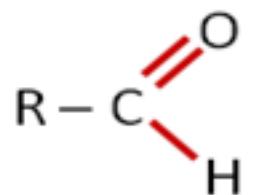


## Module – 34.1

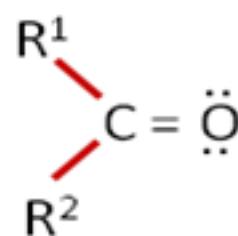
### Carbonyl Compounds

#### Introduction:

Oxygen compounds in which oxygen is bonded to a carbon atom through a double bond are known as carbonyl compounds. The functional unit ( $>\text{C}=\text{O}$ ), present in these compounds is called carbonyl group. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen or alkyl or aryl groups. If at least one of these groups is hydrogen, the compound is an **aldehyde**. If both the groups are hydrocarbon groups the compound is a **ketone**.



**Aldehyde:** R = alkyl group



**Ketone :** R<sup>1</sup> and R<sup>2</sup> = alkyl or aryl groups

Aldehydes and ketones are simple but most important carbonyl compounds.

### Nomenclature:

The naming of carboxyl compounds i.e. aldehydes and ketones, is done in two ways. They are

- Common method or trivial method and
- IUPAC method

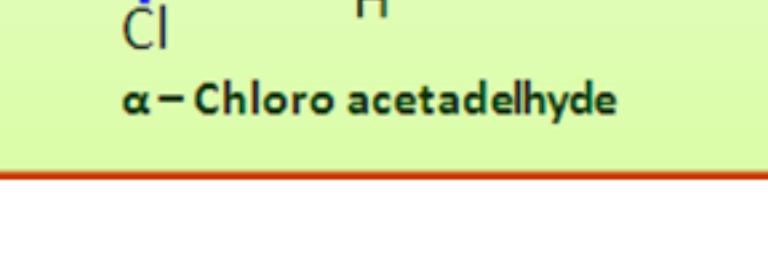
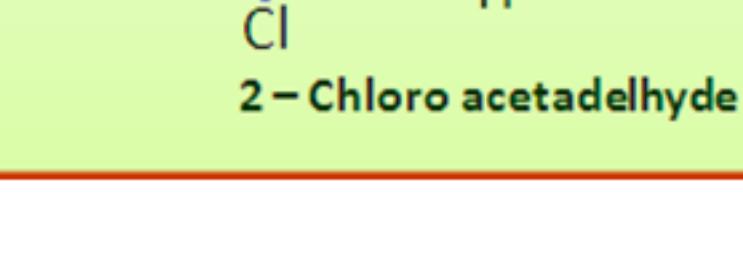
#### a. Common (naming) method:

This is used for a few compounds only. The names of the aldehydes are derived from the names of the corresponding carboxylic acid. The part “– oic acid or “– ic acid” in the name of the acid is replaced by “– aldehyde”.

**Ex:** Form (ic acid) → Formaldehyde

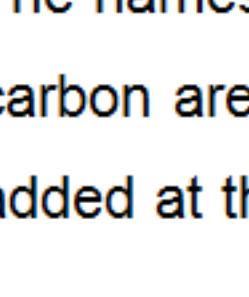
Benz (oic acid) → benzaldehyde

The carbon atoms in the chain are indicated either by the Greek alphabets  $\alpha$ ,  $\beta$ ,  $\gamma$  .... or by numerical indecies. 1, 2, 3 ..... The examples given below indicate the method of identifying the carbons in the chain.

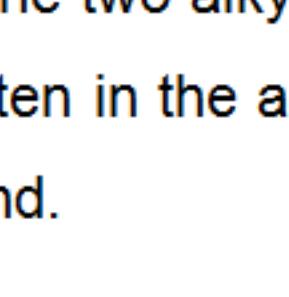
By Greek alphabets	By numerical prefixes
<p>Starts from the carbon next to carbonyl carbon.</p>  <p><b>Ex:</b> <math>\text{CH}_2 - \overset{\alpha}{\underset{\text{Cl}}{\text{C}}} = \text{O} \text{ H}</math></p> <p><math>\alpha</math>-Chloro acetadelhyde</p>	<p>Numbering starts from the aldehydic carbon in aldehydes.</p>  <p><b>Ex:</b> <math>\text{CH}_2 - \overset{2}{\underset{\text{Cl}}{\text{C}}} = \text{O} \text{ H}</math></p> <p>2-Chloro acetadelhyde</p>

#### Other examples:

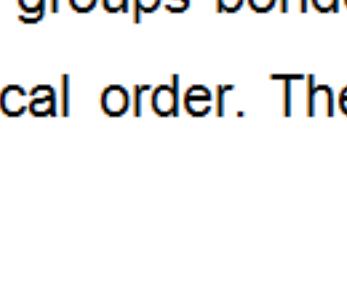
Formaldehyde



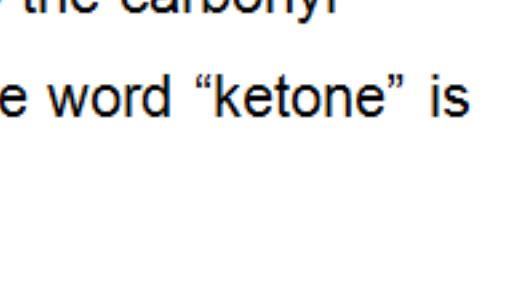
acetaldehyde



Benzaldehyde



$\beta$ -Bromo- $\alpha$ -methylbutyraldehyde



#### Nomenclature of ketones:

The names of the two alkyl or aryl groups bonded to the carbonyl carbon are written in the alphabetical order. Then the word “ketone” is added at the end.

**Ex:**  $\text{CH}_3.\text{CO.C}_2\text{H}_5$       Ethyl methyl ketone.

The locations of the substituents in the chain are indicated by Greek letters  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\beta'$  .....etc. the carbons next to the carbonyl functional group are labeled as  $\alpha$  carbons. Then the successive carbons in the chain are labeled as  $\beta$ ,  $\gamma$  etc respectively.

**Ex:**  $\text{ClCH}_2 - \overset{\alpha}{\text{CO}} - \overset{\alpha'}{\text{CH}_2} - \overset{\beta'}{\text{CH}_2\text{Br}}$

$\alpha$ -chloromethyl  $\beta'$ -bromoethyl ketone

Some ketones have historical common names. The simplest of them all is dimethyl ketone. Its common name is acetone. Aromatic ketones having phenyl group as one of the hydrocarbon groups are called as phenones.

**Ex:** 

Acetophenone



Benzophenone

## IUPAC nomenclature of aldehydes:

The IUPAC names of aliphatic aldehydes are derived from the IUPAC names of the corresponding alkanes. The ending '-e' of the alkane is replaced by '-al'.

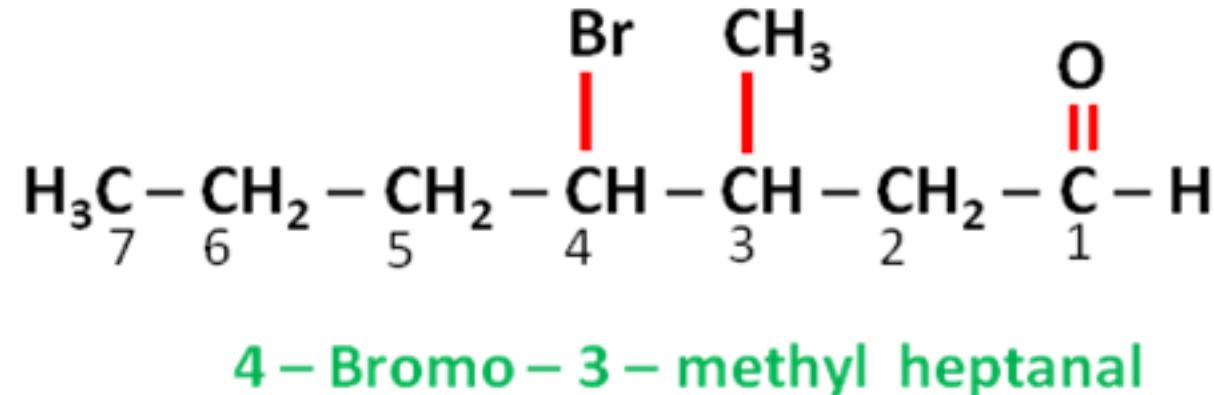
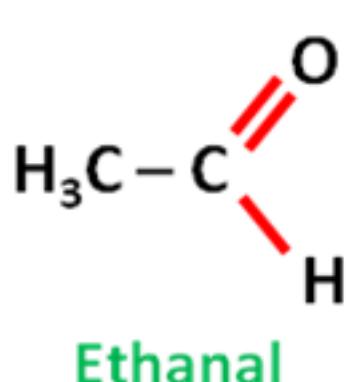
**Ex:** HCHO (Methan + al) = Methanal

CH<sub>3</sub>CHO (Ethan + al) = Ethanal

The following principles are followed

- The longest carbon chain containing the carbonyl carbon is taken to decide the name of the parent alkane.
- The carbon chain is numbered from the end nearer to the carbonyl group
- The substituents are written in alphabetical order along with Arabic numerals including their positions in the carbon chain.
- The carbon of the aldehydic group and the carbonyl carbon in cyclic ketones always get the number 1.
- When the aldehyde group is attached to a ring, the numbering of the ring carbon atoms starts from the carbon atom that is attached to the aldehyde group. Then the suffix carbaldehyde is added after the full name of the hydrocarbon.

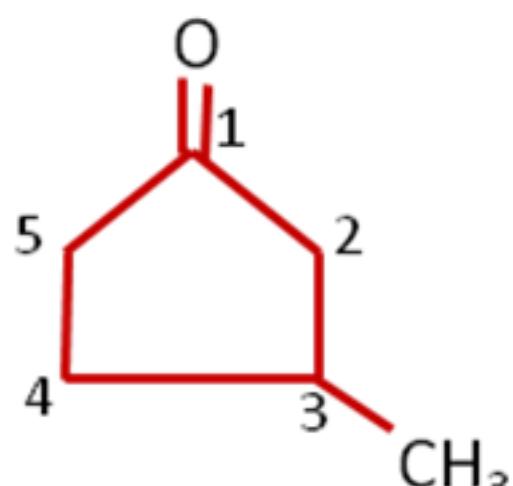
### Examples:



## IUPAC nomenclature of ketones:

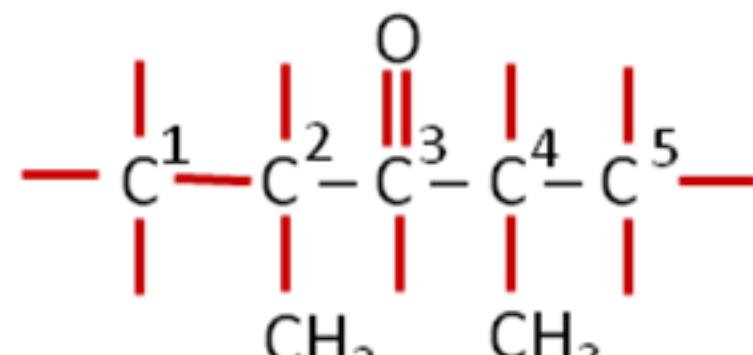
### Examples:

3 – methyl cyclopentanone



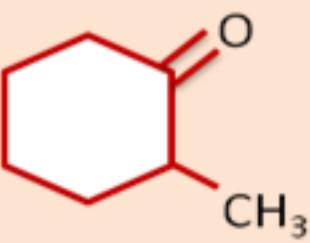
2,4 – Dimethyl pentan – 3 – one

$\alpha, \alpha^1$  - Dimethyl Pentan – 3 – one



The common (trivial) and IUPAC names of some aldehydes and ketones are given in below Table

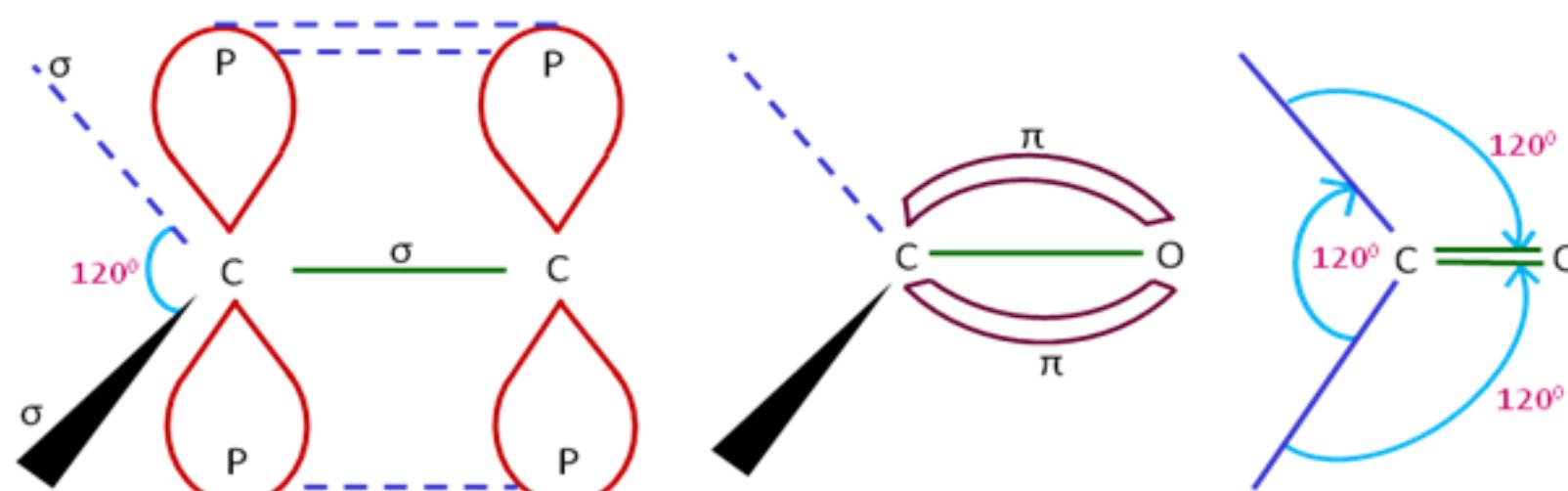
Aldehyde	Trivial Name	IUPAC Name
$\text{C}_2\text{H}_5\text{CHO}$	propionaldehyde	Propanal
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CHO} \\   \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2 – Methylpropanal
$\begin{array}{c} \text{CH}_3 - \overset{\beta}{\text{CH}} - \overset{\alpha}{\text{CHCHO}} \\   \\ \text{Br} \qquad   \\ \qquad \qquad \text{CH}_3 \end{array}$	$\beta$ – bromo – $\alpha$ – methyl butyraldehyde	3 – Bromo – 2 – methlbutanal
$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \overset{\beta}{\text{CH}} - \overset{\alpha}{\text{CH}} - \text{CHO} \\   \\ \text{Cl} \qquad   \\ \qquad \qquad \text{CH}_2 - \text{CH}_3 \end{array}$	$\beta$ – Chloro – $\alpha$ – ethyl valeraldehyde	3 – Chloro – 2 – ethyl pentanal

Ketone	Trivial	IUPAC
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	Methyl, n – propyl ketone	Pentan – 2 – one/2 – pentanone
$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2$	Diisopropyl ketone	2, 4 – Dimethylpentan – 3 – one
	$\alpha$ – Methylcyclohexanone	2 - Methylcyclohexanone
$(\text{CH}_3)_2\text{C} = \text{CHCOCH}_3$	Mesityl oxide	4 – Methylpent – 3 – en – 2 – one

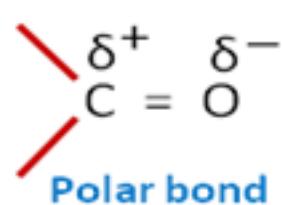
## Structure of the Carbonyl Group:

The aldehydes and ketones have at least one carbonyl group as the functional group. The carbonyl carbon is  $sp^2$  hybridized. It has three  $sp^2$  hybrid orbitals and one unhybridized p-orbital. It uses  $sp^2$  hybrid orbitals to form three  $\sigma$  – bonds. One with oxygen atom and the remaining two with two other atoms or groups (R's or Ar's or H'r). All these three sigma bonds lie in the same plane and are at an angle of  $120^\circ$ .

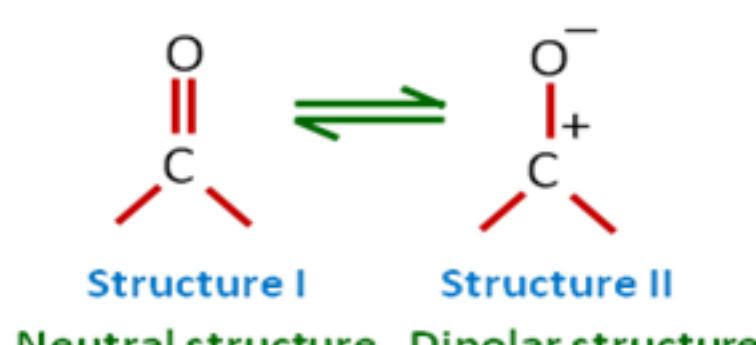
The fourth valence electron, which remains in the unhybridized p-orbital overlaps with the p-orbital of oxygen to form a  $\pi$  – bond. The oxygen atom has two lone pairs of electrons, which occupy the remaining orbitals on oxygen atom. The carbonyl carbon and the three atoms bonded to it lie in the same plane and the pi-electron cloud is above and below this plane.



Since the carbon and the oxygen atoms have different values of electronegativity, the bond between carbon and oxygen is a polar bond. The electron density around the oxygen atom is greater. This causes the development of partial positive charge ( $\delta+$ ) on carbon and a partial negative charge ( $\delta-$ ) on oxygen atoms.



Thus the carbonyl carbon is an electrophilic centre (Lewis acid) while the carbonyl oxygen is a nucleophilic (Lewis base) centre. These carbonyl compounds have significant dipole moments. The dipole moment of carbonyl compounds is due to the highly polar character of the carbonyl group. This, in turn, can be explained on the basis of resonance involving a neutral structure. (Structure I) and a dipolar structure (Structure II)



## Preparation of Aldehydes and Ketones:

Some important methods for the preparation of aldehydes and ketones.

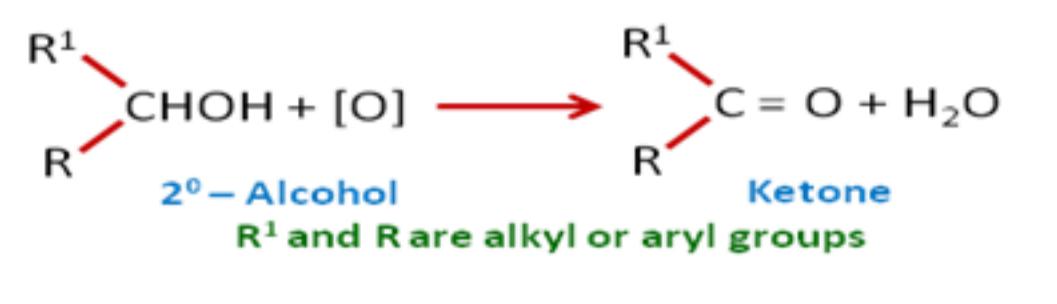
### 1. By oxidation of Alcohols:

Aldehydes and ketones are generally prepared by the oxidation of either primary or secondary alcohols respectively.

Common oxidizing agents are  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CrO}_3$ . Strong oxidizing agents oxidize the aldehyde produced from the oxidation of a primary alcohol further to carboxylic acid.

Low molecular weight primary alcohols may be oxidized to aldehydes if the reaction temperature is so adjusted that the aldehyde, being lower boiling substance, than the alcohol, distils out of the reaction mixture as soon as it is formed, thus escaping from further oxidation.

The general reaction is:



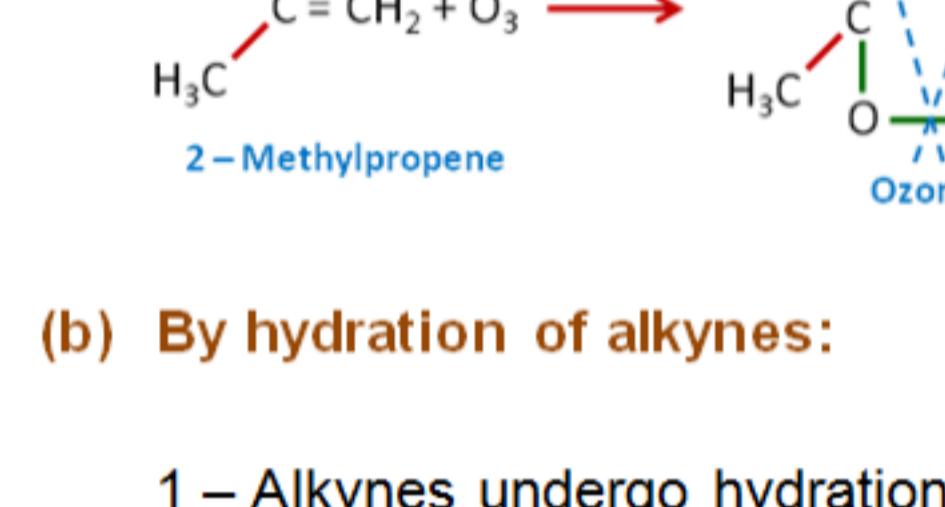
The temperature for this reaction is maintained slightly above 349 K

Collins reagent (chromium trioxide - pyridine complex) in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) is a very good oxidizing agent for converting primary alcohol to aldehydes. The reagent checks the further oxidation of aldehydes to carboxylic acids. Collins reagent is used in non-aqueous medium like  $\text{CH}_2\text{Cl}_2$ .

On mixing pyridine ( $\text{C}_5\text{H}_5\text{N}$ ),  $\text{CrO}_3$  and  $\text{HCl}$  in dichloromethane, pyridinium chloro-chromate ( $\text{C}_5\text{H}_5\text{NH}^+ \text{CrO}_3 \text{Cl}^-$ ) abbreviated as PCC, is made

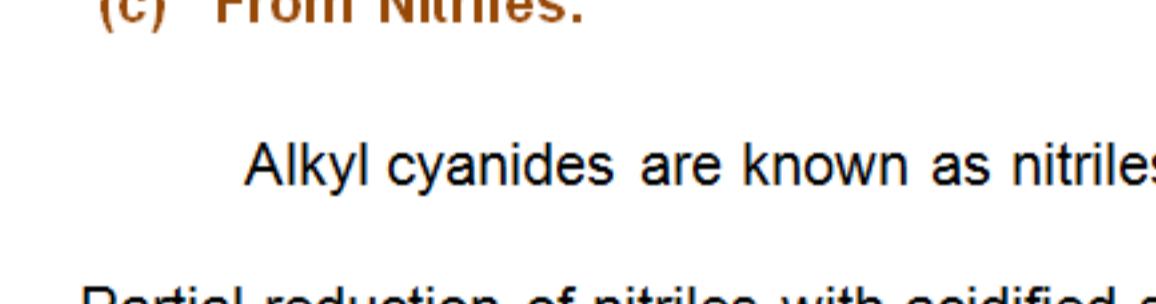


Ketones can be prepared by using similar oxidizing agents from secondary alcohols.

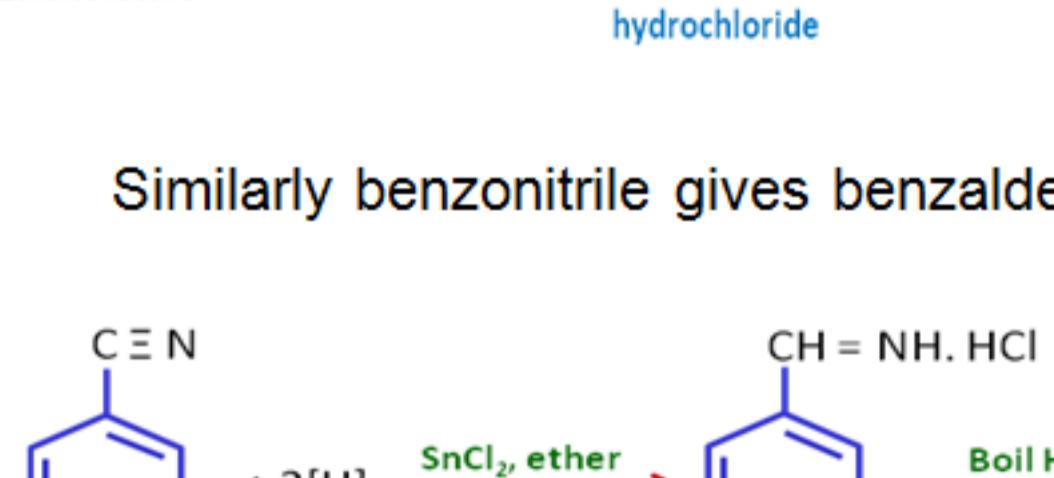


### 2. By dehydrogenation of alcohols:

When vapours of primary or secondary alcohols are passed over a hot copper gauze at 573 K, they get dehydrogenated to form aldehydes or ketones respectively.



Other heated metal catalysts like silver or copper may be used. This method is suitable for secondary alcohols and is of industrial application.

