) = \Delta H_2 - \Delta H_1$

$$\Delta Cp = \frac{\Delta H2 - \Delta H1}{T2 - T1}$$

Or

$$\Delta Cp = \sum Cp(prouct) - \sum Cp \ (reactant)$$

Entropy
It is a measure of the disorder or randomness of a system.
$S = \frac{Q}{T}$
$dS = \frac{dQ}{T}$
$dQ = TdS$

ENTROPY CHANGES
Entropy changes in a reversible process
Consider a process occurring under completely reversible conditions i.e. the heat absorbed by the system reversible and heat is lost by the surroundings also reversible.
If Qrev is heat absorbed by the system reversibly, then Q_{rev} will be the heat lost by surroundings.

ΔS system $= + \ \frac{Q_{rev}}{T}$

ΔS surroundings$= - \frac{Q_{rev}}{T}$

ΔS Universe$= \Delta S$ system $+\Delta S$ surroundings

$\qquad = \frac{Q_{rev}}{T} - \frac{Q_{rev}}{T}$
$\qquad = 0$

Thus in a reversible process, the net entropy change for the combined system and the surroundings is zero.

Entropy changes in irreversible (spontaneous) process

ΔS system$= + \ \frac{Q_{rev}}{T}$

ΔS surroundings$= - \frac{Q_{rev}}{T}$

ΔS Universe$= \Delta S$ system $+\Delta S$ surroundings

$\qquad = \frac{Q_{rev}}{T} - \frac{Q_{rev}}{T}$ ---- 1
$\qquad =$ W reverse > W irreverse

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Work done is directrly proportional to the heat absorbed or lost

Q reverse > Q irreverse ---- 2

Equation 2 is divided by T we get

$$\frac{Q_{rev}}{T} > \frac{Q_{rev}}{T}$$

$$\frac{Q_{rev}}{T} - \frac{Q_{rev}}{T} > 0 \quad ---- 3$$

From equations 1 & 3

ΔS system $+ \Delta S$ surroundings > 0

Thus in an irreversible process, the entropy change for the combined system and surroundings is greaterthan zero.

ENTROPY CHANGES
   A) Entropy changes when V and T are the variables

$dS = \frac{dq_{rev}}{T}$

But first law $dq = dE = P - dW$

 The expansion work is dW

$dW = -PdV$

$-dW = PdV$

$dq = dE + PdV$

$dE = Cv \, dT$

$dq = Cv \, dT + PdV$

$dq = Cv \, dT + RT \frac{dV}{V}$

dividing both sides with T we get

$\frac{dq}{T} = \frac{CvdT}{T} + R\frac{dV}{V}$ 　　　　but $\frac{dq}{T} = dS$

For ideal gasPV=RT

$\Delta S = Cv\int_{T1}^{T2} \frac{dT}{T} + R\int_{V1}^{V2}\frac{dV}{V}$

$\Delta S = Cv \ln\frac{T2}{T1} + R\ln\frac{V2}{V1}$

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For n moles $\Delta S = n\ C_v \ln \dfrac{T2}{T1} + n\ R \ln \dfrac{V2}{V1}$

B) Entropy changes when P and T are the variables

$P_1V_1 = RT_1$ initial state

$P_2V_2 = RT_2$ final state

But $\dfrac{V_2}{V_1} = \dfrac{P_1 T_2}{P_2 T_1}$

$\Delta S = C_v \ln \dfrac{T2}{T1} + R \ln \dfrac{V2}{V1}$

$\Delta S = C_v \ln \dfrac{T2}{T1} + R \ln \dfrac{T2}{T1} - R \ln \dfrac{P2}{P1}$

But $C_p - C_v = R$

$C_v = C_p - R$

$\Delta S = C_v \left(\ln \dfrac{T2}{T1} - R \ln \dfrac{P2}{P1} \right)$

For n moles $\Delta S = n\ C_p \ln \dfrac{T2}{T1} - n\ R \ln \dfrac{P2}{P1}$

GIBB'S HELMHOLTZ EQUATION

$G = H - TS$

But $H = E + PV$

$G = E + PV - TS$

$dG = dE + PdV + VdP - TdS - SdT$ but $dE = TdS - PdV$

$dG = TdS - PdV + PdV + VdP - TdS - SdT$

$dG = TdS + VdP - TdS - SdT$ ---- 1

$dG = VdP - SdT$ ---- 2

According to first law of thermodynamics

$dq = dE + dW$

$dq = dE + PdV$ but $dS = \dfrac{dq}{T}$ $dq = TdS$

$TdS = dE + PdV$ ----- 3

Equation 2 value is substituted in equation 1

$dG = TdS + VdP - TdS - SdT$

$dG = VdP - SdT$

According to first law of thermodynamics

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Dq= dE + PdV   but dS=$\frac{dQ}{T}$

dQ=TdS   ----- 4

substitute equ 4 in equ 2 we get

dG= TdS + VdP – TdS – SdT   ----- 5

dG= VdP – SdT

If pressure is constant dP=0

dG= - SdT

$\left(\frac{\delta G}{\delta T}\right)_p = - S \left(\frac{\delta T}{\delta T}\right)$

$\left(\frac{\delta G}{\delta T}\right)_p = - S$

$\left(\frac{\delta G}{\delta P}\right)_p = V$

$\Delta G = G_2 – G_1$

$\int_{P_1}^{P_2} VdP.$

$\Delta G = RT\int_{P_1}^{P_2} \frac{dP}{P}$

$\Delta G = RT \ln \frac{P_2}{P_1}$ ----- a

<div align="center">Or</div>

$\Delta G = G_2 – G_1$

Differentiating with respect to t we get

$\frac{d}{dT}(\Delta G) = \frac{d}{dT} G_2 - \frac{d}{dT} G_1$

But $\left(\frac{\delta G2}{\delta T}\right) = - S_2 , \left(\frac{\delta G1}{\delta T}\right)_p = - S_1$

$\frac{d}{dT}(\Delta G) = -S_2 + S_1$

$\frac{d}{dT}(\Delta G) = - \Delta S$ ….(1)

Substitute (1) in G=H - TΔS

$\Delta G = \Delta H + T \left(\frac{d\Delta G}{dT}\right)p$

This is called Gibb's – Helmholtz equation.

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