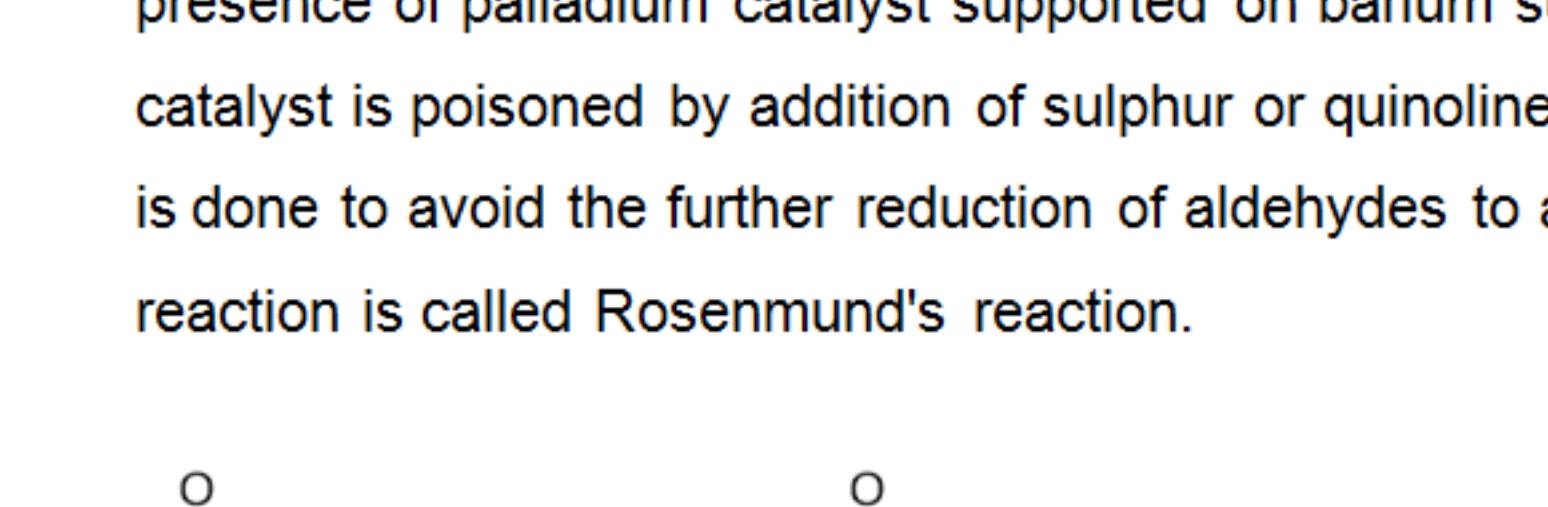


The dehydrogenation reaction is a better method of preparation because there is no risk of further oxidation of aldehyde.

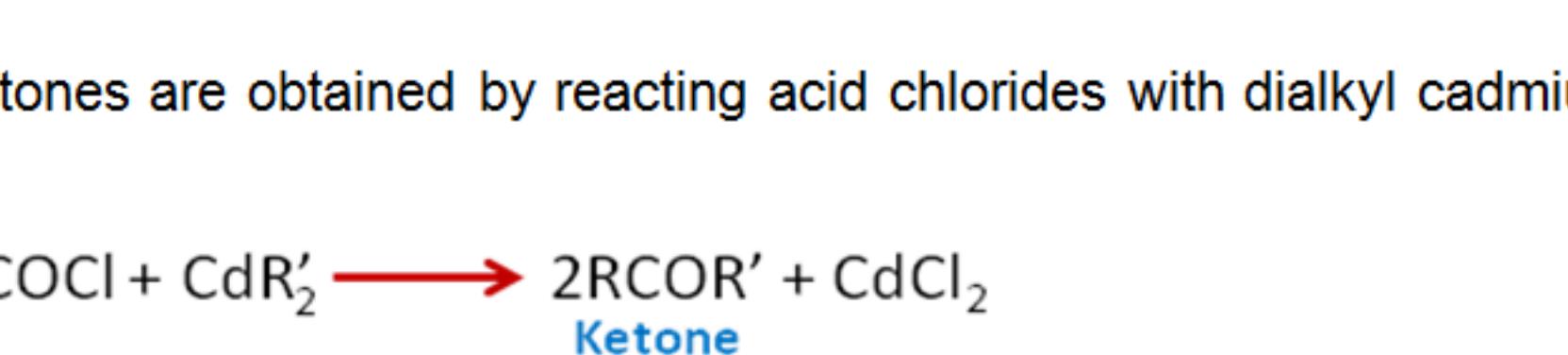
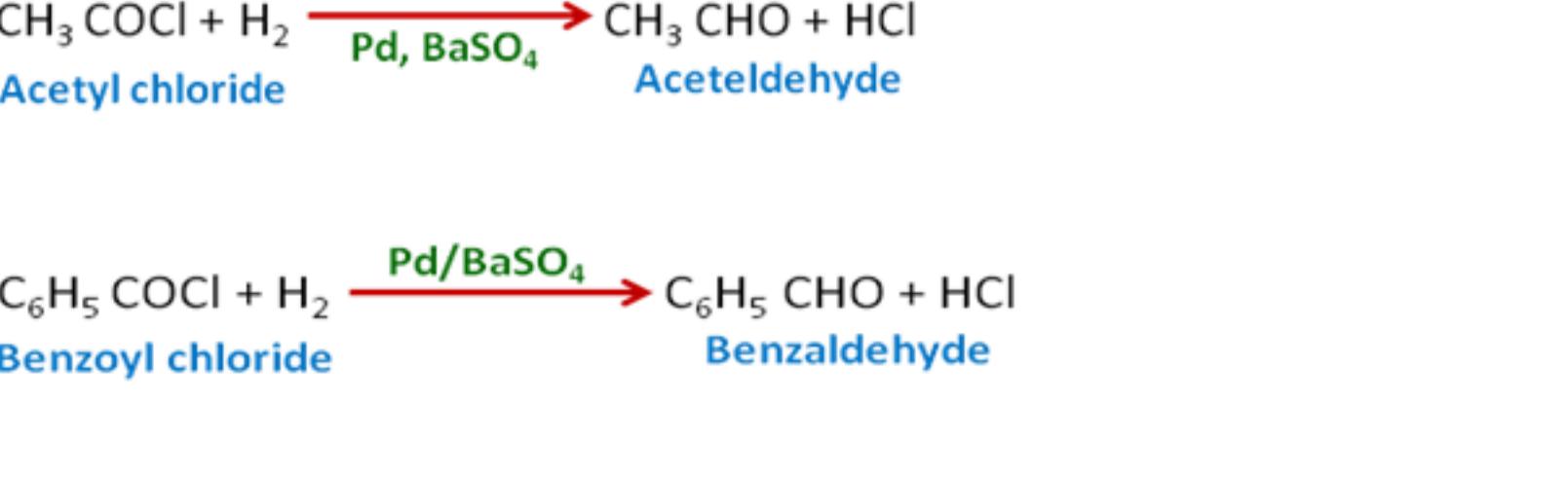
### 3. From Hydrocarbons:

#### (a) By ozonolysis of alkenes:

From the chapter on alkanes, it is known that alkenes give carbonyl compounds on ozonolysis.



#### Example:



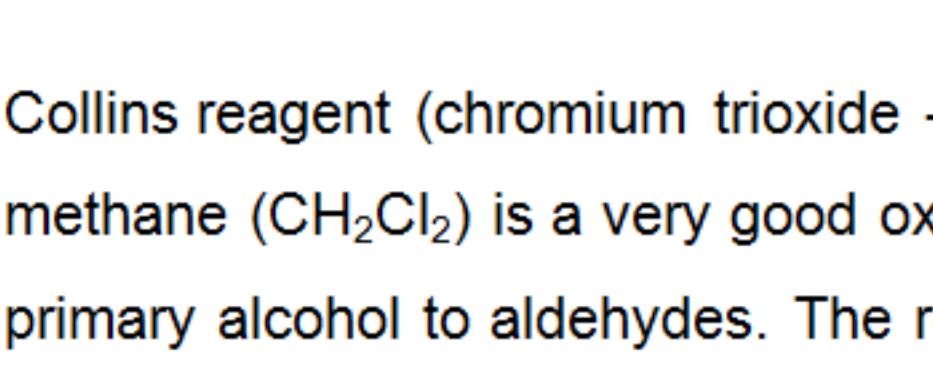
#### (b) By hydration of alkynes:

1 – Alkynes undergo hydration with dil  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$  and give carbonyl compounds.

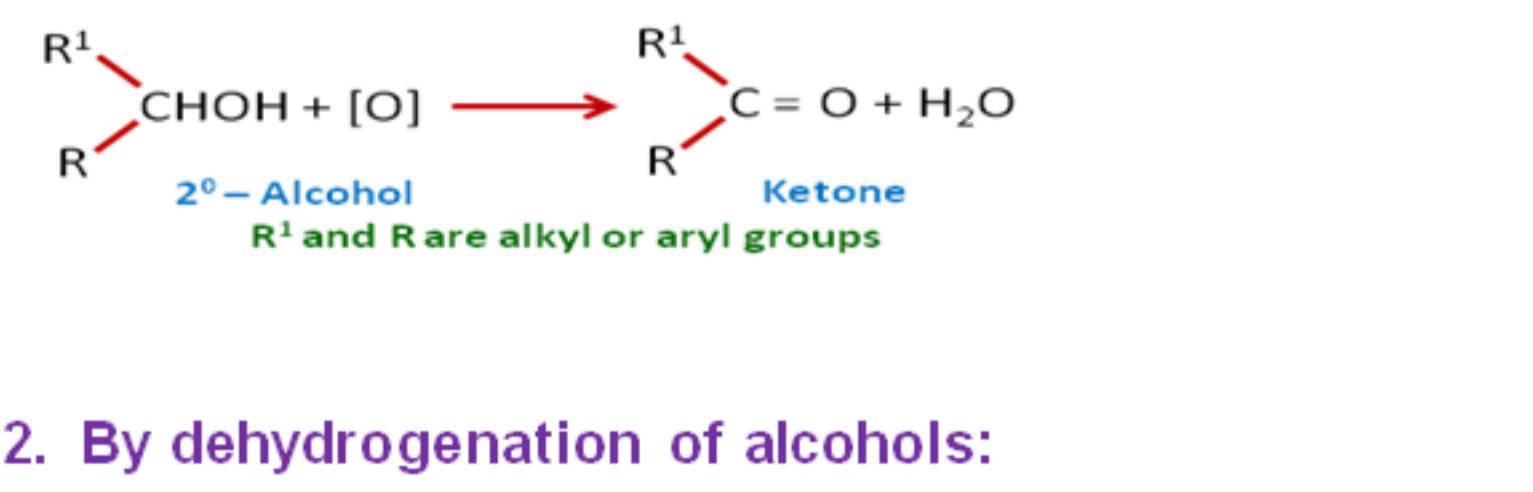
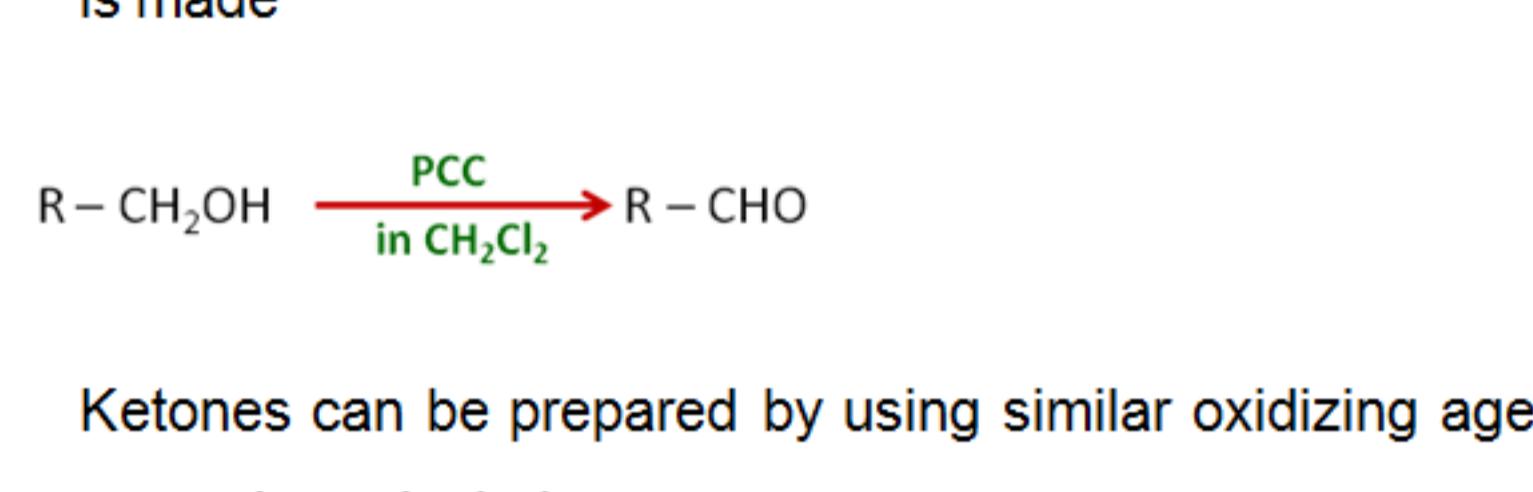
**Ex:** Ethyne adds water in the presence of Dil. $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  to give acetaldehyde.



Hydration of other alkynes under similar condition gives ketones.

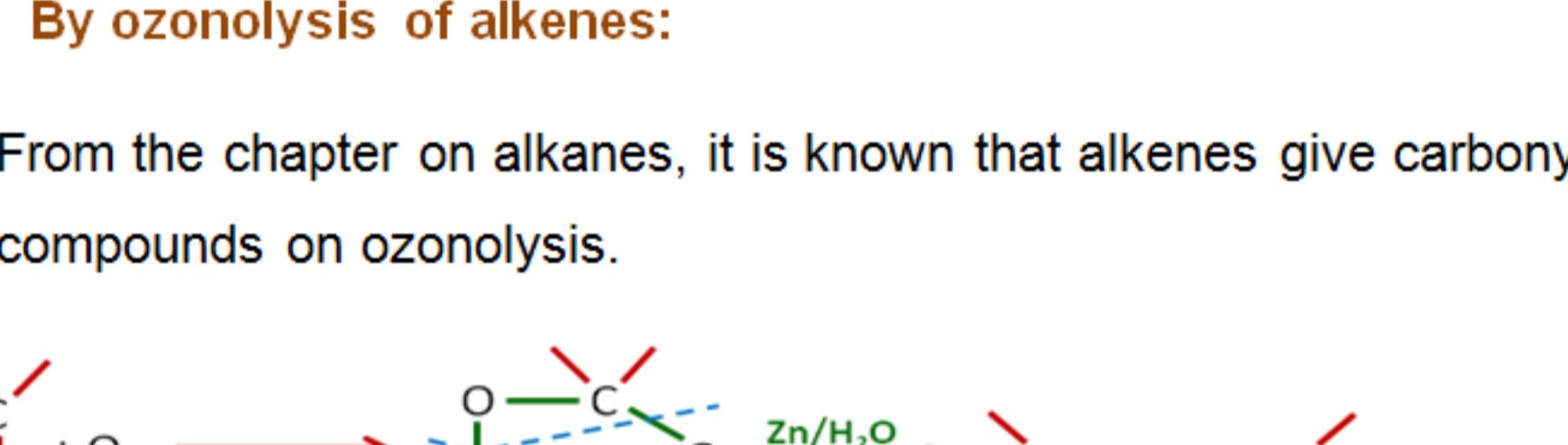
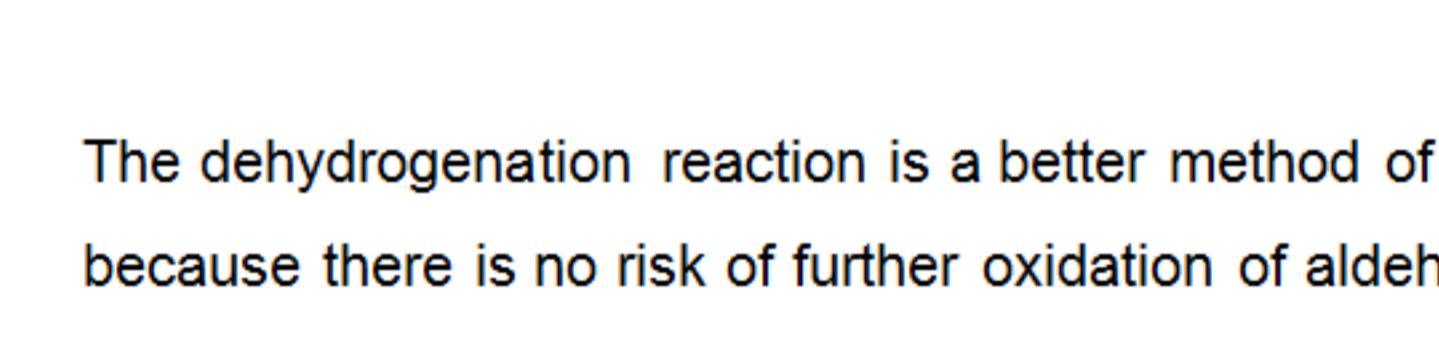
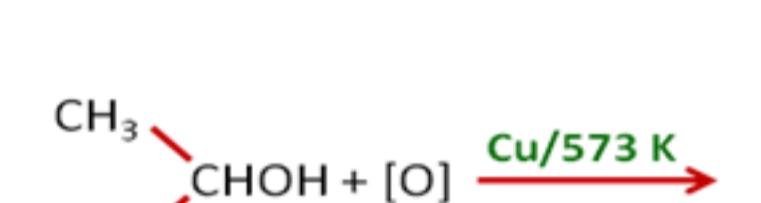


Similarly benzonitrile gives benzaldehyde.

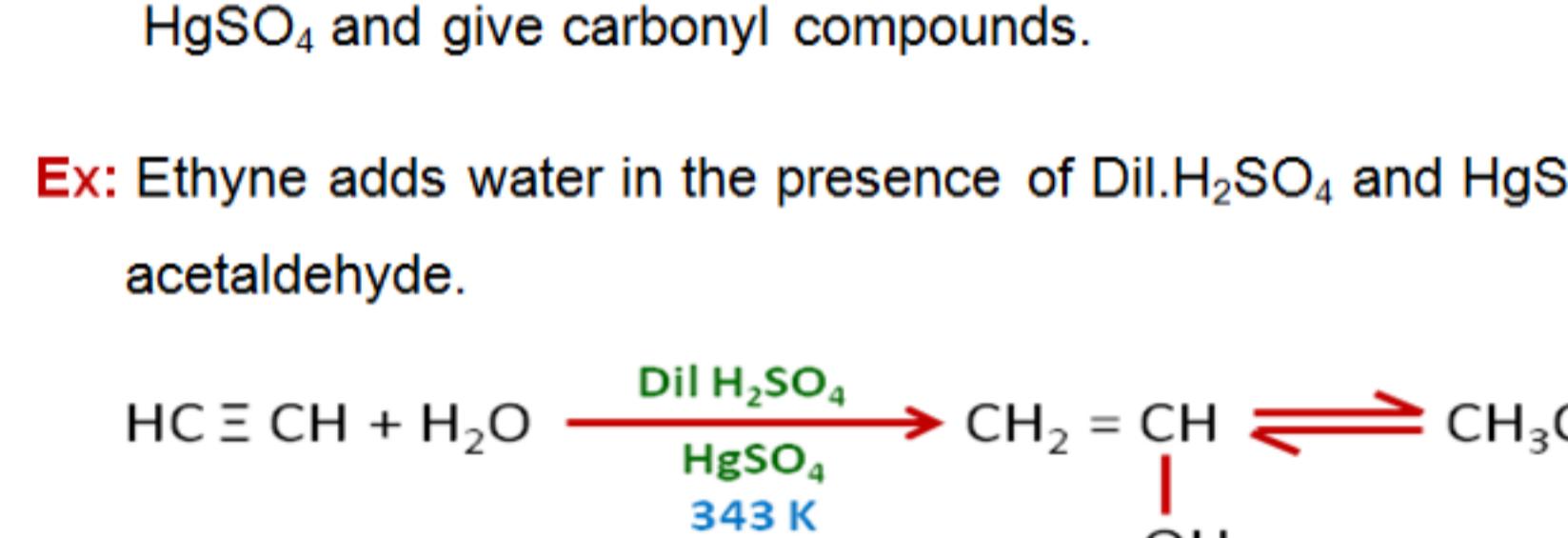
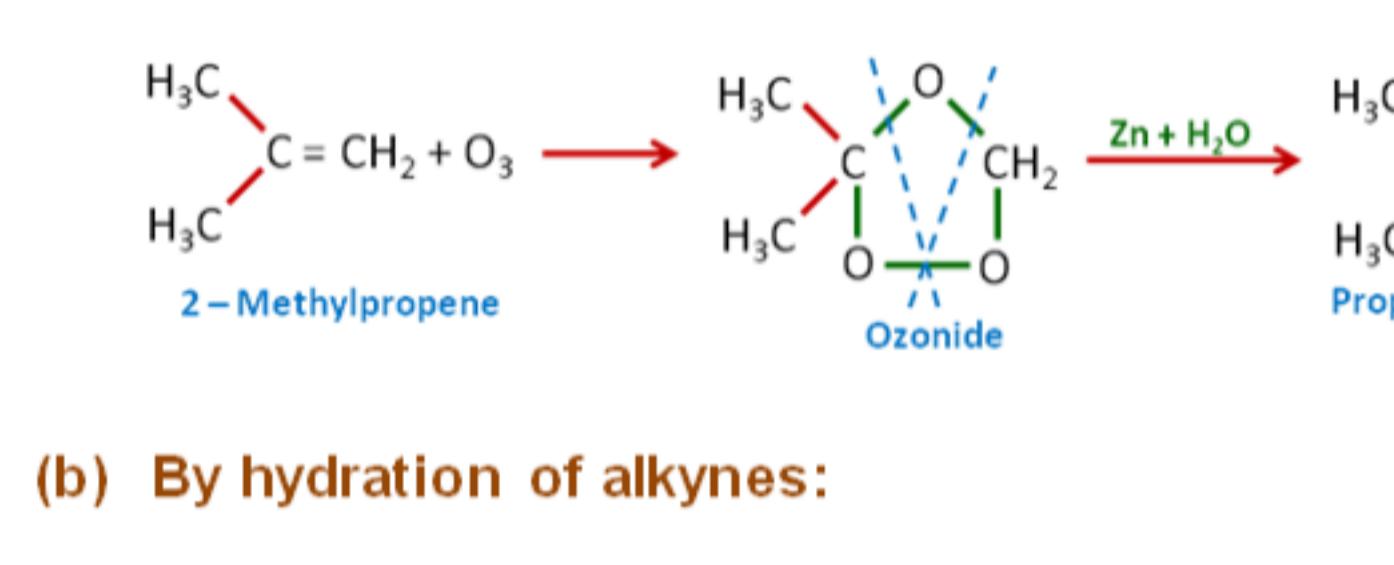


#### (d) From Acid Chlorides:

Aldehydes are prepared from acid chlorides by reaction with  $\text{H}_2$  in the presence of palladium catalyst supported on barium sulphate. The catalyst is poisoned by addition of sulphur or quinoline. The poisoning is done to avoid the further reduction of aldehydes to alcohols. This reaction is called Rosenmund's reaction.



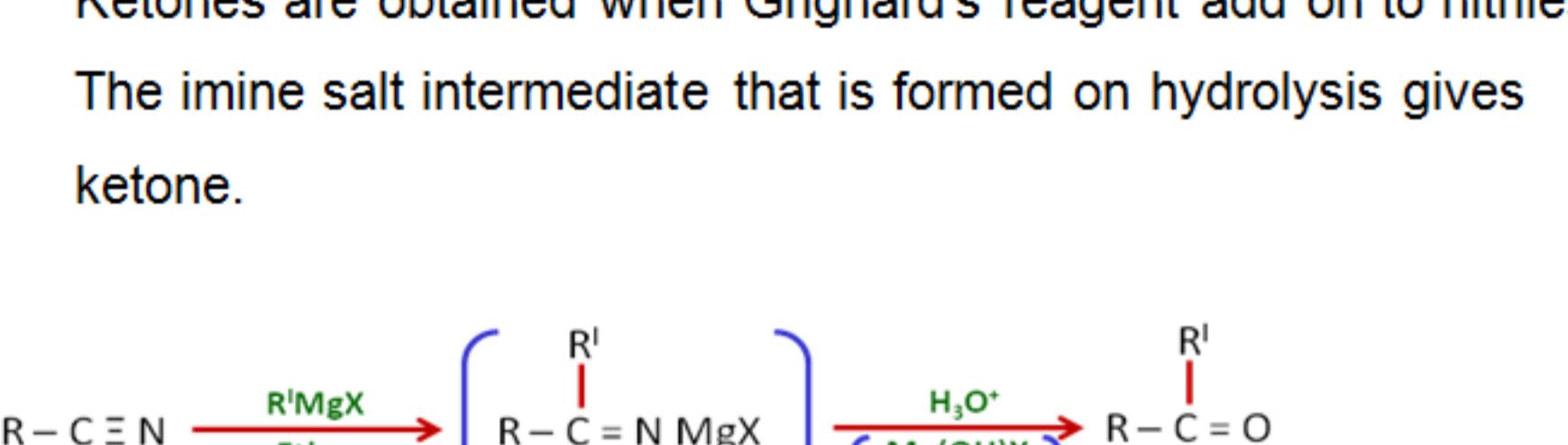
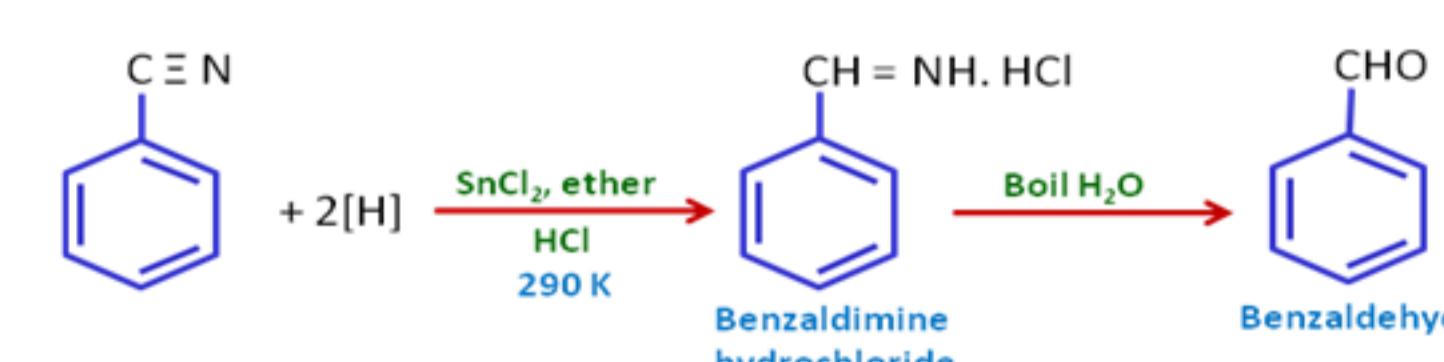
Ketones are obtained when Grignard's reagent add on to nitriles. The imine salt intermediate that is formed on hydrolysis gives ketone.



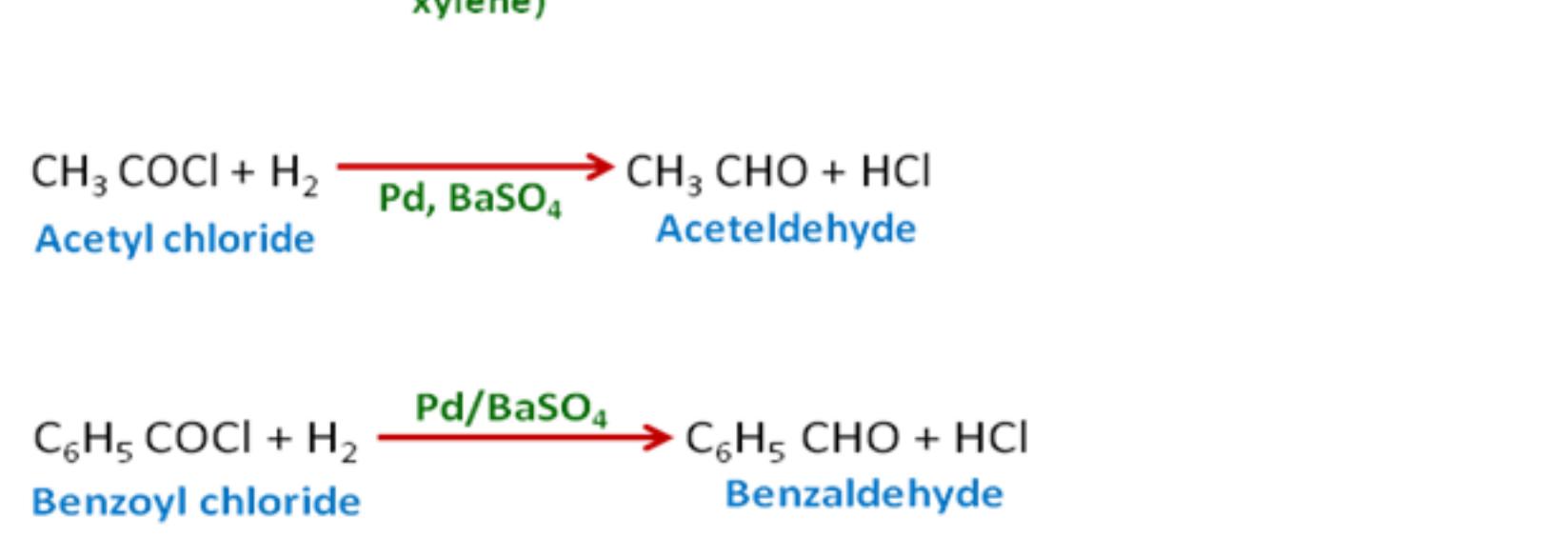
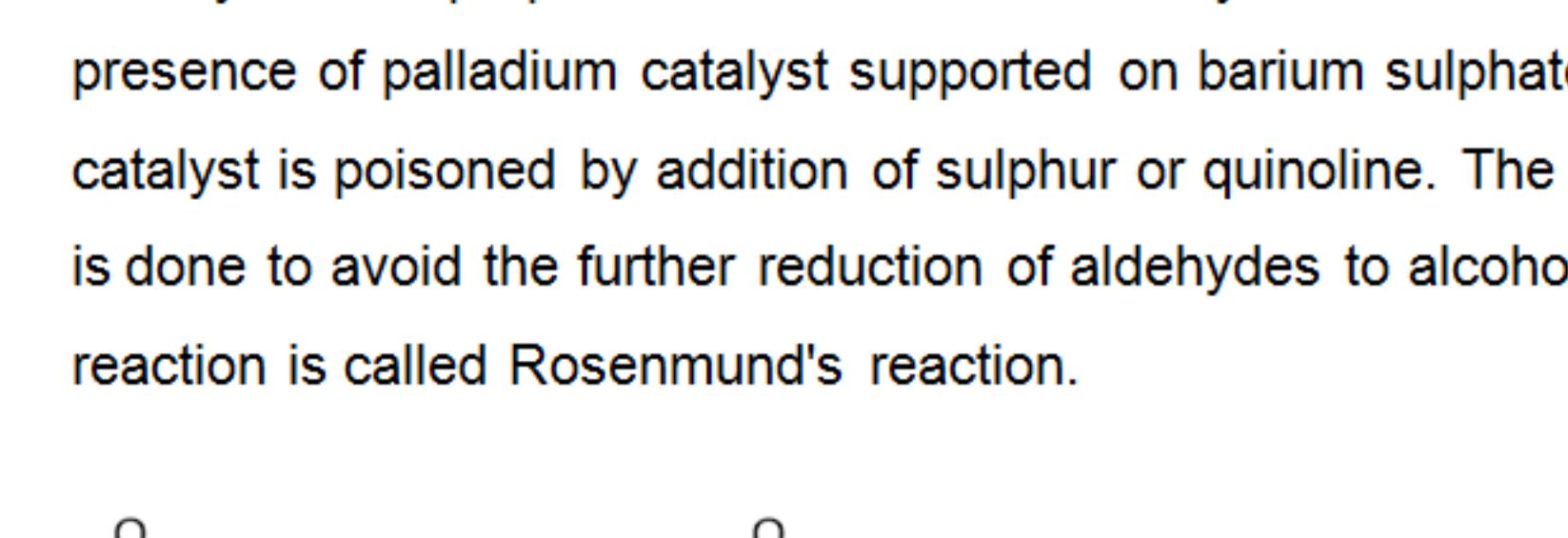
#### (e) From Nitriles:

Alkyl cyanides are known as nitriles ( $\text{R.CN}$ )

Partial reduction of nitriles with acidified stannous chloride  $\text{SnCl}_2/\text{HCl}$  at room temperature gives aldehydes. In the first step imine hydrochloride is obtained which on subsequent hydrolysis with boiled water gives aldehyde. This specific type of reduction of nitriles is called Stephen's reduction.



Ketones are obtained when Grignard's reagent add on to nitriles. The imine salt intermediate that is formed on hydrolysis gives ketone.



#### (f) From Acid Chlorides:

Aldehydes are prepared from acid chlorides by reaction with  $\text{H}_2$  in the presence of palladium catalyst supported on barium sulphate. The catalyst is poisoned by addition of sulphur or quinoline. The poisoning is done to avoid the further reduction of aldehydes to alcohols. This reaction is called Rosenmund's reaction.

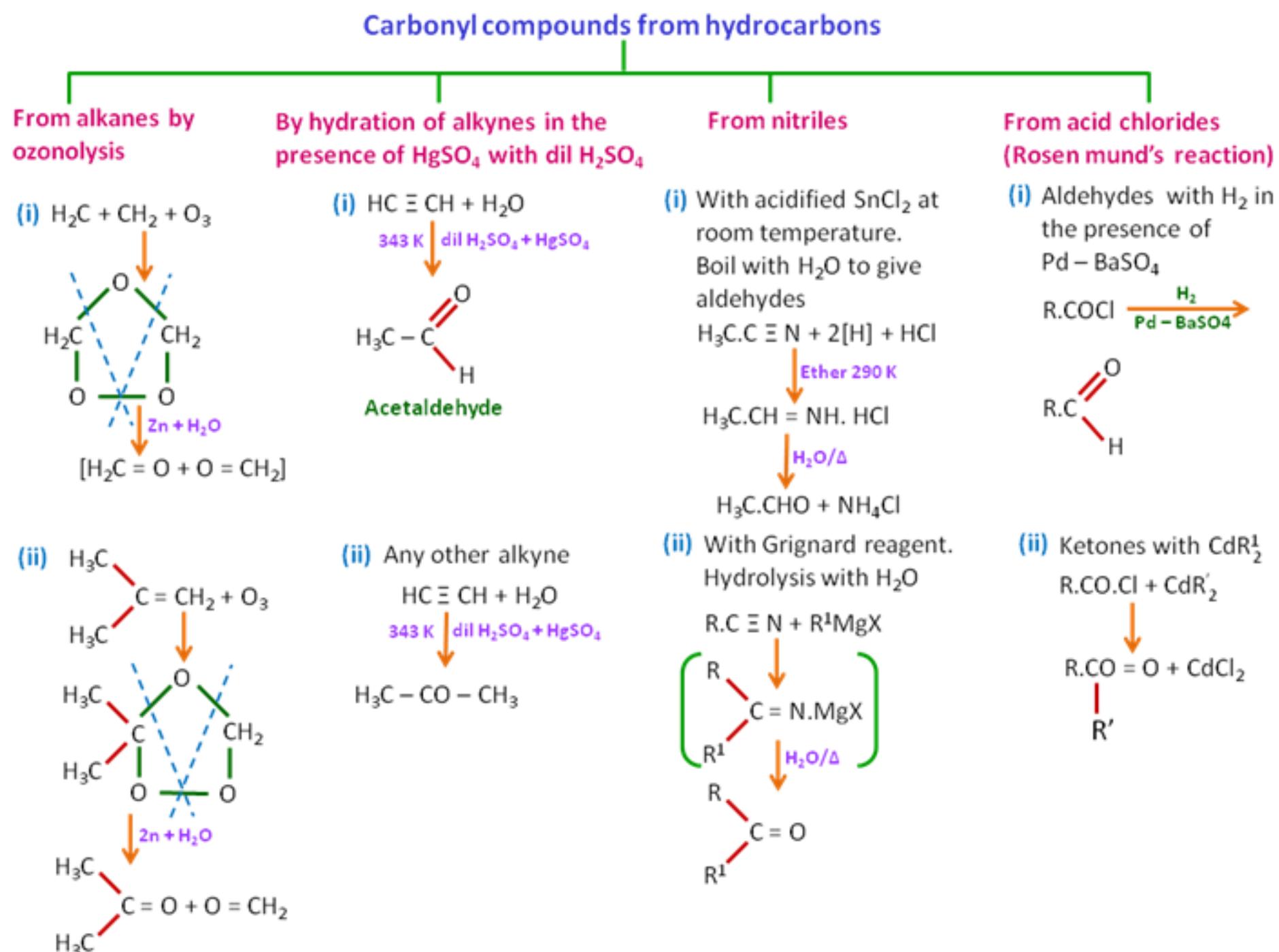


Ketones cannot be obtained by Rosenmund's reaction.

Ketones are obtained by reacting acid chlorides with dialkyl cadmium.



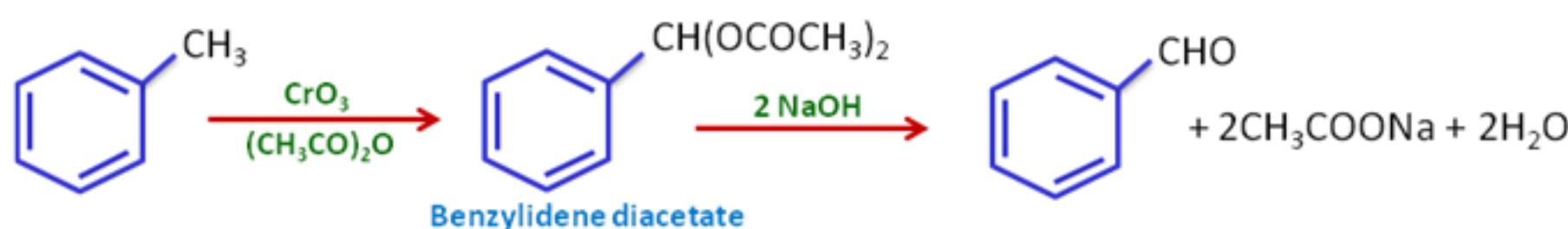
## Structure of carboxyl compounds:



#### 4. Aromatic aldehydes from aromatic hydrocarbons:

##### (a) By oxidation of methylbenzenes:

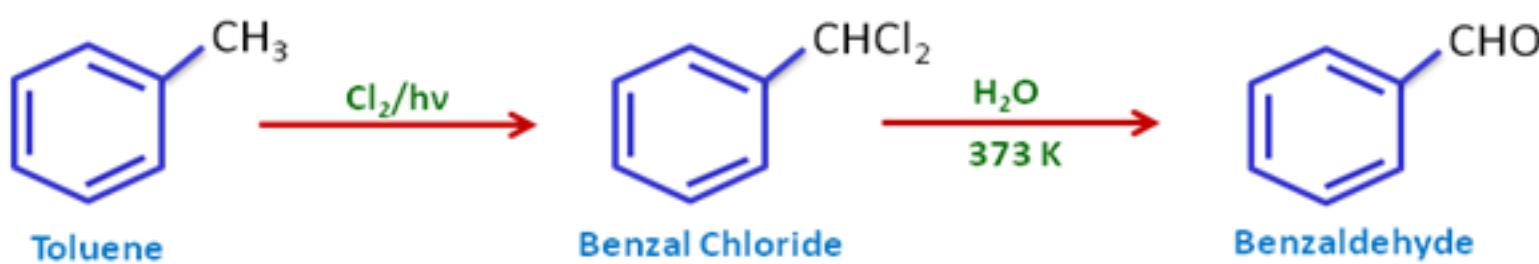
Oxidation of an aromatic compound having a methyl group on the benzene ring with  $\text{CrO}_3$  in the presence of acetic anhydride followed by hydrolysis gives the corresponding benzaldehyde.



Further oxidation of the benzaldehyde to benzoic acid is prevented as the aldehyde forms a non-oxidisable benzylidene diacetate derivative. This reaction is called the Etard reaction.

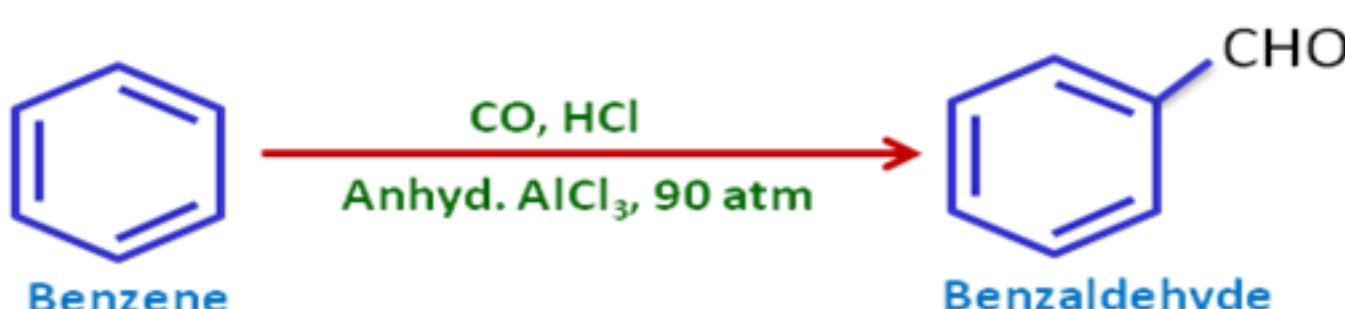
##### (b) By side chain chlorination followed by hydrolysis:

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



##### (c) By Gattermann – Koch reaction:

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



## Physical Properties:

### (a) Physical state:

Lower aldehydes are either gases or low boiling liquids. Other aldehydes and ketones are liquids or solids at room temperature.

Lower aldehydes have sharp pungent odors. As the size of the molecule increases, the odor becomes less pungent and more fragrant.

Lower ketones are colorless liquids and have pleasant smell. The higher members are colorless solids. Aromatic ketones are usually solids with a pleasant smell.

### (b) Boiling points:

Aldehydes and Ketones have relatively high boiling point as compared to hydrocarbons of comparable molecular masses. This is because the aldehydes and ketones contain polar carbonyl group and therefore have stronger intermolecular dipole - dipole interactions between the opposite ends of C=O dipoles.

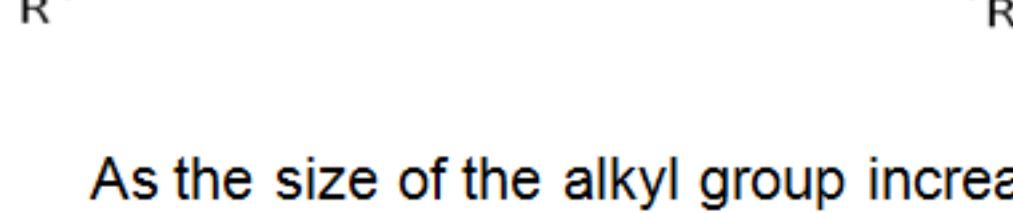
However, their boiling points are lower than those of alcohols of comparable molecular masses because unlike alcohols, they cannot form intermolecular hydrogen bonds.

Name of the compound	b.pt.(K)	Molar Mass
n – Butane	273	58
Propanal	322	58
Acetone	329	58
Propan – I – ol	370	60

Ketones are relatively more polar than their corresponding isomeric aldehydes due to the presence of two electrons repelling alkyl groups around the carbonyl carbon. Thus boiling points of ketones are slightly higher than those of isomeric aldehydes.

### (c) Solubility:

Lower members of aldehydes and ketones (methanal, ethanal, propanone) are completely miscible with water because they form hydrogen bonds with water.



As the size of the alkyl group increases the solubility decreases rapidly. It is because of the increase in the magnitude of non polar part in the molecule. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.

# Aldehydes, Ketones and Carboxylic acids

## Module 34.2: Chemical properties of Carbonylcompounds

The reactions with acetaldehyde and acetone are given as examples. All other aldehydes and ketones give similar reactions. Aldehydes and ketones are highly reactive compounds. They undergo similar reactions because of the presence of a carbonyl group in both of them.

### i. OxidationReactions:

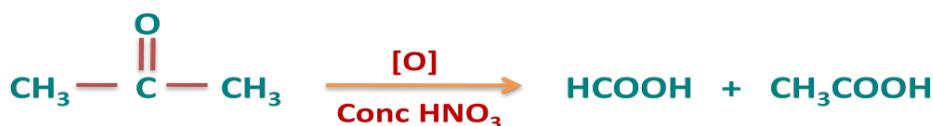
Aldehydes differ from ketones in their oxidation reactions. Aldehydes are oxidized to carboxylic acids on treatment with common oxidizing agents like nitric acid, potassium permanganate, potassium dichromate etc.

Aldehydes are easily oxidizing to carboxylic acids containing the same number of carbon atoms, as in parent aldehyde.



Even weak oxidizing agents like  $\text{Br}_2/\text{H}_2\text{O}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  etc. are effective. As a result aldehydes act as strong reducing agents.

Ketones are not easily oxidized. Under various conditions, their oxidation involves carbon-carbon bond cleavage giving a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.



These oxidation reactions can be used to distinguish aldehydes from ketones.

### a. Tollen's test:

Aldehydes give the Tollen's test. On warming of an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's reagent) in a clean test tube in a water bath; a bright silver mirror is produced due to deposition of silver metal on the sides of the test tube. The reaction occurs in alkaline medium.

Ketones do not respond to this test.



### b. Fehling's test:

Fehling's solution is an alkaline solution of copper sulphate containing sodium potassium tartrate (Rochelle salt) as a complexing agent. Aldehydes on warming with solution, give a red precipitate of cuprous oxide as a result of the redox reaction. Aromatic aldehydes give very poor result in this test.



Ketones do not reduce Fehling solution.

### c. Oxidation of ketones:

Ketones get oxidized only with strong oxidizing reagents like potassium dichromate but not with mild oxidizing agents like  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  etc. Oxidation of ketones involves carbon – carbon bond cleavage. The carboxylic acid formed contains less number of carbon atoms than those in ketone.



#### d. Haloform reaction:

Aldehydes and ketones containing the group “ $\text{CH}_3\text{CO}-$ ”, form iodoform when treated with  $\text{I}_2$  in alkali.



#### ii. Reduction Reactions:

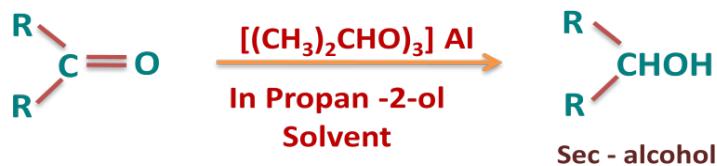
Aldehydes and ketones can be reduced to a variety of compounds under suitable conditions with different reducing agents.

##### a. Reduction to alcohols:

Aldehydes and ketones on mild reduction give their corresponding primary or secondary alcohols respectively. This type of reduction is carried out either catalytically with  $\text{H}_2$  in the presence of Ni, Pt or Pd or chemically by  $\text{LiAlH}_4$  (Lithium Aluminum Hydride) or  $\text{NaBH}_4$  (Sodium borohydride).



Ketones can be reduced to secondary alcohols with aluminum isopropoxide in propane-2-ol solution.

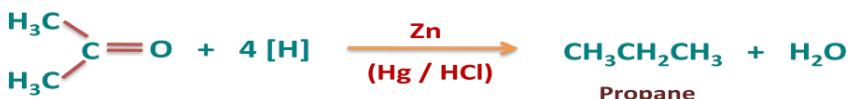


This reaction is called **Meerwein-Ponndorf-Verley reduction**.

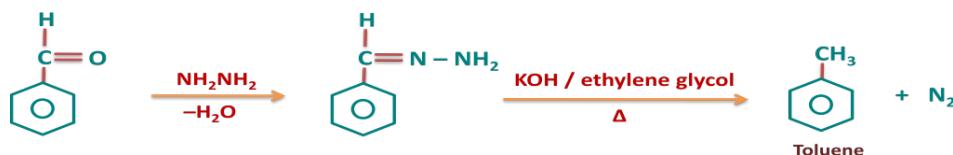
### b. Reduction to hydrocarbon:

The carbonyl group ( $\text{C}=\text{O}$ ) can be reduced to methylene ( $\text{CH}_2$ ) group resulting in the formation of alkanes by any of the following reagents.

- i. Zinc amalgam and concentrated hydrochloric acid reduce and the reaction is called **Clemmensen reduction**.



- ii. Wolff-Kishner reduction use hydrazine followed by heating with  $\text{NaOC}_2\text{H}_5$  (highly boiling point).



### iii. Addition reactions:

#### a. Addition of hydrogencyanide:

Addition of hydrogen cyanide to aldehydes and ketones give  **$\alpha$ -cyanoalcohols**, usually called **Cyanohydrins**. This reaction is carried out in the presence of a base catalyst.

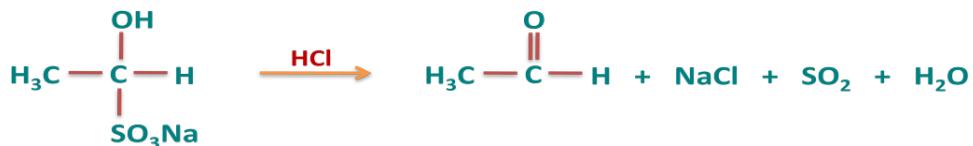


### b. Addition of sodium bisulphite:

When an aldehyde or a ketone is treated with a saturated solution of sodium bisulphite, many aldehydes form crystalline solids.

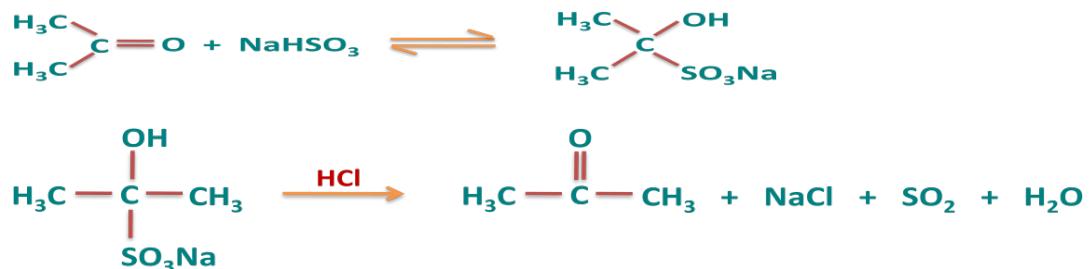


The bisulphite addition compound can be decomposed with dilute acids or bases to regenerate the original carbonyl compound.



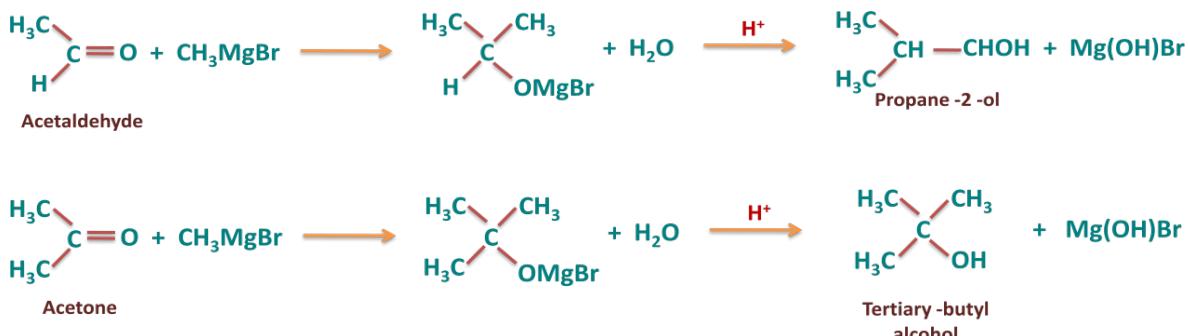
Therefore, the formation and decomposition of bisulphite addition compounds is used for the purification and separation of carbonyl compounds from the mixture.

Normally  $\text{CH}_2\text{O}$  ( $\text{HCHO}$ ) exists as a polymer. The monomer of  $\text{HCHO}$  can be separated by this method.



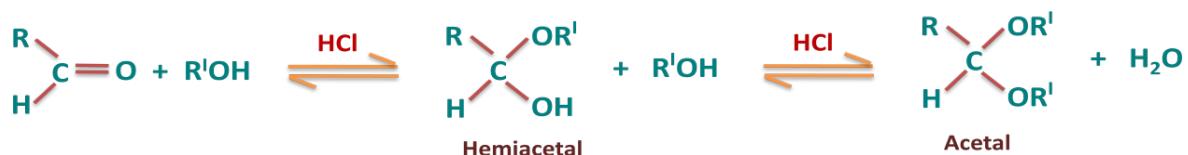
### c. Addition of Grignard's reagent:

Grignard reagents add on Aldehydes and ketones to form addition products these compounds on acidic hydrolysis yield alcohols.

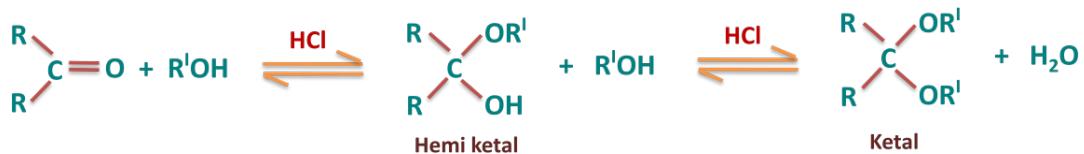


### d. Addition of alcohols:

Aldehydes react with alcohols in the presence of an acid (usually HCl) to form **Hemiacetals**. Hemiacetals are unstable and react with molecules of alcohols to form **acetals**.



Similarly, ketones react with alcohols in presence of HCl to form **Hemiketals** and **ketals**.

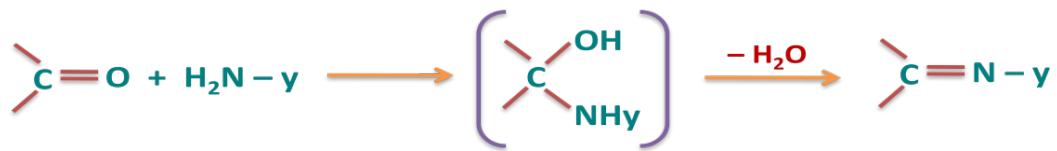


### e. Addition of $\text{H}_2\text{N}-y$ type compounds:

Acetaldehyde and acetone react with compounds of general formula  $\text{H}_2\text{N}-\text{X}$ . Here  $y = -\text{H}, -\text{OH}, -\text{NH}_2, -\text{NHC}_6\text{H}_5, -\text{NHCONH}_2, -\text{NHC}_6\text{H}_3(\text{NO}_2)_2$ .

These are derivatives of ammonia.

The general reaction with these compounds is written as

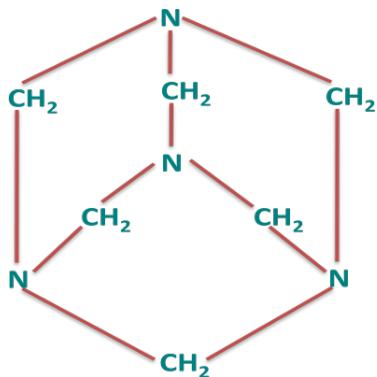


### i. Addition of Ammonia:

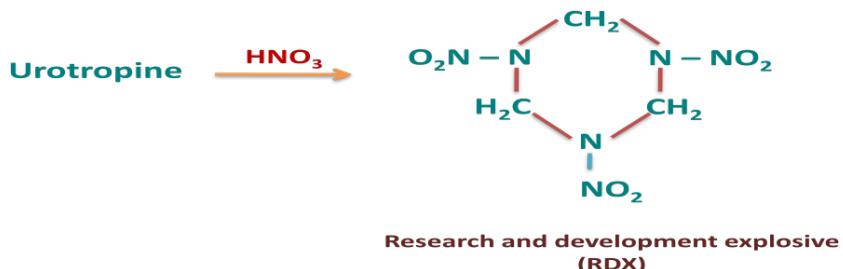
Formaldehyde reacts with ammonia to give **hexamethylenetetramine (Urotropine)**. It is a medicine for urinary infection.



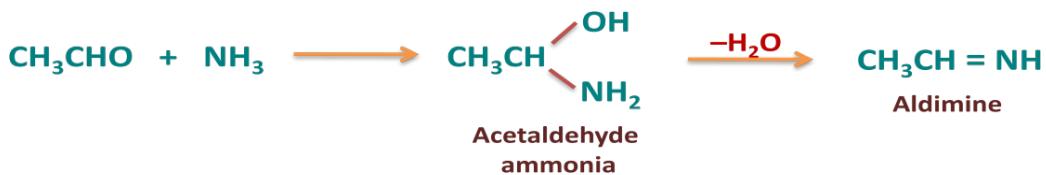
Its structure is



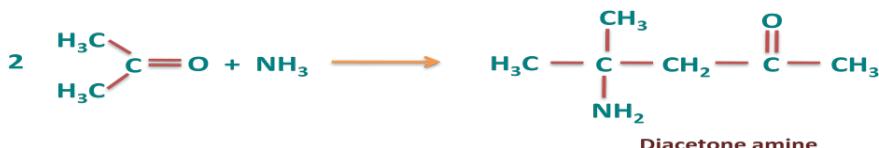
Nitration of Urotropine under controlled conditions gives a well known explosive (**RDX**)



Aldehydes react with ammonia to form **aldehyde ammonia**, which is unstable and loses water at once to form aldimine.

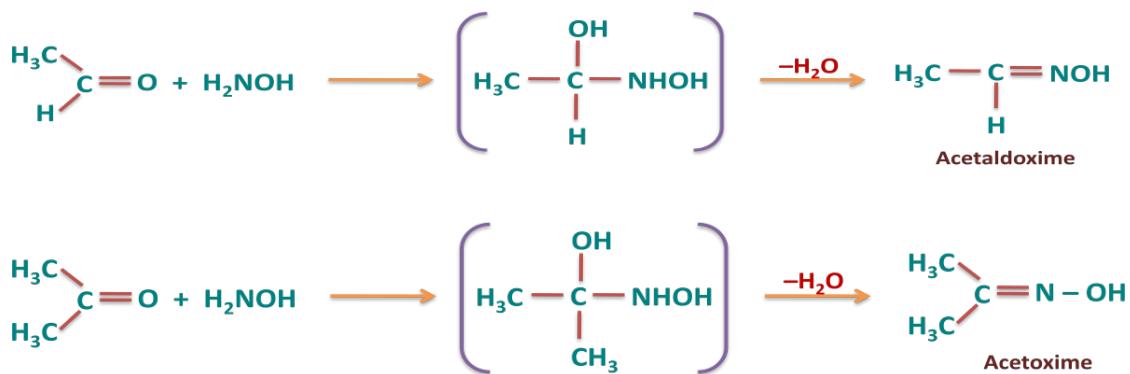


Acetone reacts with ammonia to form Diacetone amine.



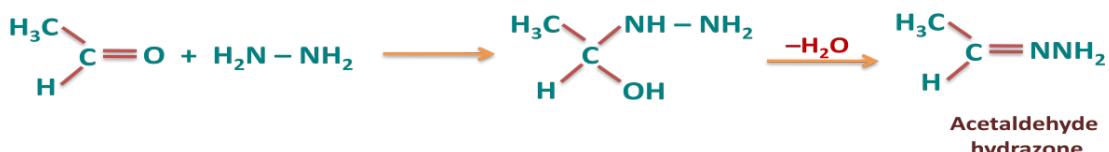
### ii. With hydroxylamine:

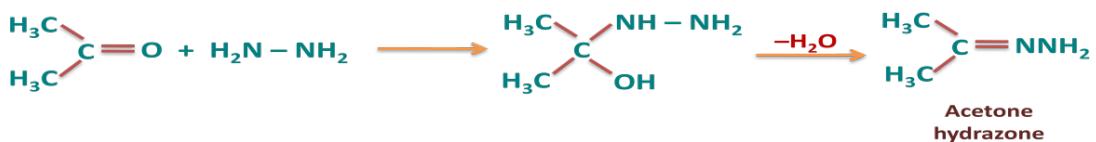
Aldehydes and ketones react with hydroxylamine to form corresponding oximes.



### iii. With hydrazine:

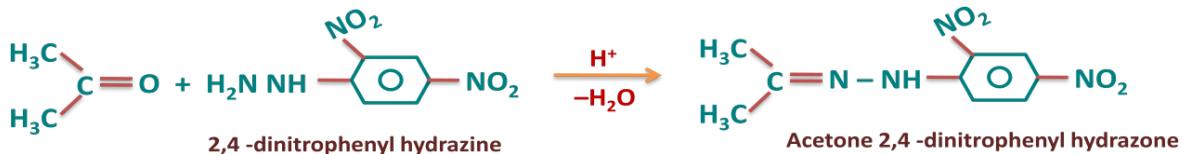
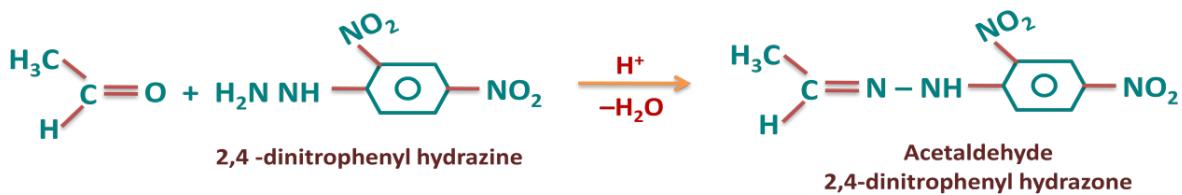
Aldehydes and ketones react with hydrazine to form the corresponding aldehyde hydrazones and ketone hydrazones.





#### iv. With 2, 4-dinitrophenylhydrazine:

Aldehydes and ketones react with 2, 4-dinitro phenyl hydrazine's commonly known as DNP or Brady's reagent. 2, 4-DNP hydrazones are yellow or orange or red solids useful for characterization of aldehydes and ketones.



#### Self check questions:

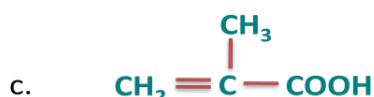
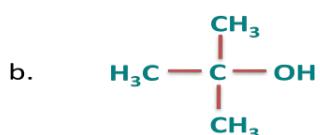
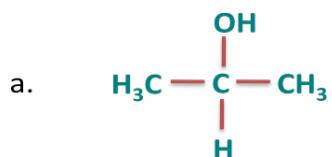
- The reducing agent in Clemmensen reduction is
  - $\text{Zn-Hg} / \text{Conc. HCl}$
  - $\text{LiAlH}_4$
  - $\text{Pd/BaSO}_4$
  - $\text{PdCl}_2/\text{CuCl}_2$

**Solution:** a)

- The reduction of  $\text{C=O}$  to  $-\text{CH}_2-$  using  $\text{NH}_2\text{NH}_2$  and  $\text{NaOC}_2\text{H}_5$  is known as
  - Wolff-Kishner reduction
  - Clemmensen reduction
  - Birch reduction
  - Reimer-Tiemann reaction

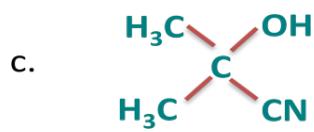
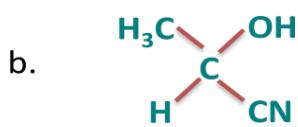
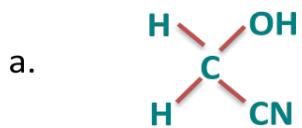
**Solution:** a)

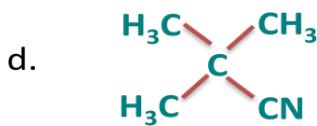
3. Identify the compound X in the following sequences.



**Solution:** b)

4. When the  $\text{CH}_3\text{CHO}$  treated with  $\text{NaCN}$  and dil. $\text{H}_2\text{SO}_4$ , addition of  $\text{HCN}$  on carbonyl group produces





**Solution:** b)

5. Which compound gives a positive haloform test and a positive Fehling's solution test?
  - a. Acetone
  - b. Acetaldehyde
  - c. Ethanol
  - d. Formaldehyde

**Solution:** b)

6. The reaction of acetaldehyde with Tollen's reagent gives
  - a. Methyl alcohol
  - b. Acetic acid
  - c. Silver mirror
  - d. Formaldehyde

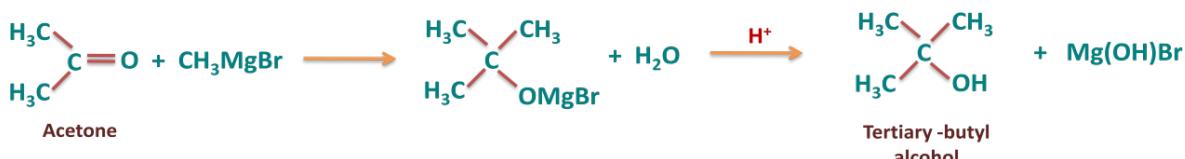
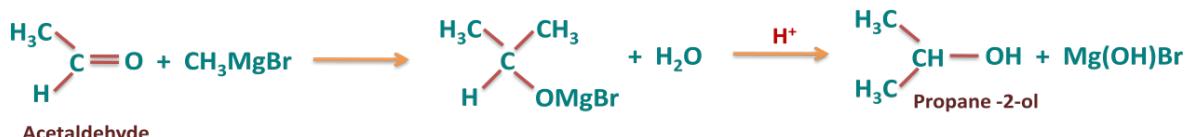
**Solution:** c)

7. What are the products obtained when
  - i. An Aldehyde and
  - ii. Acetone  
are treated with Grignard's reagent ?

**Solution:**

#### Addition of Grignard's reagent:

Addition of Grignard reagent on aldehydes and ketones produces addition products, these compounds on acidic hydrolysis yield alcohols.



8. Write the reaction of Tollen's reagent with  $\text{CH}_3\text{CHO}$ .

**Solution:**

**Tollen's test:**

Aldehydes give the Tollen's test on warming an aldehyde with freshly prepared ammonical silver nitrate solution (Tollen's reagent) in a clean test tube in a water bath, a bright silver mirror is produced due to deposition of silver metal on the sides of the test tube. The reaction occurs in alkaline medium.

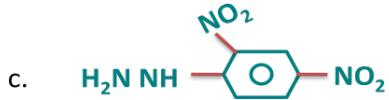
Ketones do not respond to this test.



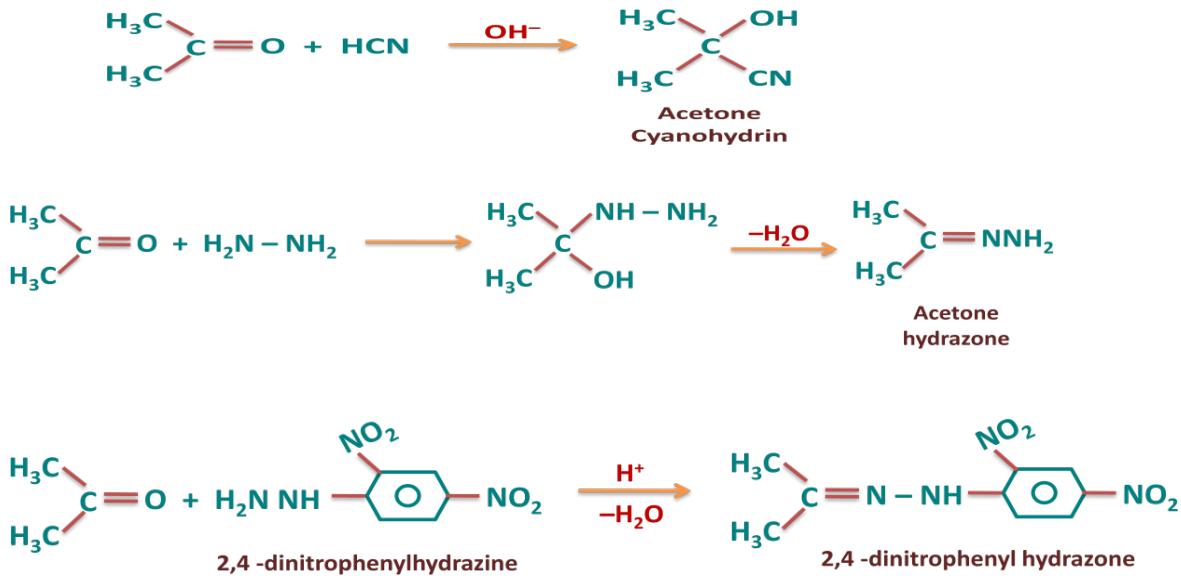
9. How does acetone react with

a. **HCN**

b.  **$\text{H}_2\text{N}-\text{NH}_2$**



**Solution:**



**Problem set:**

1. Fehling's solution gives a precipitate with H<sub>3</sub>CCHO, Then the precipitate is \_\_\_\_\_ in colour
- White
  - Green
  - Red
  - Blue

**Solution:** c)

2.



Identify B and C in the above sequences of reactions.

- a. B=Ethylene; C = Ethyleneglycol
- b. B=Acetylene; C = Oxalicacid
- c. B=Ethanol; C = Aceticacid
- d. B=2-Propanol; C =Acetone

**Solution:** a)

3. In the following reaction X is \_\_\_\_\_



- a. HCHO
- b. CH<sub>3</sub>CHO
- c. CH<sub>3</sub>COCH<sub>3</sub>
- d. All the above

**Solution:** c)

4. C<sub>2</sub>H<sub>5</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> can be distinguish by testing with

- a. Phenyl hydrazine
- b. Hydroxylamine
- c. Fehlingsolution
- d. Sodiumbisulphite

**Solution:** c)

5.



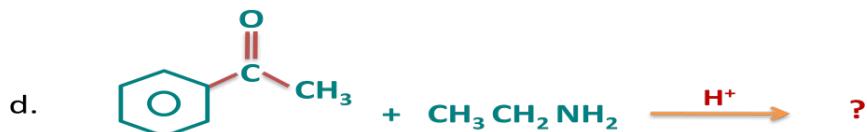
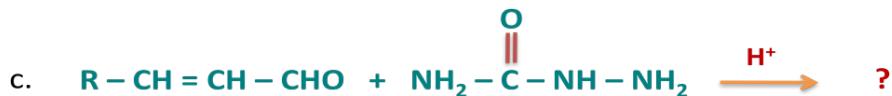
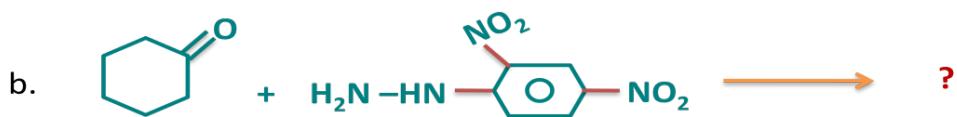
A and B are

- a. Positionisomers

- b. Chainisomers
- c. Tautomers
- d. Homomers

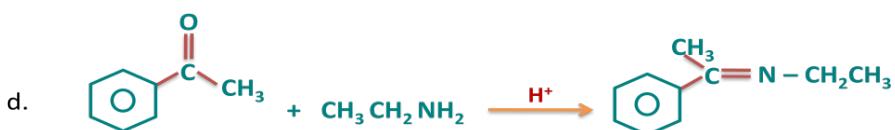
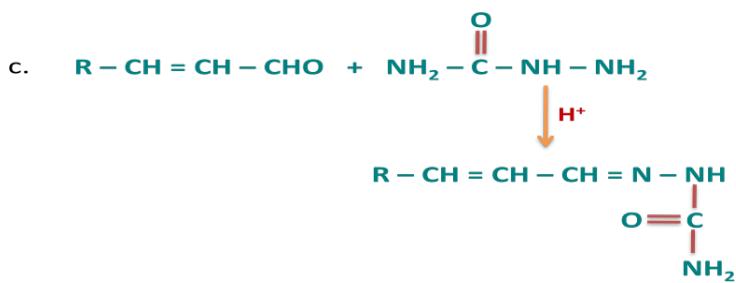
**Solution:** d)

6. Predict the products of the following reactions:

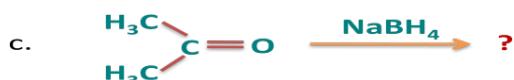
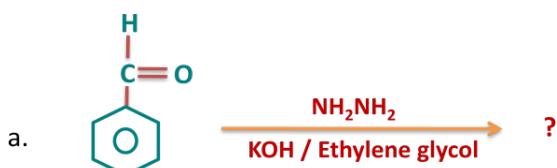


**Solution:**

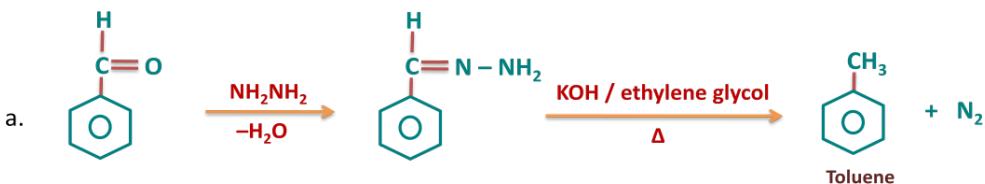




7. Complete the following reactions



**Solution:**

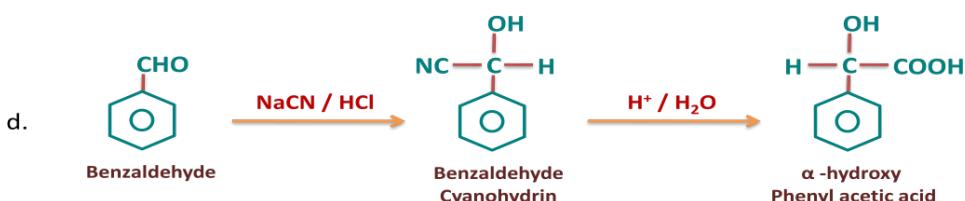
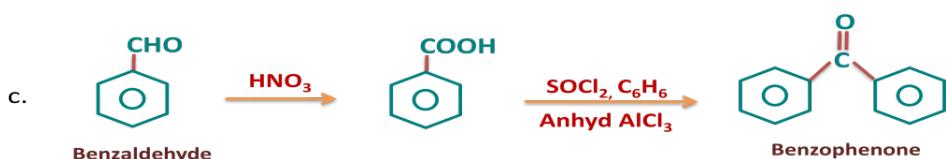
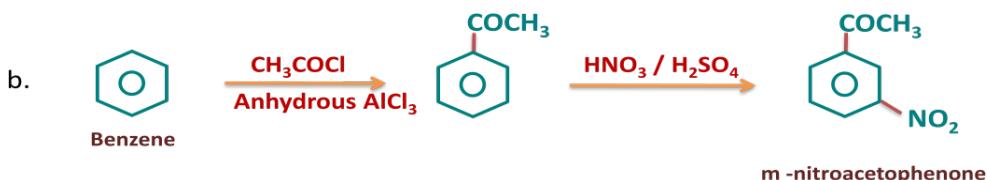
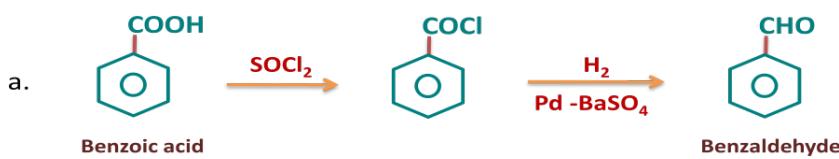




8. How will you bring about the following conversions in not more than two steps?

- Benzoic acid to Benzaldehyde
- Benzene to m-nitroacetophenone
- Benzaldehyde to Benzophenone
- Benzaldehyde to  $\alpha$ -hydroxyphenyl acetic acid.

**Solution:**



### Exercise questions:

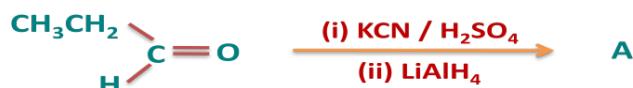
1. Complete the following reaction.



2. How will you convert butan-2-one to propanoic acid?

3. A ketone A, which undergoes haloform reaction, gives the compound B on reduction. B on heating with conc.  $\text{H}_2\text{SO}_4$  gives compound C, which forms mono-ozonide D. D on hydrolysis in the presence of zinc dust gives only acetaldehyde. Identify A, B and C. write down the reactions involved.

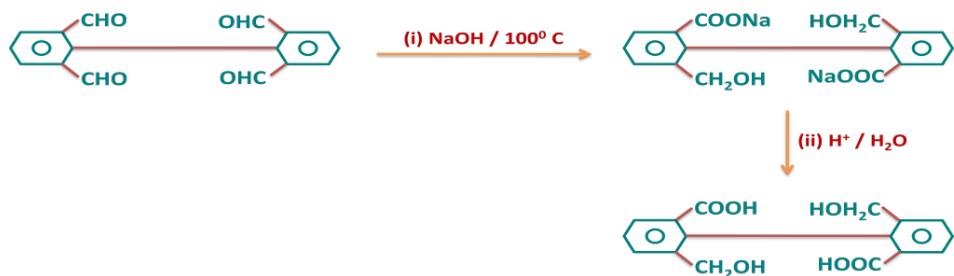
4. Complete the following reaction with appropriate structure.



5. Write the structure of the major organic product expected from the following reaction.

### Solutions:

1.



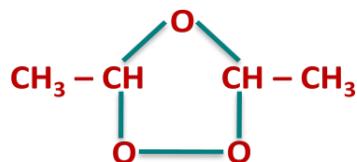
The above reaction is based on Cannizaro reaction.

2. Oxidation:





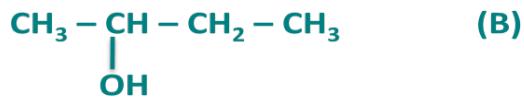
3. Ketone A undergoes haloform reaction, thus, it must contain  $\text{H}_3\text{CCO}^-$  group. The product (Acetaldehyde) is obtained on hydrolysis in the presence of Zn-dust, the compound D would be as follows



The compound C gives mono-ozonide D, which shows that the compound C contains a multiple bond. Since, the hydrolysis of D gives only acetaldehyde, the compound C would be as follows; It contains doublebond.



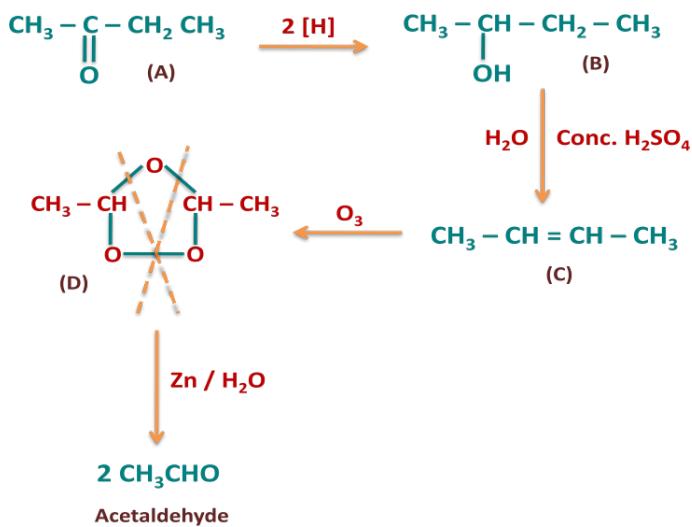
The compound C is obtained by dehydration of the compound B. Hence, the compound B would be



The compound B is obtained by the reduction of compound A (which contains  $\text{CH}_3\text{CO}^-$  group). Hence, the compound A would be;



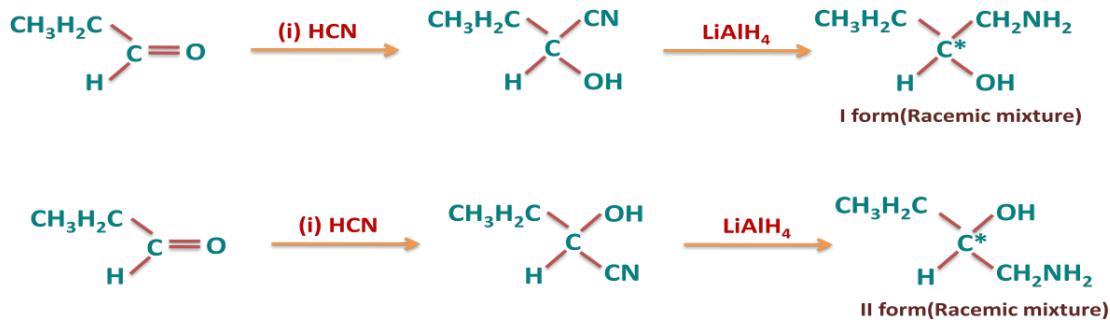
The reaction involved is as follows;



4. In the above equation



This HCN gives addition reaction on  $\text{C=O}$  group as follows



5.



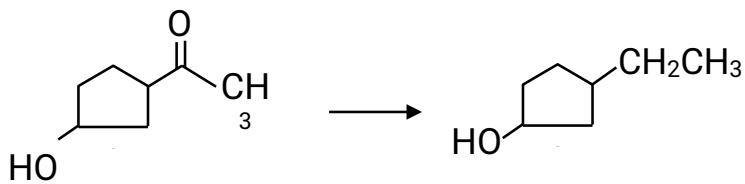
(It is crossed Cannizaro reaction.)

### IIT Questions:

1. The compound that will not give iodoform on treatment with alkali and iodine is
  - a) acetone
  - (b) ethanol
  - (c) diethyl ketone
  - (d) isopropylalcohol
2. The enol form of acetone, after treatment with D<sub>2</sub>O, gives



3. The formation of oximes and other ammonia derivative requires slightly \_\_\_\_\_ media for maximum rate.
4. When acetaldehyde is heated with Fehling's solution, it gives a precipitate of:
  - a. Cu
  - b. CuO
  - c. Cu<sub>2</sub>O
  - d. Cu + Cu<sub>2</sub>O + CuO
5. Which of the following will react with water?
  - a. CHCl<sub>3</sub>
  - b. Cl<sub>3</sub>C.CHO
  - c. CCl<sub>4</sub>
  - d. ClCH<sub>2</sub>CH<sub>2</sub>Cl
6. The appropriate reagent for the following transformation:



- a. Zn(Hg), HCl
- b. NH<sub>2</sub>NH<sub>2</sub>, OH<sup>-</sup>
- c. H<sub>2</sub>/Ni
- d. NaBH<sub>4</sub>

7. Compound A (molecular formula  $C_3H_8O$ ) is treated with acidified potassium dichromate to form a product B (molecular formula  $C_3H_6O$ ). B forms a shining silver mirror on warming with ammonical silver nitrate. B when treated with an aqueous solution of  $H_2NCONHNH_2$  and sodium acetate gives a product C. Identify the structure of C.
- a.  $CH_3CH_2CH = N . NHCONH_2$
- c.  $CH_3 - \begin{matrix} C = N \\ | \\ CH_3 \end{matrix} . NHCONH_2$
- b.  $CH_3 - \begin{matrix} C = N \\ | \\ CH_3 \end{matrix} . CONHNH_2$
- d.  $CH_3CH_2CH = N . CONHNH_2$
8. How will you convert butan-2-one to propanoic acid?
- a. Tollen's reagent
- b. Fehling's solution
- c.  $NaOH/I_2/H^+$
- d.  $NaOH/NaI/H^+$
9. Which of the following compounds will give a yellow precipitate with iodine and alkali?
- a. 2-hydroxy propane
- b. Acetophenone
- c. Methyl acetate
- d. Acetamide
10. Among the following compounds, which will react with acetone to give a product containing  $> C = N -$ ?
- a.  $C_6H_5NH_2$
- b.  $(CH_3)_3N$
- c.  $C_6H_5NHC_6H_5$
- d.  $C_6H_5NHNH_2$
11. Write down the reactions involved in the preparation of the following using the reagents indicated against in parenthesis  
"Acetoxime from acetaldehyde."  
[ $K_2Cr_2O_7/ H^+$ ,  $Ca(OH)_2$  and  $NH_2OH . HCl$ ]

12. Give reasons in one or two sentences for the following:

"Hydrazones of aldehydes and ketones are not prepared in highly acidic medium".

13. How may the following transformation be carried out (in not more than six steps)?

"Benzaldehyde to cyanobenzene"

14. Answer the following with suitable equations wherever necessary:

- Suggest a reagent to distinguish acetaldehyde from acetone
- What happens when excess chlorine is passed through boiling toluene in the presence of sun-light?

15. An aldehyde *A* ( $C_{11}H_8O$ ), which does not undergo self aldol condensation, gives benzaldehyde and two moles of *B* on ozonolysis. Compound *B*, on oxidation with silver ion gives oxalic acid. Identify the compounds *A* and *B*.

### Solutions:

1. c

Diethyl ketone ( $C_2H_5COC_2H_5$ ) will not show iodoform test.

2. a

The enolic form of acetone contains active hydrogen, replaceable by deuterium.

3. acidic

In acidic medium, the carbonyl group becomes more electrophilic and reactive due to the formation  $\begin{array}{c} \text{C}^+-\text{O} \\ | \\ \text{H} \end{array}$  In more strongly acid solution of

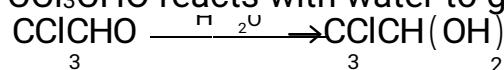
( $pH < 3.5$ ), the unshared pair of electrons of N is protonated to give electrophile  $\text{H}_3\text{NG}^+$ , a species which cannot react. In basic medium, there is no protonation of  $\text{C=O}$ .

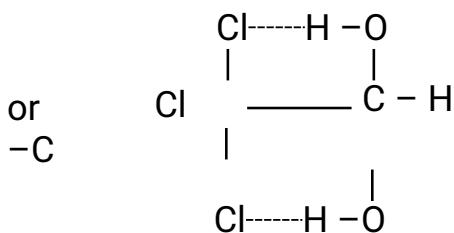
4. (c)



5. (b)

$\text{CCl}_3\text{CHO}$  reacts with water to give stable chloral monohydrate.





**Chloral monohydrate**  
(stability due to intramolecular H-bond)

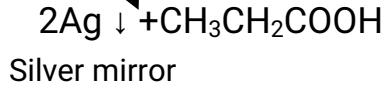
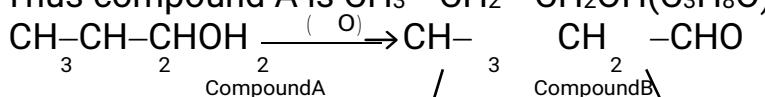
6. (b)

Wolff-kishner reagent ( $\text{NH}_2-\text{NH}_2, \text{OH}^-$ ) is preferred for reduction of  $> \text{C}=\text{O}$  group into  $- \text{CH}_2-$  to Clemmensen's reagent to avoid reduction of phenolic  $- \text{OH}$  group simultaneously.

7. (a)

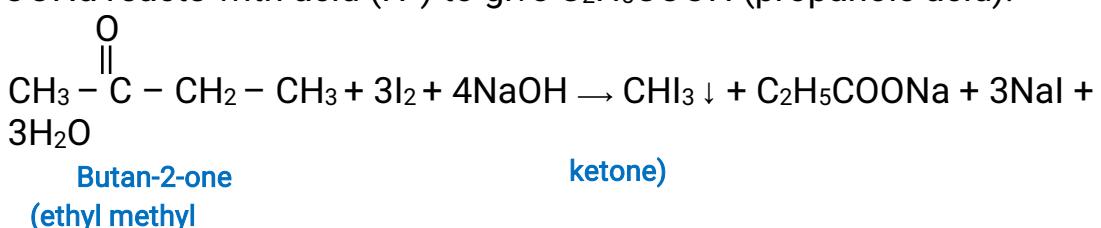
Compound A is primary alcohol because on oxidation it gives an aldehyde 'B' which form shining silver mirror with ammonical silver nitrate (Tollen's reagent)

Thus compound A is  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH} (\text{C}_3\text{H}_8\text{O})$

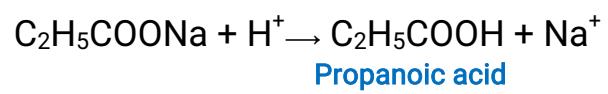


8. (a)

Tollen's reagent, Fehling solution and  $\text{NaOH}/\text{I}_2/\text{H}^+$  are not able to change butane-2-one (ketone) into propanoic acid because these are mild oxidizing agents, so  $\text{NaOH}/\text{I}_2$  firstly form iodoform along with  $\text{C}_2\text{H}_5\text{COONa}$  with butan- 2-one (ethyl methyl ketone). In these  $\text{C}_2\text{H}_5\text{COONa}$  reacts with acid ( $\text{H}^+$ ) to give  $\text{C}_2\text{H}_5\text{COOH}$  (propanoic acid).



iodoform

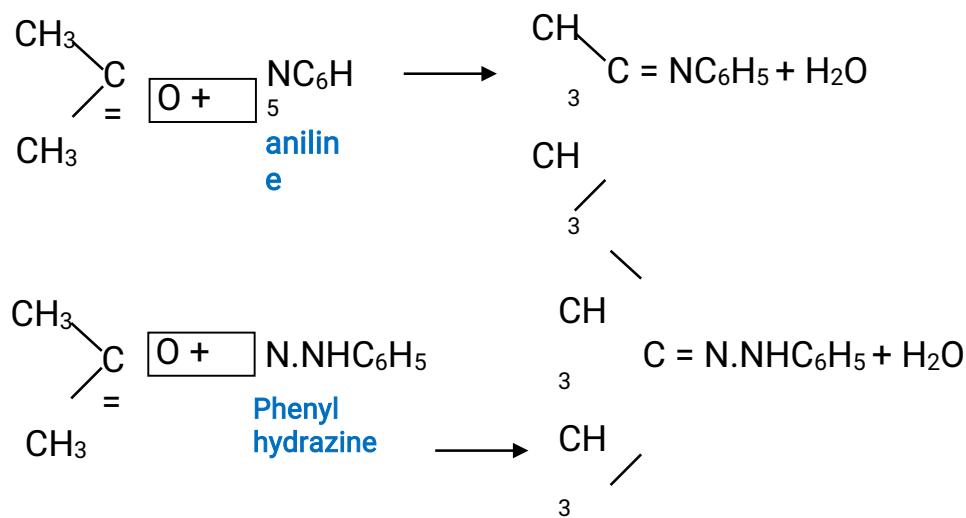


9. Both a) and b)

All alcohols having  $\text{CH}_3\text{CHOH} - \text{R}$  groups and carbonyl compounds containing  $\text{CH}_3\text{CO} - \text{R}$  group give yellow ppt. with iodine and alkali (i.e. iodoform test).

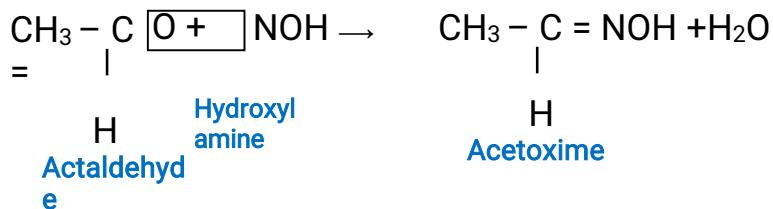
10. Both a) and d)

Carbonyl compound (acetone) forms condensation product with hydrazine, phenyl hydrazine, aniline etc.



Hence, in these reactions  $> \text{C} = \text{N}$  bonds are formed in products.

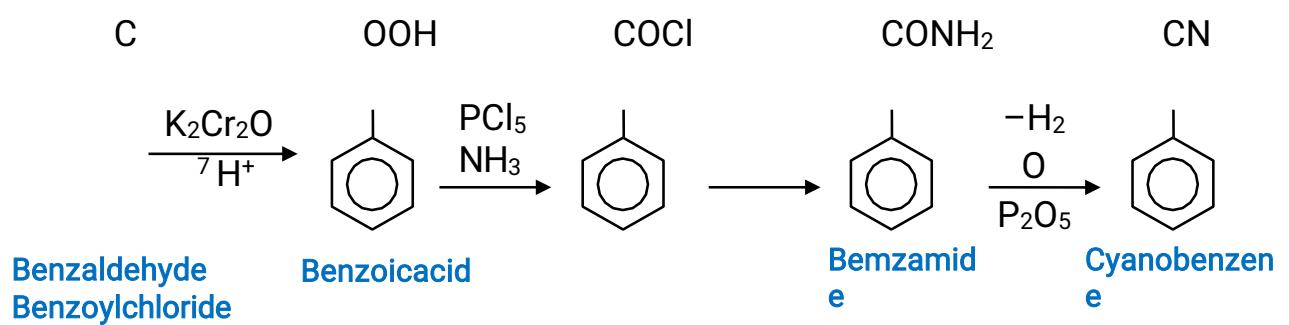
11.



12. Because in acidic medium, hydrazines get protonated and their nucleophilicity decreases.

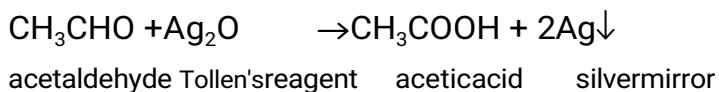
13.



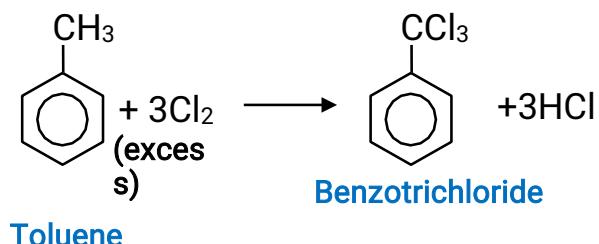


14.

- (i) **Tollen's reagent test:** Acetaldehyde reduces the Tollen's reagent to form silver mirror while acetone does not give this test.

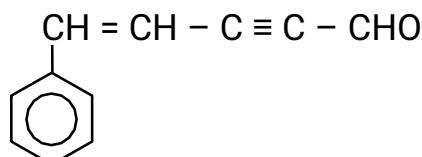


- (ii) When excess chlorine is passed through boiling toluene in the presence of sun-light, benzotrichloride is obtained.

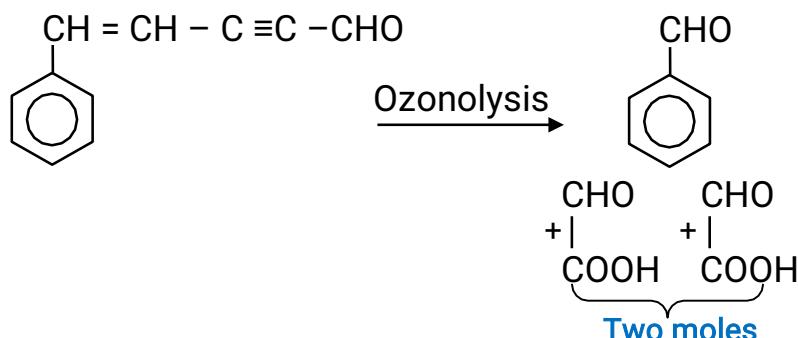


15. Aldehyde does not have  $\alpha$ -hydrogen atoms but ozonolysis to give two moles of compound *B* and benzaldehyde. Compound *B* on oxidation with  $\text{Ag}^+$

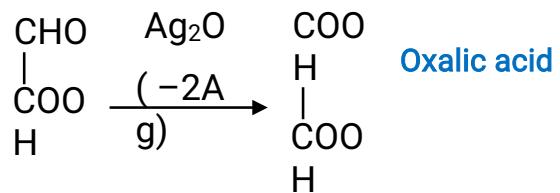
(Tollen's reagent) to give oxalic acid. So Aldehyde *A* may be



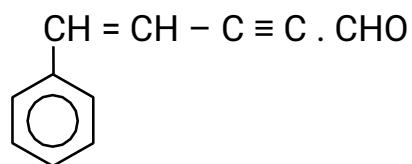
This aldehyde on ozonolysis gives following product:



(On ozonolysis  $-\text{CH} = \text{CH}-$  gives aldehyde and group  $-\text{C} \equiv \text{C}-$  gives acidic group)



Hence, compound A is



# Aldehydes,Ketonesand Carboxylicacids

## Module34.3:MechanismofNucleophilicAdditionReaction

AldehydesandKetonesarehighlyreactivecompounds.Theyundergosimilารreactionsbecauseofthepresenceofacarbonylfunctionalgroupinbothofthem.

### NucleophilicAdditionReactions:

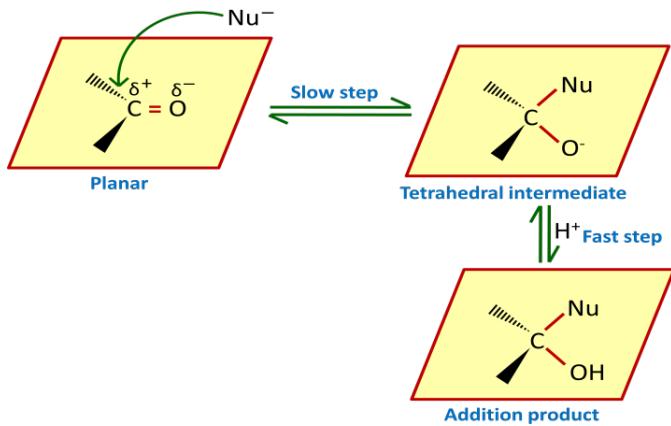
Aldehydes and ketones contain a carbonyl group. The carbonyl group ( $>\text{C} = \text{O}$  bond) has a multiple bond. Hence aldehydes and ketones undergo addition reactions at the carbonyl group. They have a polar carbonyl group. The carbon of the carbonyl group being electrophilic, is readily attacked by the nucleophiles. Hence the most typical reactions of aldehydes and ketones are nucleophilic addition reactions to carbon-oxygen double bond.

### Mechanismofnucleophilicaddition:

The nucleophile ( $\text{Nu}^-$ ) attacks the carbonyl carbon from above or below the plane of the carbonyl group leading to a  $\text{C}-\text{Nu}$  bond formation.

This is accompanied by heterolytic cleavage of the weaker carbon-oxygen pi-bond. The electron pair of the pi-bond is completely transferred to the oxygen atom. The electronegative oxygen atom thus gets a negative charge. During this process, the hybridization of the carbonyl carbon changes from trigonal to tetrahedral and the oxygen atom is pushed out of the plane of the carbonyl group.

The negatively charged tetrahedral intermediate is basic and captures a proton from the medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon-oxygen double bond.



### Relative Reactivity of Aldehydes and Ketones:

In general ketones are less reactive than aldehydes on account of the following facts.

#### (i) Electronreleasingeffect:

In the mechanism of nucleophilic addition, the first step involving the formation of the tetrahedral intermediate is accelerated by electron withdrawing groups and retarded by electron donating groups.

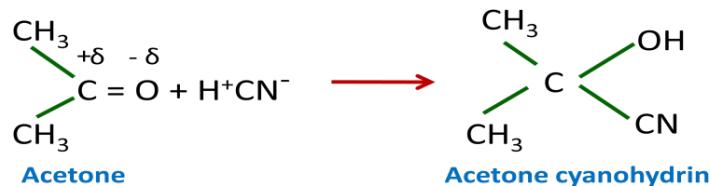
In ketones, the carbonyl carbon is attached to two alkyl groups, which are electron releasing in nature. These alkyl groups push electrons towards carbonyl carbon and thus decrease the magnitude of positive charge on it and make it less susceptible to nucleophilic attack. In an aldehyde there is only one electron donating group as against two in ketones.

#### (ii) Stericeffect:

The tetrahedral intermediate is more crowded when bulkier groups are attached to carbonyl carbon. In ketones the presence of two bulky alkyl groups hinders the approach of the nucleophile to the carbonyl carbon. This factor is called the **stericfactor**.

Some important examples of nucleophilic addition reactions are given below:

### A. The addition of HCN to acetone is an example of nucleophilic addition.

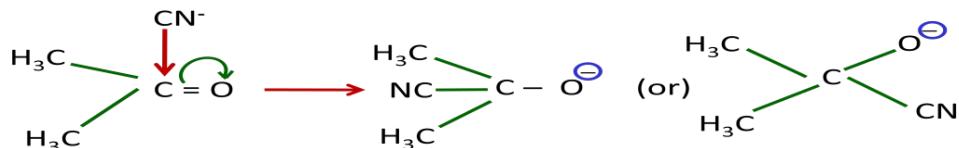


The mechanism of the reaction involves the following steps:

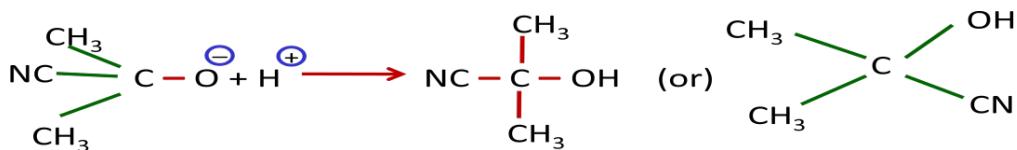
**Step 1:** HCN gives a proton ( $\text{H}^+$ ) and a nucleophile, cyanide ion  $(\text{CN})^-$

$$\text{HCN} \longrightarrow \text{H}^+ + \text{CN}^-$$

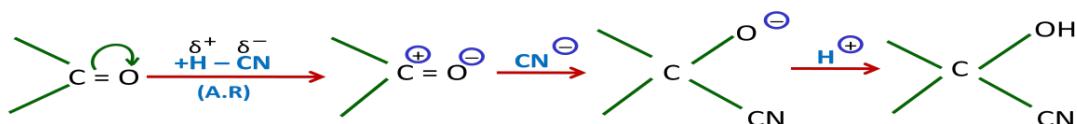
**Step 2:** The nucleophile  $(\text{CN})^-$  attacks the positively charged carbon so as to form an anion [H $^+$  does not initiate the negatively charged oxygen as an anion is more stable than a cation].



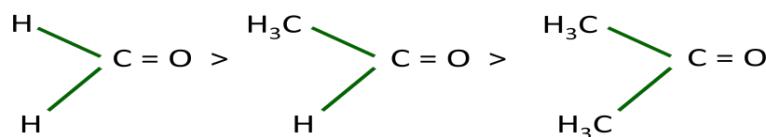
**Step 3:** The proton ( $\text{H}^+$ ) combines with an ion to form the addition product.



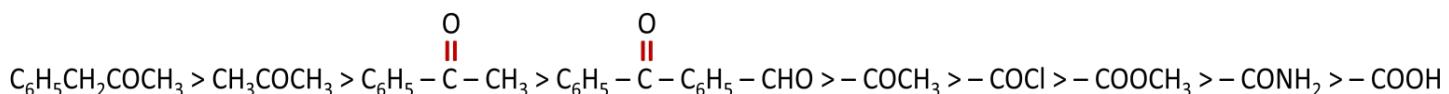
In  $\text{C}=\text{O}$  compounds, the addition of liquid HCN gives cyanohydrin and the addendum is  $\text{CN}^-$  ion and not HCN directly (addition is catalyzed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds).



Ease of nucleophilic addition ( $A_N$ ) reactions on carbonyl compounds will be in order.

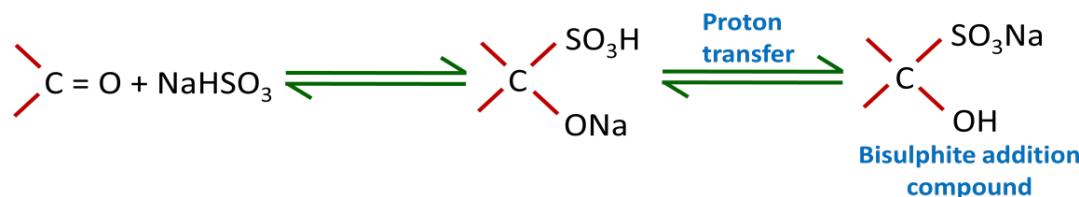


**Example:**



### B. Addition of sodium bisulphite ( $\text{NaHSO}_3$ )

$\text{NaHSO}_3$  adds to aldehydes and ketones to form crystalline addition products.



The bisulphite addition compound can be converted back to the original carbonyl compound by treating it with dilute mineral acid and/or an alkali. Therefore the bisulphite addition compounds are useful for separation and purification of aldehydes.

**Review questions:**

**Example set:**

1. The formation of cyanohydrins from a ketone is an example of
  - a. Electrophilic addition
  - b. Nucleophilic addition
  - c. Electrophilic substitution
  - d. Nucleophilic substitution

**Solution:** b)

2. The general order of reactivity of carbonyl compounds for nucleophilic addition reaction is

- a.  $\text{H}_2\text{CO} > \text{RCHO} > \text{C}_6\text{H}_5\text{CHO} > \text{R}_2\text{CO} > (\text{C}_6\text{H}_5)_2\text{CO}$
- b.  $(\text{C}_6\text{H}_5)_2\text{CO} > \text{R}_2\text{CO} > \text{C}_6\text{H}_5\text{CHO} > \text{RCHO} > \text{H}_2\text{CO}$
- c.  $(\text{C}_6\text{H}_5)_2\text{CO} > \text{R}_2\text{CO} > \text{H}_2\text{CO} > \text{C}_6\text{H}_5\text{CHO} > \text{RCHO}$
- d.  $\text{H}_2\text{CO} > \text{RCHO} > \text{R}_2\text{CHO} > \text{C}_6\text{H}_5\text{CHO} > (\text{C}_6\text{H}_5)_2\text{CO}$

**Solution:a)**

3. Which of the following statements regarding carbonyl groups is NOT correct?
- a. The carbon atom of carbonyl group in aldehydes is  $\text{sp}^2$  hybridized
  - b. The carbon atom of carbonyl group in the transition state formed during the addition reaction across the carbonyl group is  $\text{sp}^3$  hybridized
  - c. The aryl group in aromatic aldehydes speeds up the addition reaction across the carbonyl group
  - d. An aryl group stabilizes the aldehyde more than the transition state

**Solution:c)**

4. Carbonyl compounds undergo nucleophilic addition because of
- a. More stable anion with negative charge on oxygen atom and less stable carbonium ion
  - b. Electronegativity difference between carbon and oxygen atoms
  - c. Electromeric effect
  - d. All the above

**Solution:a)**

5. Write the mechanism of nucleophilic addition reaction of carbonyl compounds

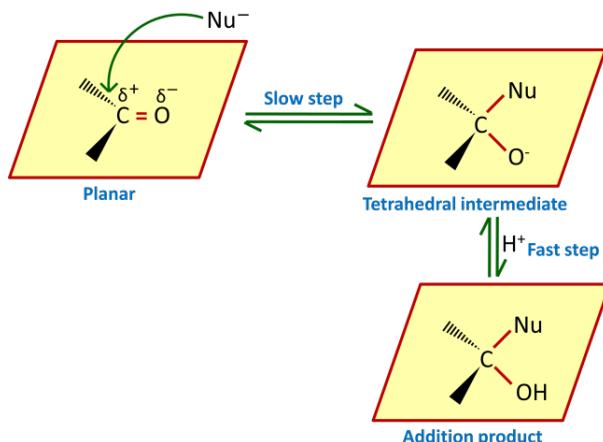
**Solution:**

#### Mechanism of nucleophilic addition:

The nucleophile ( $\text{Nu}^-$ ) attacks the carbonyl carbon from above or below the plane of the carbonyl group leading to a C-N bond formation.

This is accompanied by heterolytic cleavage of the weaker carbon-oxygen pi-bond. The electron pair of the pi-bond is completely transferred to the oxygen atom. The electronegative oxygen atom thus gets a negative charge. During this process, the hybridization of the carbonyl carbon changes from trigonal to tetrahedral and the oxygen atom is pushed out of the plane of the carbonyl group.

The negatively charged tetrahedral intermediate is basic and captures a proton from the medium to give the electrically neutral product. The net result is addition of  $\text{Nu}^-$  and  $\text{H}^+$  across the carbon-oxygen double bond.



6. Explain why ketones are less reactive than aldehydes?

**Solution:**

#### Relative Reactivity of Aldehydes and Ketones:

In general ketones are less reactive than aldehydes on account of the following facts.

##### i) Electron releasing effect:

In the mechanism of nucleophilic addition, the first step involving the formation of the tetrahedral intermediate is accelerated by electron withdrawing groups and retarded by electron donating groups.

In ketones, the carbonyl carbon is attached to two alkyl groups, which are electron releasing in nature. These alkyl groups push electrons towards carbonyl carbon and thus decrease the magnitude of positive charge on it and make it less susceptible to nucleophilic attack. In an aldehyde there is only one electron donating group as against two in ketones.

##### ii) Steric effect:

The tetrahedral intermediate is more crowded when bulkier groups are attached to carbonyl carbon. In ketones the presence of two bulky alkyl groups hinders

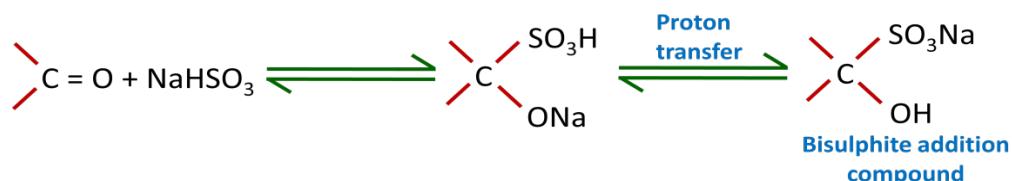
the approach of the nucleophile to the carbonyl carbon. This factor is called the **steric factor**.

7. What happens when sodium bisulphite reacts with a carbonyl compounds

**Solution:**

Addition of sodium bisulphite ( $\text{NaHSO}_3$ )

$\text{NaHSO}_3$  adds to aldehydes and ketones to form crystalline addition products.



The bisulphite addition compound can be converted back to the original carbonyl compound by treating it with dilute mineral acid and or an alkali. Therefore the bisulphite addition compounds are useful for separation and purification of aldehydes.

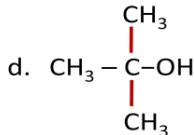
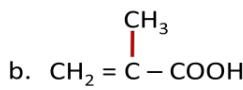
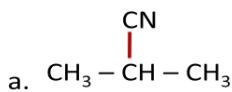
**Problem set:**

- Among the following the one having the most reactive carbonyl group is
  - $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$
  - $\text{HCHO}$
  - $\text{CH}_3\text{CHO}$
  - $\text{CH}_3\text{COCH}_3$

**Solution:** b)

- Identify the compound X in the following sequence





**Solution:**(b)

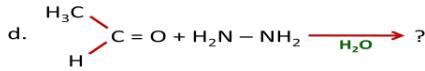
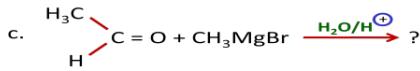
3. When  $\text{CH}_3\text{CHO}$  treated with  $\text{NaCN}$  and dil  $\text{H}_2\text{SO}_4$ , the carbonyl group attack on  $\text{HCN}$  to form
- Acetonecyanohydrin
  - Acetaldehydecyanohydrin
  - Formaldehydecyanohydrin
  - Alkylcyanide

**Solution:**(b)

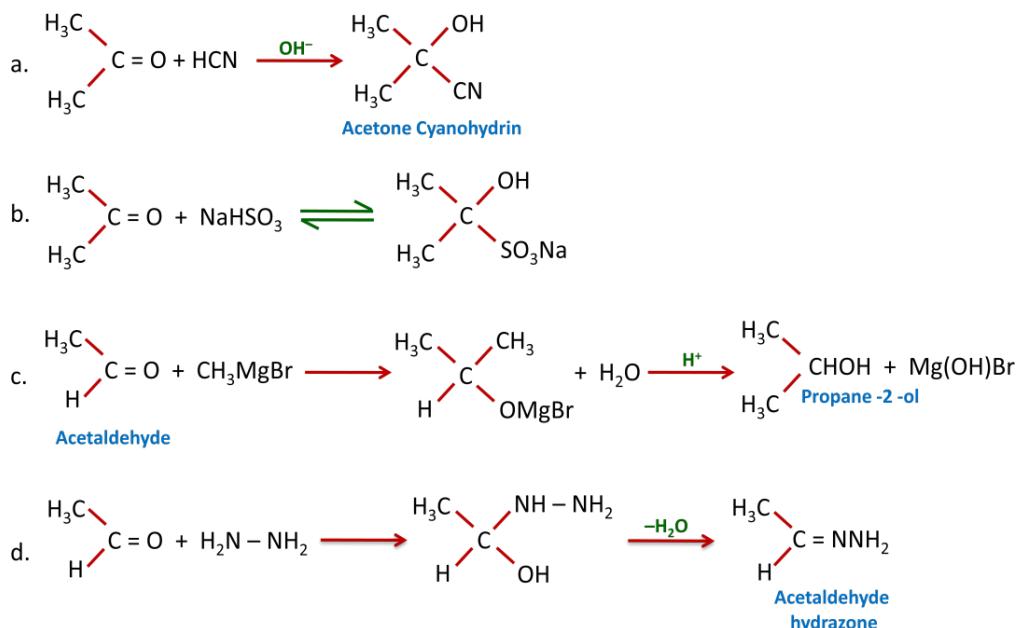
4. Which of the following statements regarding aldehydes is FALSE?
- The addition reactions occurring across the  $\text{C}=\text{O}$  is electrophilic type
  - The addition reactions occurring across the  $\text{C}=\text{O}$  bond is nucleophilic type
  - Aldehydes undergo addition reactions more readily than ketones
  - The addition reactions shown by  $\text{C}=\text{O}$  group is catalyzed by acids

**Solution:**(a)

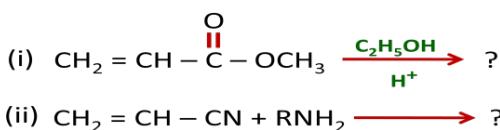
5. Predict the products in the following reactions



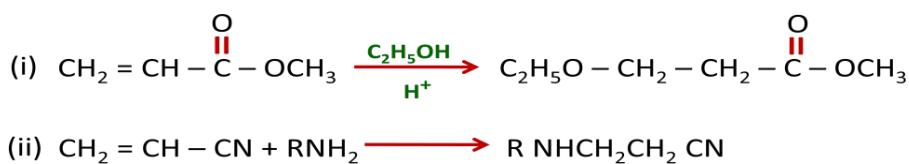
**Solution:**



6. Complete the following reaction



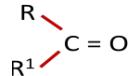
**Solution:**



**Exercise questions:**

1. Aldehydes generally undergo nucleophilic additions more readily than ketones. Explain
2. The nucleophilic addition of carbonyl is catalysed by an acid. Explain why?
3. Acetaldehyde forms  $\beta$ -hydroxybutyraldehyde in the presence of a dilute base or an acid. Then

- i) Name the reaction and
  - ii) Give the mechanism of the reaction and explain how it can be called as a nucleophilic addition reaction
4. Carbonyl compounds are reduced by  $\text{NaBH}_4$ . Name the product given by reduction. It is a nucleophilic reaction. Justify
5. Acids, esters, aldehydes and ketones can be reduced to the corresponding alcohols. Write the sequence of the ease of reduction of these compounds.



### Solutions to exercise questions:

1. The important step in the nucleophilic addition reaction is the formation of a bond to the electron deficient. i.e., electrophilic, carbonyl carbon. The carbonyl group is more susceptible to the attack by electron-rich, i.e., nucleophilic reagents, or bases.

In the nucleophilic addition reaction the transition state is formed by attack of a nucleophile. In the transition state, the trigonal carbon begins to acquire a tetrahedral configuration. Thus the attacked groups are brought closer together. Then we might expect steric hindrance in the addition reaction. i.e., the larger alkyl or aryl groups will tend to resist crowding more compared to smaller groups like hydrogen's.

The higher reactivity of the aldehydes seems to be due to a combination of electronic and steric factors. A ketone contains a second alkyl or aryl group in the place where an aldehyde contains a hydrogen atom. Therefore a ketone resists strongly the bonding of another group to the carbon atom so that an intermediate complex (or transition state). An alkyl group releases electrons, and destabilizes the transition state by increasing the negative charge density developing on oxygen.

An aryl group is an electron-withdrawing group. It is expected, therefore, to stabilize the transition state. Thus the nucleophilic addition is expected to be aided by the aryl group. But the aryl group is stabilized more due to resonance. And therefore the transition state is more deactivated than getting activated. Therefore ketones react less readily as compared to the corresponding aldehydes.

2. If an acid (i.e. a  $\text{H}^+$  ion or a Lewis acid) is present, the hydrogen ion becomes attached to the carbonyl oxygen. This protonation prior to the nucleo-

philic

attack lowers the energy of activation ( $E_{activation}$ ). This permits oxygen to acquire the  $\pi$  electrons without having to accept a negative charge. Thus nucleophilic addition to aldehydes and ketones can be catalysed by acids. i.e.  $\text{H}^+$  ion or sometimes Lewis acids.

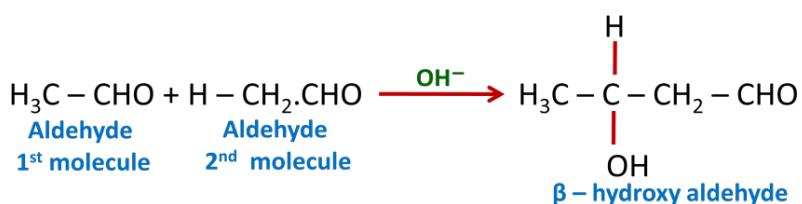
3.

i) **Aldol condensation:** Under the influence of a dilute acid or base, two molecules of an aldehyde or a ketone having an  $\alpha -$  hydrogen may combine to form a  $\beta$ -hydroxy ketone. In each case one molecule of aldehyde (or a ketone) adds onto a second molecule of the compound. In this process the

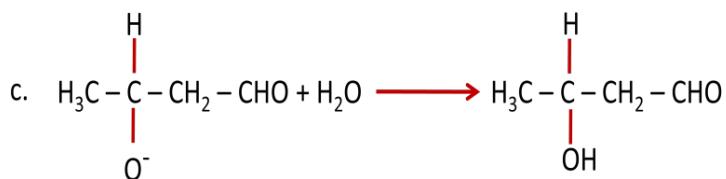
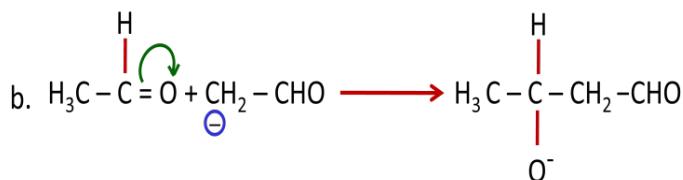
$\alpha -$

carbon of the first molecule becomes attached to the carbonyl carbon of the second.

**Ex:**



ii) **Mechanism of the reaction:**

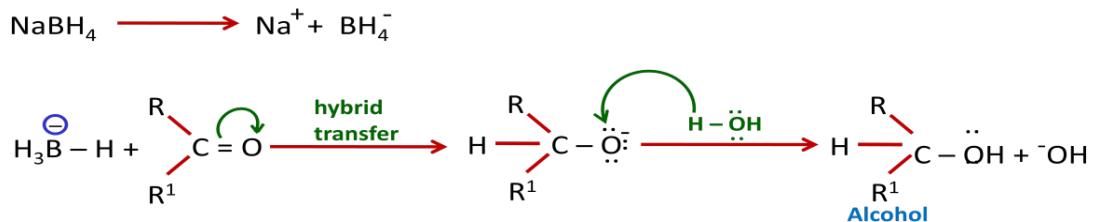


In the mechanism step (b) involves the nucleophilic attack of  $\text{CH}_2\text{CHO}$  on the aldehyde.

Hence the reaction may be called a nucleophilic addition reaction.

4.

- i)  $(NaBH_4 + \text{Aldehyde or ketone})$  gives the corresponding alcohol
- ii) Nucleophilic addition reaction:



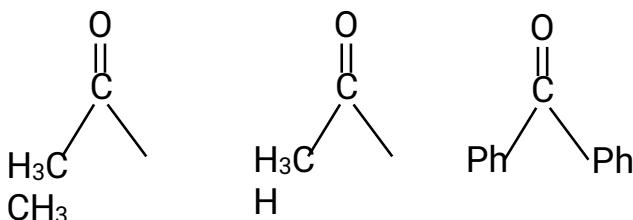
The addition of the Borohydride ion involves the transfer of a hydride ion to the carbonyl. It is a nucleophilic addition.

5.



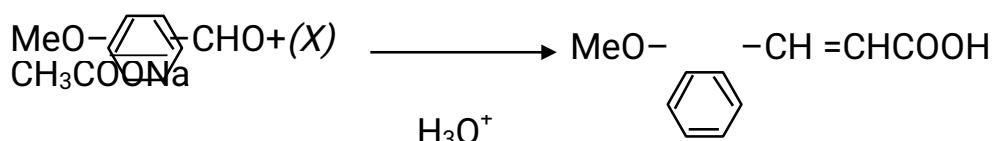
### IITquestions:

1. The order of reactivity of phenylmagnesium bromide with the following compounds is



- a. (II) > (III) > (I)
- b. (I) > (III) > (II)
- c. (II) > (I) > (III)
- d. All react with the same rate

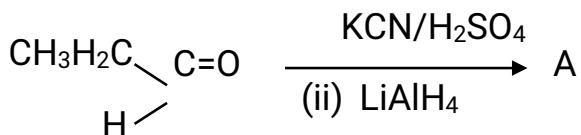
2.



The compound (X) is:

- a.  $\text{CH}_3\text{COOH}$
- b.  $\text{BrCH}_2\text{COOH}$
- c.  $(\text{CH}_3\text{CO})_2\text{O}$
- d.  $\text{CHO-COOH}$

3. Complete the following reaction with appropriate structure:

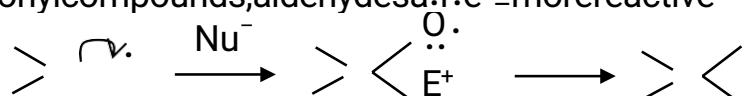


### Solution:

1. (c)

In phenylmagnesium bromide ( $\text{PhMgBr}$ ), Ph is attached with that C-atom of

carbonyl group which have low electron density (higher electropositive charge). In carbonyl compounds, aldehydes are more reactive ..



O-E

C=O

Slow  
Nu

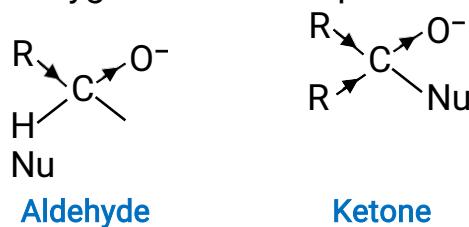
C

Fast

C

Nu

towards nucleophile in nucleophilic addition reaction because in ketones alkylgroups (due to + I effect) decrease the electropositive charge of carbon of carbonyl group. Hence, attraction of nucleophile decreases. Moreover in the tetrahedral intermediate aldehyde have less steric repulsion than ketones and also the aldehyde increases the negative charge on oxygen less in comparison of ketones.

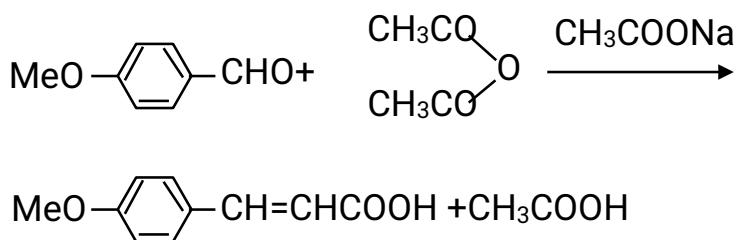


Thus, on the basis of above reason the order of reactivity of acetone (I), acetaldehyde (II) and benzaldehyde (III) with PhMgBr is

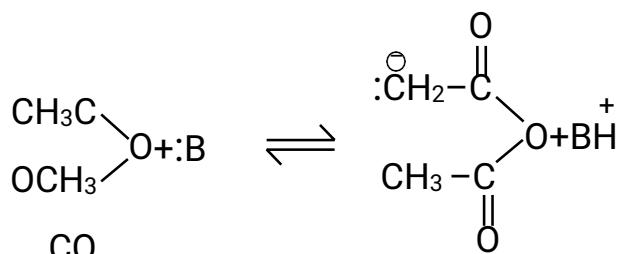


2. (c)

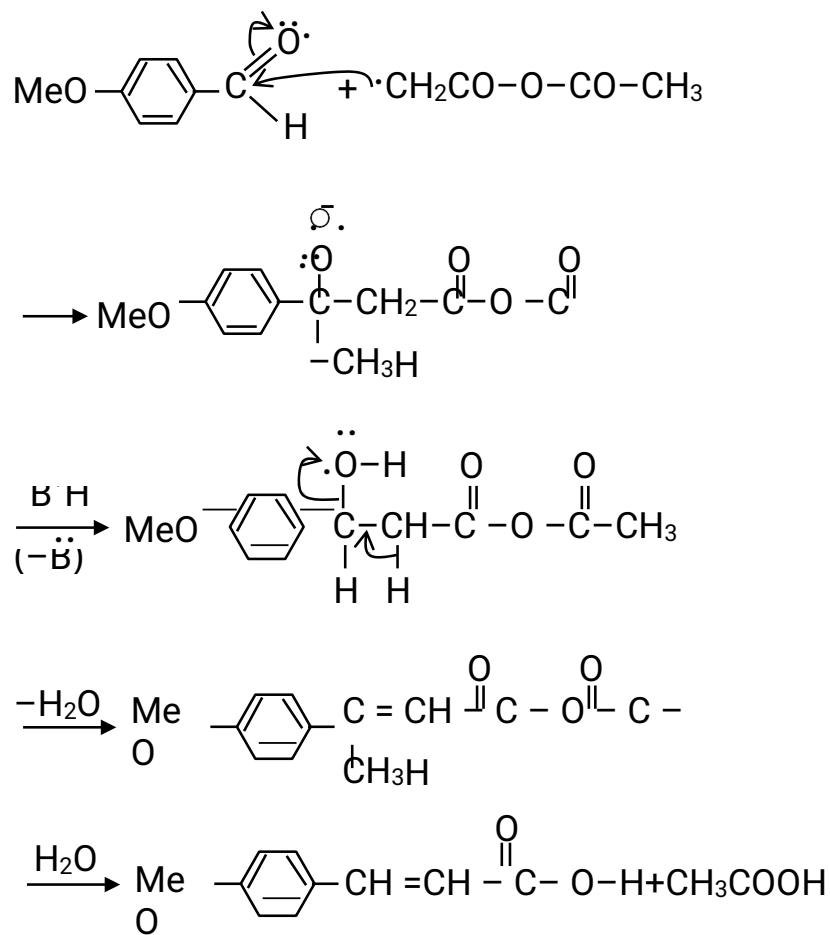
This reaction is an example of Perkin's reaction because it is  $\alpha,\beta$ -unsaturated acid obtained with aromatic aldehydes. Therefore, (X) is acetic anhydride i.e.,  $(\text{CH}_3\text{CO})_2\text{O}$ .



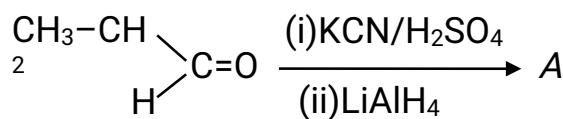
Mechanism of this reaction is represented as follows



(Base =  $\text{CH}_3\text{COONa}$ )

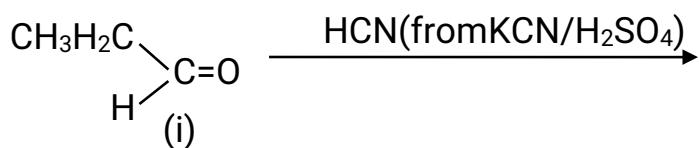


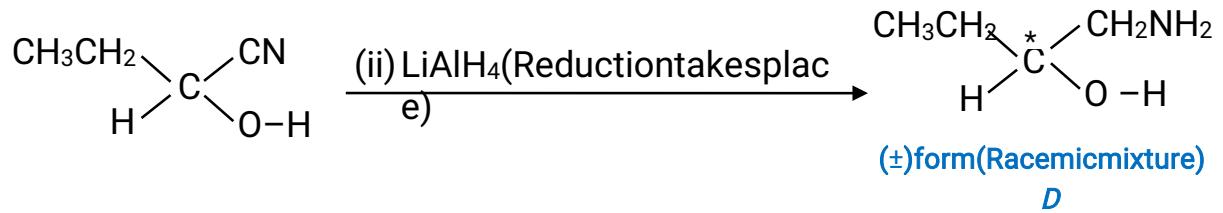
3.



In it: (i)  $\text{KCN} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCN}$

This HCN gives nucleophilic addition reaction on  $\text{C=O}$  group as follows:

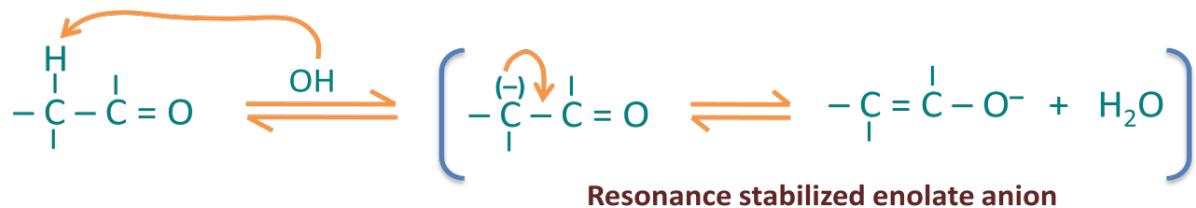




Such \*Cis asymmetric C-atom, so here racemic mixture is formed.

## Acidity of $\alpha$ -hydrogen of aldehydes and ketones:

The  $\alpha$ -hydrogen in aldehydes and ketones is weakly acidic and may be removed by a base such as NaOH. The acidity of  $\alpha$ -hydrogen is due to resonance stabilization of the conjugate base called the **enolate anion**.



In the next step nucleophilic addition of the enolate anion occurs. The  $\alpha$ -carbon of the enolate anion has considerably negative character and is thus nucleophilic. It adds to the carbonyl group of the unreacted aldehyde or ketone to give the aldol product.

## Aldol condensation:

Aldehydes containing  $\alpha$ -hydrogen undergo self-addition in the presence of a base to form products called Aldols. This reaction is called Aldol condensation.

The term aldol is derived from the combination of the words aldehyde and alcohol, the two function groups present in the product.

**Example:** two molecules of acetaldehyde combine with each other in the presence of dilute NaOH to form 3-hydroxy butanal.

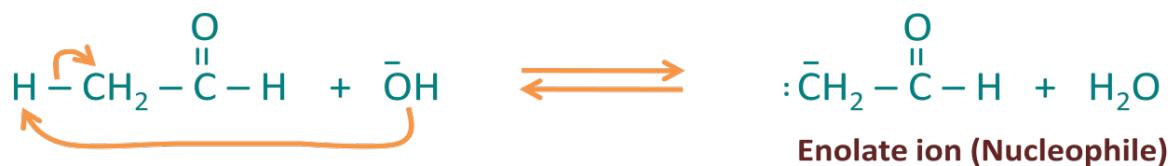


## Mechanism:

The reaction is reversible and involves the following steps.

### Step-1:

The enolate ion is formed.



### Step-2:

The enolate ion attacks the carboxyl carbon of another un-ionized aldehyde molecule.



### Step-3:

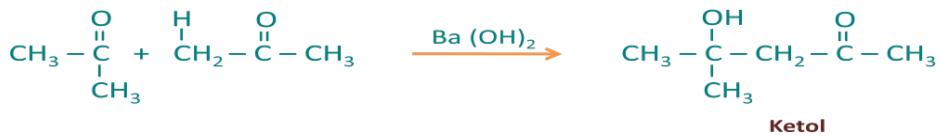
The negative oxygen in the product accepts a proton from water to give aldol.



Aldols are easily dehydrated either by heating or by treatment with dilute acid to form  $\alpha, \beta$ -unsaturated aldehydes.



Ketones containing  $\alpha$ -hydrogen also undergo aldol condensation to form ketols.

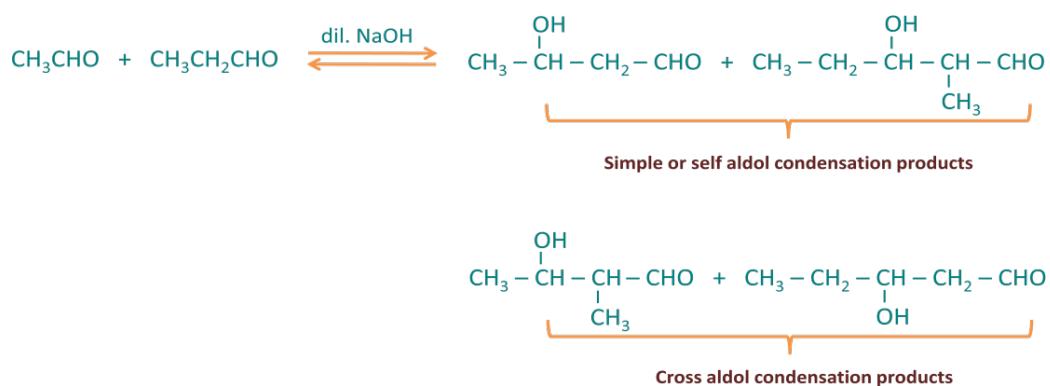


Ketols are also easily dehydrated by heating or by treatment with dilute acid to form  $\alpha, \beta$ -unsaturated ketones.



## Cross aldol condensation:

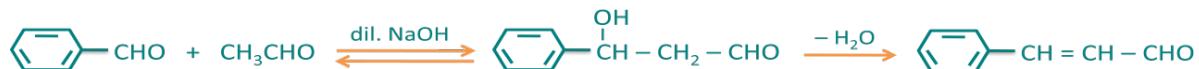
Aldol condensation of a mixture of two different aldehydes and ketones each containing an  $\alpha$ -hydrogen gives a mixture of four products. In this reaction, each carbonyl compound produces the corresponding enolate anion. This enolate anion may add on to the compound with the same carbonyl group to give a simple aldol condensation product. The other products arise when a different carbonyl compound may add. This is cross aldol condensation and gives rise to the formation of cross aldol condensation products.



This cross aldol condensation has no synthetic value except when one of the carbonyl compound has no  $\alpha$ -hydrogen.

**Example:**

In the reaction between benzaldehyde and acetaldehyde, the cross aldol product easily loses water molecule to give Cinnamaldehyde.



In Conclusion, all aldehydes and ketones which contain  $\alpha$ -hydrogen atom undergo aldol condensation. Those which do not contain  $\alpha$ -hydrogen like  $\text{HCHO}$ ,  $\text{C}_6\text{H}_5\text{CHO}$  etc do not undergo this reaction. However cross aldol condensation can occurs between carbonyl compound having no  $\alpha$ -H atom with aldehyde or ketones possessing  $\alpha$ -H atom.

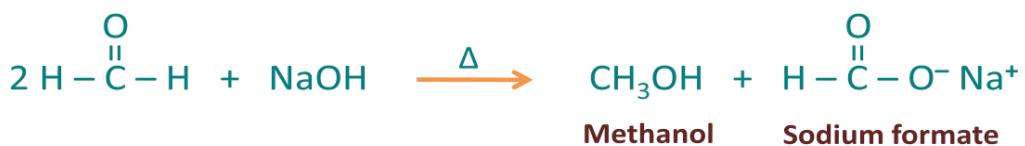
**Cannizzaro reaction:**

Aldehydes which lack an  $\alpha$ -hydrogen, when heated with concentrated  $\text{NaOH}$ , undergo a disproportionation reaction. One half of the aldehyde molecules are oxidized to a carboxylic acid and one half are reduced to an alcohol. This reaction is known as Cannizzaro reaction.

**Note:**

Aldehydes with  $\alpha$ -hydrogens do not undergo this reaction. Under these conditions, they undergo an aldol condensation reaction.

**Example:**



**Note:**

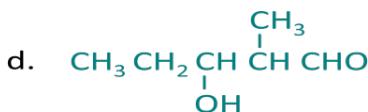
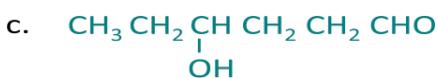
Ketones do not undergo this reaction.

## Uses:

- Formaldehyde is well known as formalin (40 % formaldehyde) solution used to preserve biological specimens and to prepare Bakelite.
- Acetaldehyde is used as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde is used in perfumery and in dye industries.
- Acetone is used in the manufacture of thermo softening plastic Perspex.
- Acetone is used in the production of chloroform and diacetone alcohol.
- Many aldehydes and ketones; **Ex:-** Butyraldehyde, vanillin, acetophenone camphor etc are well known for their odors and flavors.

### Example set:

1.



### Solution: b)

2. A  $\beta$ -hydroxy carbonyl compound is obtained by the action of NaOH on:
- $\text{R}_3\text{CCHO}$
  - $\text{C}_6\text{H}_5\text{CHO}$
  - $\text{CH}_3\text{CHO}$
  - $\text{HCHO}$

**Solution:** c)

3. The aldol condensation of acetaldehyde involves the formation of an intermediate product which is
- A carbanion
  - A carbocation
  - A free radical
  - Both b) and c)

**Solution:** a)

4. Cannizzaro reaction is not given by
- Formaldehyde
  - Trimethyl aldehyde
  - Acetaldehyde
  - Benzaldehyde

**Solution:** c)

5. When formaldehyde is treated with 50 % NaOH solution it undergoes:
- Cannizzaro reaction
  - Wurtz reaction
  - Aldol condensation
  - Hydrolysis

**Solution:** c)

6. Write a note on
- Aldol condensation
  - Cross aldol condensation

**Solution:**

**a) Aldol condensation:**

Aldehydes containing  $\alpha$ -hydrogen undergo self-addition in the presence of a base to form products called Aldols. This reaction is called Aldol condensation.

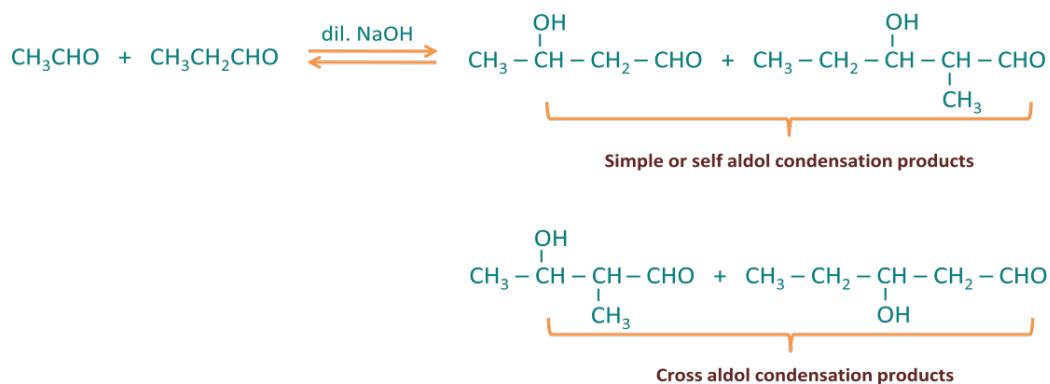
The term aldol is derived from the combination of the words aldehyde and alcohol, the two functional groups present in the product.

**Example:** two molecules of acetaldehyde combine with each other in the presence of dilute NaOH to form 3-hydroxy butanal.



### b) Cross aldol condensation:

Aldol condensation of a mixture of two different aldehydes and ketones each containing an  $\alpha$ -hydrogen gives a mixture of four products. In this reaction, each carbonyl compound produces the corresponding enolate anion. This enolate anion may add on to the compound with the same carbonyl group to give a simple aldol condensation product. The other products arise when a different carbonyl compound may add. This is cross aldol condensation and gives rise to the formation of cross aldol condensation products.



This cross aldol condensation has no synthetic value except when one of the carbonyl compound has no  $\alpha$ -hydrogen.

### 7. Write a note on Cannizzaro reaction?

**Solution:**

#### Cannizzaro reaction:

Aldehydes which lack an  $\alpha$ -hydrogen, when heated with concentrated NaOH, undergo a disproportionation reaction. One half of the aldehyde molecules are oxidized to a carboxylic acid and one half are reduced to an alcohol. This reaction is known as Cannizzaro reaction.

**Note:**

Aldehydes with  $\alpha$ -hydrogens do not undergo this reaction. Under these conditions, they undergo an aldol condensation reaction.

**Example:**



**Note:**

Ketones do not undergo this reaction.

8. Give any four uses of carbonyl compounds?

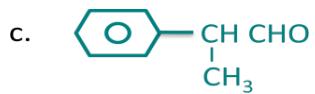
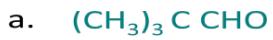
**Solution:**

**Uses:**

- Formaldehyde is well known as formalin (40 % formaldehyde) solution used to preserve biological specimens and to prepare Bakelite.
- Acetaldehyde is used as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
- Benzaldehyde is used in perfumery and in dye industries.
- Acetone is used in the manufacture of thermo softening plastic Perspex.
- Acetone is used in the production of chloroform and diacetone alcohol.
- Many aldehydes and ketones; **Ex:-** Butyraldehyde, vanillin, acetophenone camphor etc are well known for their odors and flavors.

**Problem set:**

1. Which of the following gives aldol condensation reaction?



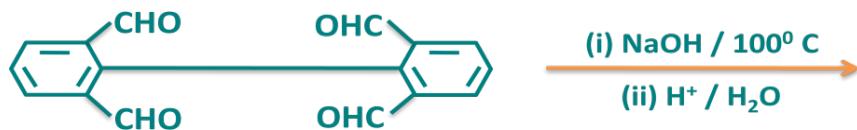
Solution: c)

2.

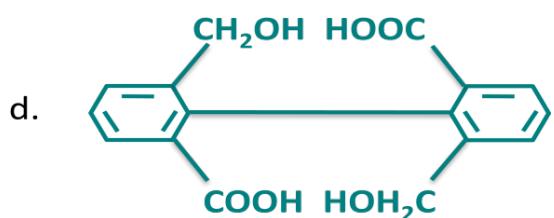
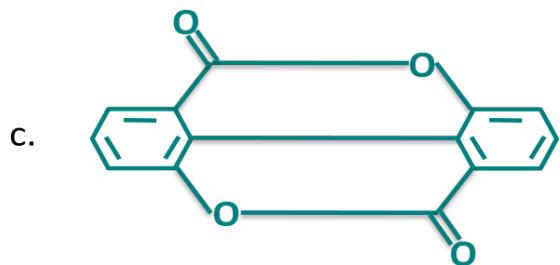


Solution: a)

3.



Major product is:



**Solution:** d)

4. The important step in Cannizzaro reaction is the intermolecular shift of;
- Proton
  - H-atom
  - Hydride ion
  - Hydronium ion

**Solution:** c)

5. Write down the product for the following reaction;



**Solution:**



6. What happened when chloral is heated with aqueous hydroxide? Give equation:

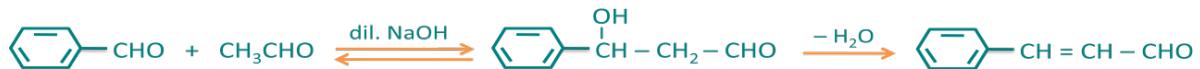
**Solution:**



7. Complete the following reaction with appropriate structures:



**Solution:**



**Exercise questions:**

1. Identify A, B, C, D and E in the following reactions:

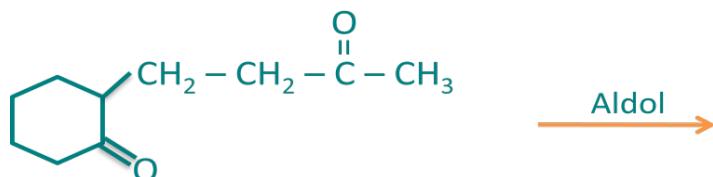


2. Give the aldol condensation product



3. Can  $C_6H_5COCHO$  undergo Cannizzaro reaction? Explain.

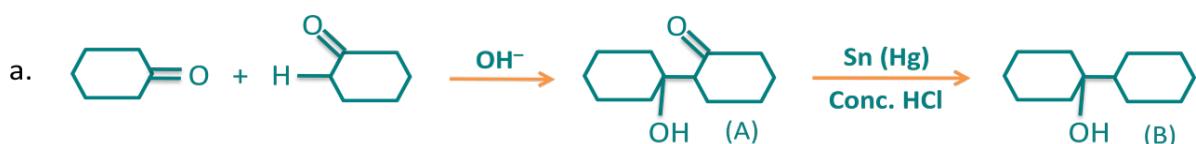
4. What is aldol condensation product of A?



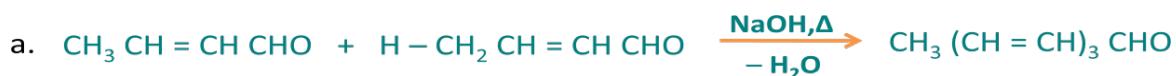
5. An aldehyde A ( $C_{11}H_8O$ ), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B

### Solutions:

1.



2.

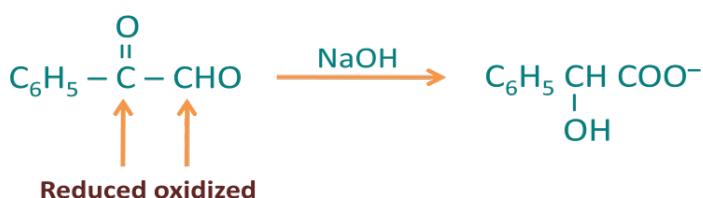


In this case, condensation of alkylic H, and not that of vinylic H, takes place.

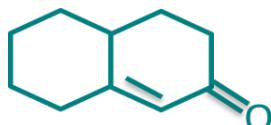


3.

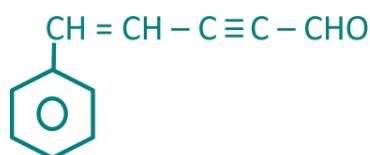
Yes,  $C_6H_5COCHO$  undergoes intra molecular Cannizzaro reaction



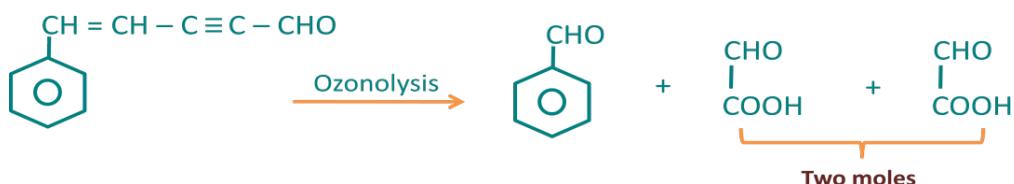
4.



5. Aldehyde does not have  $\alpha$ -hydrogen atoms but ozonolysis to give two moles of compound B and benzaldehyde compound B on oxidation with  $Ag^+$  (Tollen's reagent) to give oxalic acid so aldehyde A may be



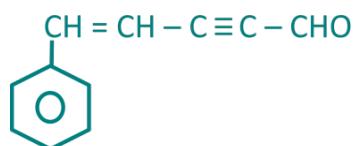
This aldehyde on ozonolysis gives following product.



[On ozonolysis –  $CH = CH -$  gives aldehyde and –  $C \equiv C -$  gives acidic group].



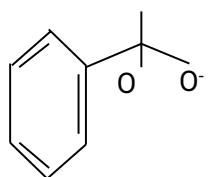
Hence, compound A is



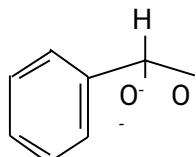
**IIT Questions:**

1. In a Cannizaro reaction, the intermediate that will be the best hydride donor is

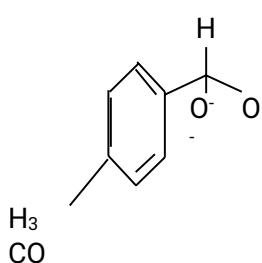
(a)



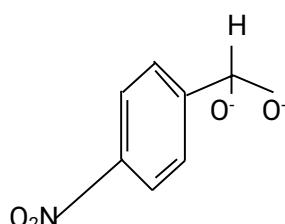
(b)



(c)



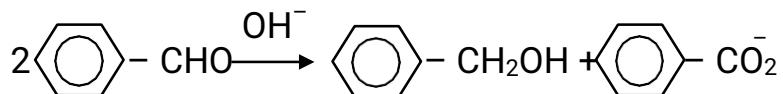
(d)



2. The Cannizaro's reaction is not given by:

- a. Trimethyl acetaldehyde
- b. Acetaldehyde
- c. Benzaldehyde
- d. Formaldehyde

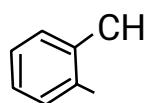
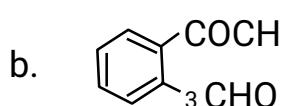
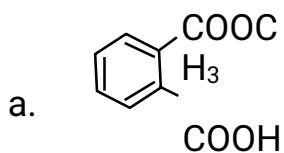
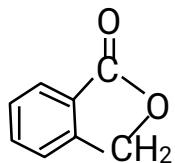
3. In the Cannizaro's reaction given below:



The slowest step is :

- a. The attack of  $\text{OH}^-$  at the carbonyl group
- b. The transfer of hydride to the carbonyl group
- c. The abstraction of proton from the carboxylic acid
- d. The deprotonation of  $\text{Ph}-\text{CH}_2\text{OH}$

4. Which of the following has the most acidic hydrogen?
- 3-hexanone
  - 2, 4-hexadione
  - 2,5 hexadione
  - 2, 3-hexanedione
5. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives:
- Benzyl alcohol and sodium formate
  - Sodium benzoate and methyl alcohol
  - Sodium benzoate and sodium formate
  - Benzyl alcohol and methyl alcohol
6. Base catalysed aldol condensation occurs with:
- Propionaldehyde
  - Benzaldehyde
  - 2-methyl propionaldehyde
  - 2, 2-dimethyl propionaldehyde
7. A new carbon-carbon bond formation is possible in :
- Cannizaro's reaction
  - Friedal Craft's reaction
  - Clemmensen reduction
  - Reimer-Tiemann reaction
8. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following by acidification gives following lactone as the :

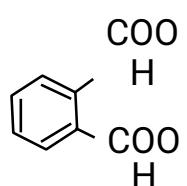


O

c.



d.



9. Show with balanced equation what happens when the following are mixed:  
 "Chloral is heated with aqueous hydroxide"
10. An organic compound *A*  $C_6H_{10}O$ , on reaction with  $CH_3MgBr$  followed by acid treatment gives compound *B*. The compound *B* on ozonolysis gives compound  
*C*. which in presence of a base gives 1-acetyl cyclopentane *D*. The compound *B* on reaction with HBr gives compound *E*. Write the structures of *A*, *B*, *C*, *D* and  
*E*. Show how *D* is formed from *C*.
11. An alkene (*A*)  $C_{16}H_{16}$  on ozonolysis gives only one product (*B*)  $C_8H_8O$ . Compound (*B*) on reaction with  $NaOH / I_2$  yields sodium benzoate. Compound (*B*) reacts with  $KOH/NH_2NH_2$  yielding a hydrocarbon (*C*)  $C_8H_{10}$ . Write the structures of compounds (*B*) and (*C*). Based on this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation ( $H_2 / Pd - C$ ) gives a racemic mixture.

### Solutions:

1. c

The methoxy group is being electron-releasing group makes the release of hydride group more easy.

2. b)

Aldehydes having no  $\alpha$ -hydrogen gives Cannizaro's reaction. Acetaldehyde has  $\alpha$ -hydrogen atom, hence does not give this reaction.

3. b)

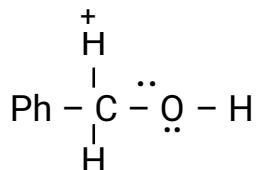
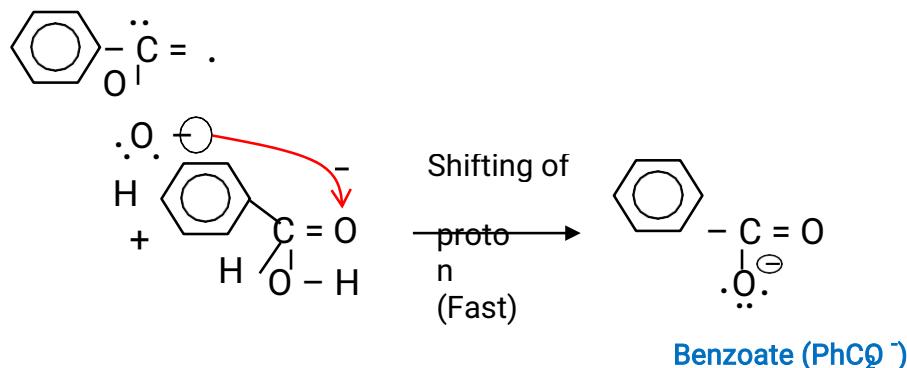
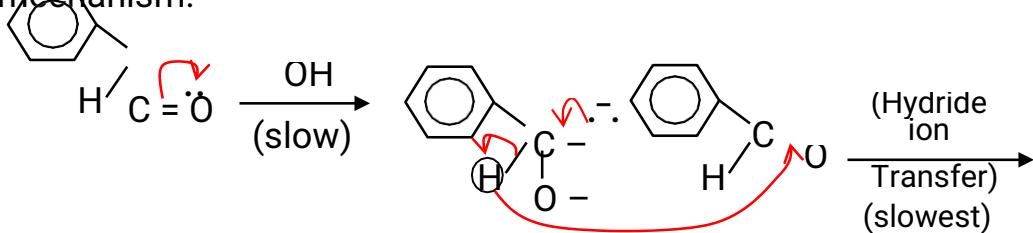
In the Cannizaro's reaction given below



-



The slowest step is transfer of hydride ion to the carbonyl group of second mole of aldehyde. Hence it is represented in following reaction mechanism.



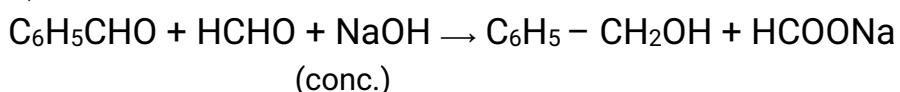
**Benzyl alcohol ( $\text{Ph}-\text{CH}_2\text{OH}$ )**

4. b)

When  $>\text{CH}_2$  group is surrounded by two electronegative (electronegative) carbonyl groups. Therefore, it is most reactive and its both hydrogen atoms are acidic in character.

Thus,  $\text{CH}_3\text{COCH}_2\text{COCH}_2\text{CH}_3$  (2, 4-hexanedione) is one of the reactive methylene compounds.

5. a)



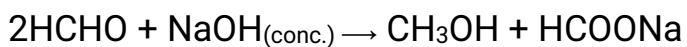
It is crossed Cannizaro's reaction.

6. Both a) and c)

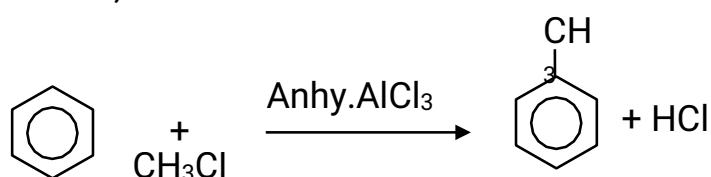
Aldol condensation given by the aldehydes having  $\alpha$ -hydrogen atom.

7. Both b) and d)

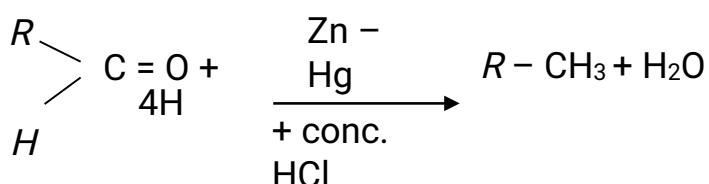
In Cannizaro's reactions



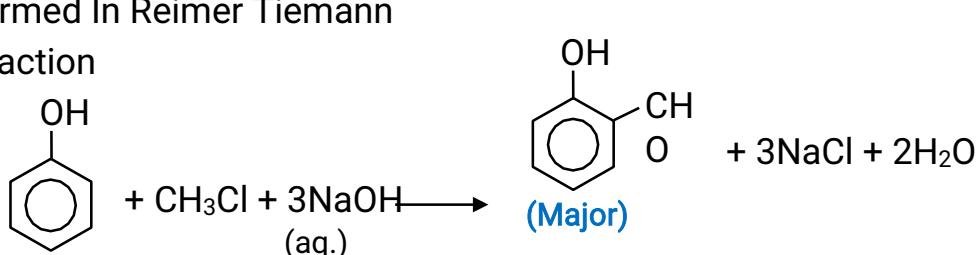
New C – C bond is not formed In Friedal-Craft reaction,



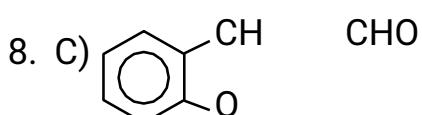
New C – C bond is formed. In Clemmensen reduction

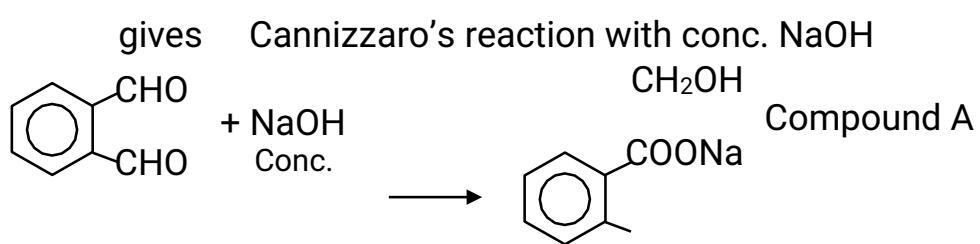


New C – C bond is not formed In Reimer Tiemann reaction



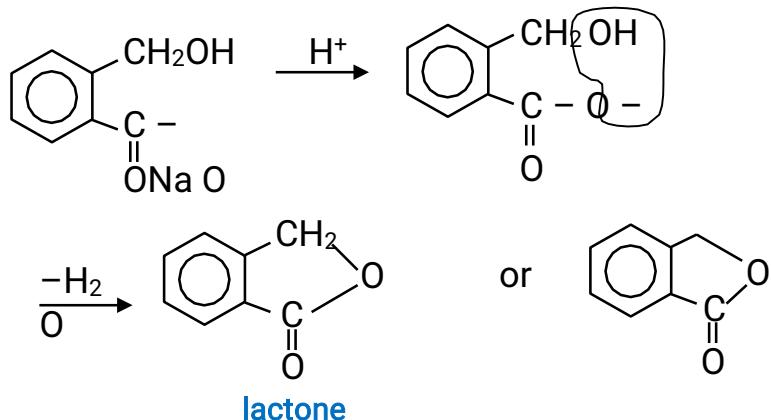
New C – C bond is formed



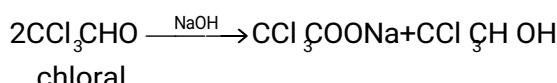


This compound on acidification to give a compound which have  $\text{CH}_2\text{OH}$  and

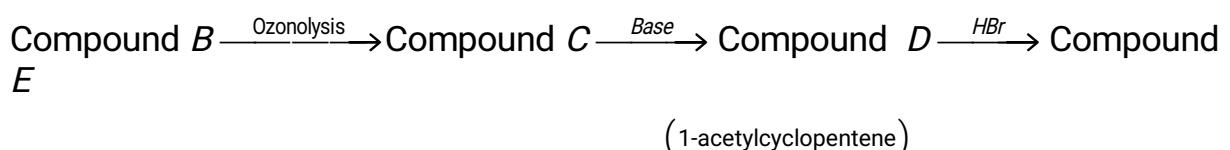
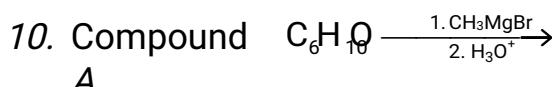
$-\text{COOH}$  group, such groups on dehydration to give lactone.



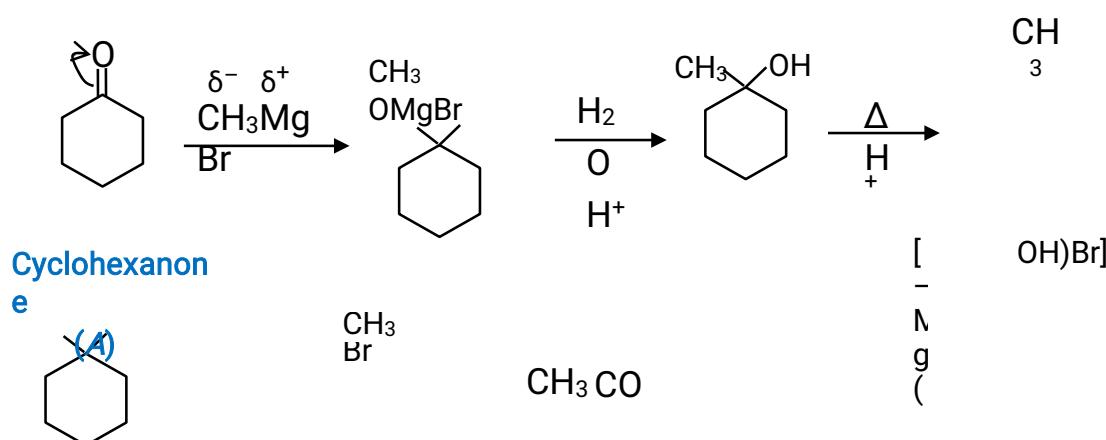
9.

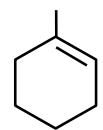


(It is Cannizaro's reaction)

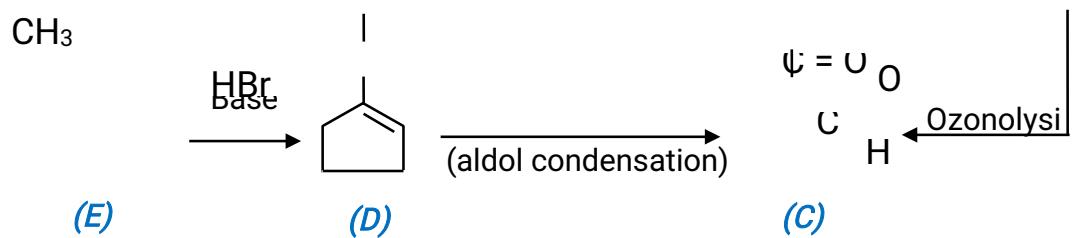


Compound *A* is cyclic carbonyl compound which gives following reaction according to given problem.

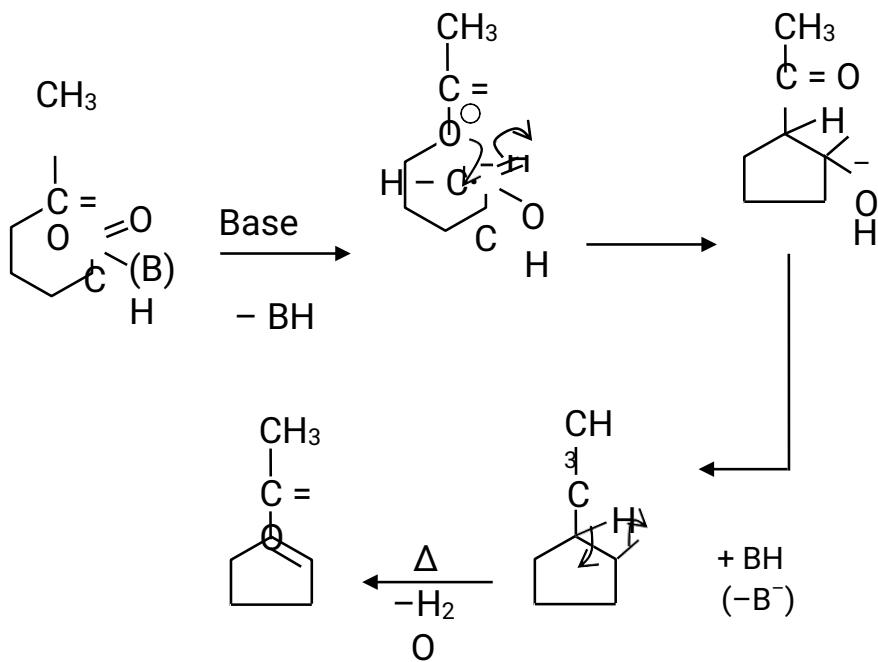




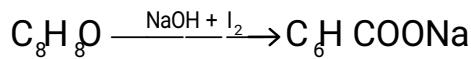
(-H<sub>2</sub>O)  
1-methyl  
Cyclohexene  
(B)



Formation of *D* with *C* is represented in from of following mechanism.



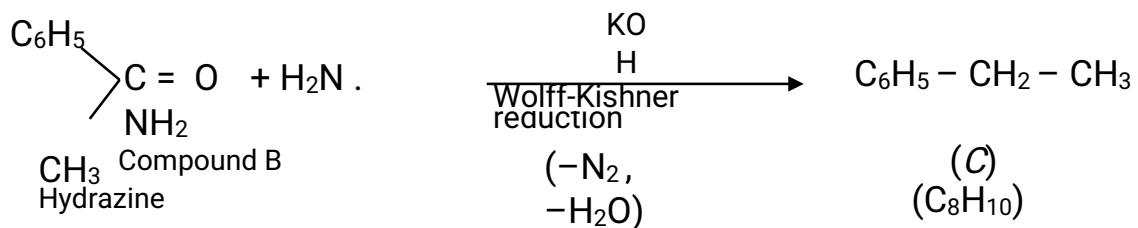
11. Alkene *A* is symmetric because it gives a carbonyl compound ( $C_8H_8O$ ) on ozonolysis.



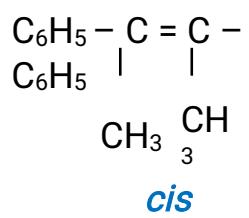
Compound B

Hence, it gives iodoform test with a mixture of NaOH and  $I_2$ , so it must have  $CH_3CO -$  group. Thus the possible structure of compound *B* is  
 $C_6H_5 - CO - CH_3$   $C_6H_5COCH_3 + 4NaOH + 3I_2 \rightarrow CHI_3 \downarrow + C_6H_5COONa + 3H_2O + 3NaI$

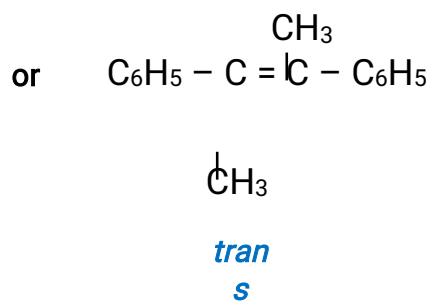
### iodoform



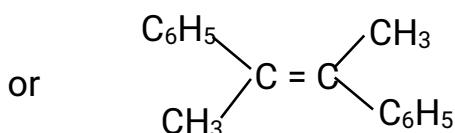
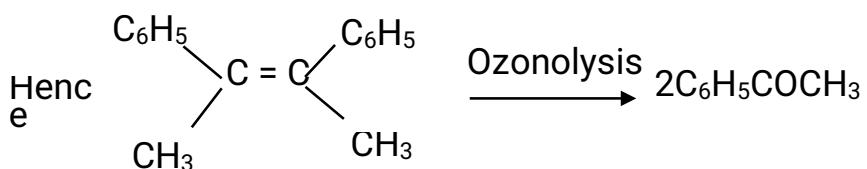
On the basis of structure of compound *B*, the compound *A* is



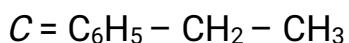
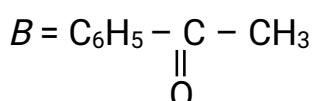
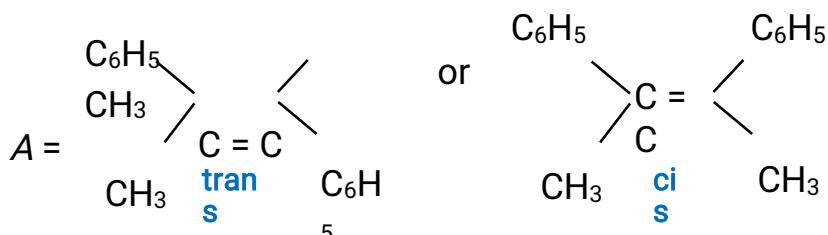
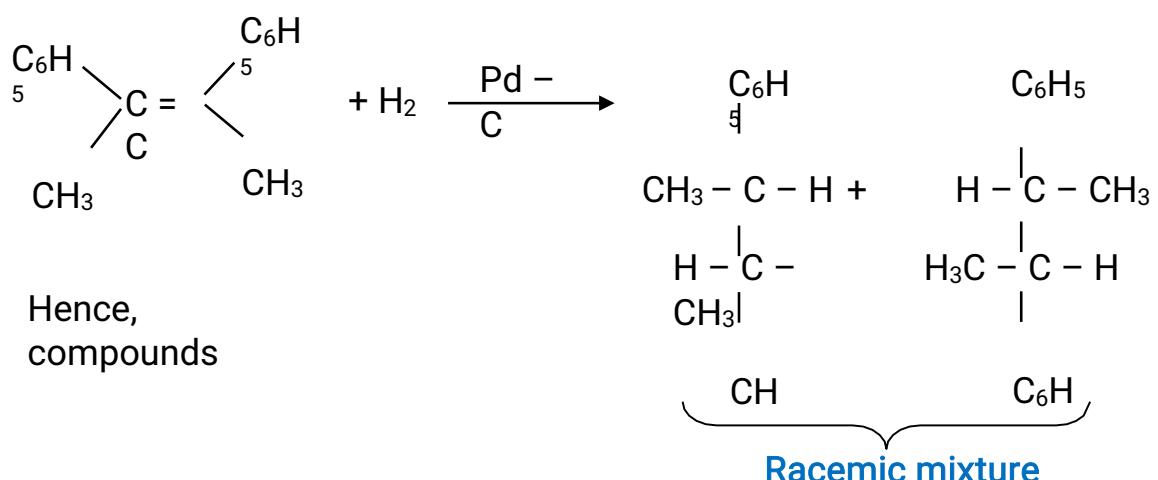
*cis*



*trans*  
*s*



Symmetric alkenes show the properties of geometrical isomerism. Hence, its *cis* and *trans* isomers are possible. In these isomers *trans* isomer gives racemic mixture on hydrogenation ( $\text{H}_2 / \text{Pd} - \text{C}$ ).



## Module 34.5: Carboxylic Acids

Carboxylic acids are organic acids characterized by the presence of a carboxyl group. It has the formula,  $\text{C}(\text{OH})(\text{O})$  usually written  $-\text{COOH}$  or  $-\text{CO}_2\text{H}$ . Carboxylic acids are Bronsted – Lowry acids – they are proton donors. Salts and anions of carboxylic acids are called carboxylates. Organic compounds with alcohols are known as esters.

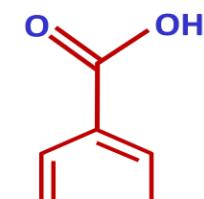
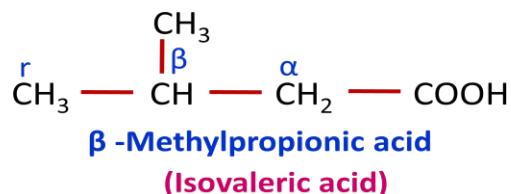
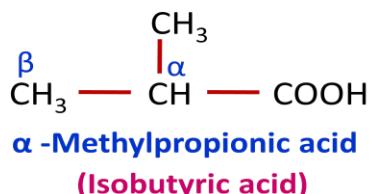
### Nomenclature:

The naming of carboxylic acids is done in two ways. They are

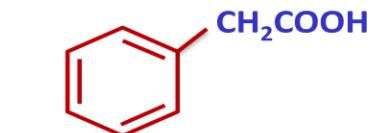
- Common method or trivial method and
- IUPAC method

#### a. Common (naming) method:

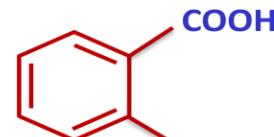
Since carboxylic acids are amongst the earliest organic compounds to be isolated from nature, a large number of them are known by their common names. The common names end with the suffix –ic acid and have been derived from Latin or Greek names of their natural sources. For *e.g.*, formic acid ( $\text{HCOOH}$ ) was first obtained from red ants (formica means ant), acetic acid ( $\text{CH}_3\text{COOH}$ ) from vinegar (acetum means vinegar) butyric acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ) from rancid butter (butyrum means butter) caproic acid ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ ) from goats (caper means goat). The positions of the substitutes are indicated by Greek letters  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  etc the  $\alpha$ -carbon being the one directly attached to the carboxyl group,  $\beta$ - the next and so on.



**Benzoic acid**



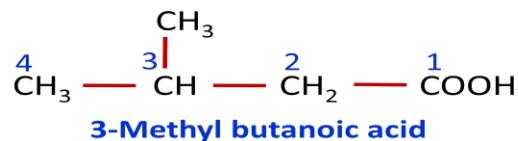
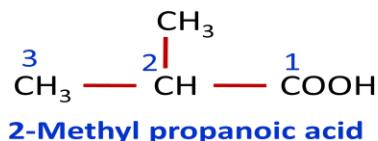
**phenylacetic acid**



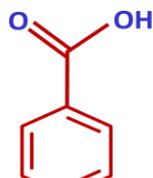
**Phthalic acid**

### b. IUPAC nomenclature:

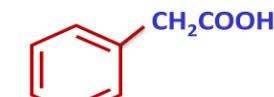
In the IUPAC system, the monocarboxylic acids are named as alkanoic acids. The name of the acid is derived by replacing the terminal 'e-' in the name of the corresponding alkane with '-oic acid'. Carboxyl carbon is always given number one while numbering the carbon atoms of the parent chain.



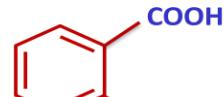
Aromatic carboxylic acids are named by adding the suffix **-carboxylic acid** in place of 'e' of the hydrocarbon name the suffix "**-oic acid**" can be used.



**Benzoic acid**



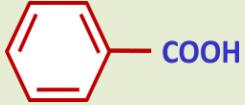
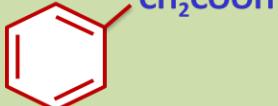
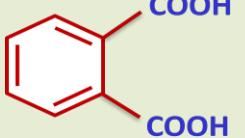
**2-phenylethanoic acid**



**Benzene-1, 2-dicarboxylic acid**

Dicarboxylic acids are named as alkanedioic acids in the IUPAC system. Simple dicarboxylic acids having the general formula  $\text{HO}_2\text{C} - (\text{CH}_2)_n - \text{CO}_2\text{H}$  where ( $n = 0$  to  $5$ ) are known by the common names: Oxalic ( $n = 0$ ), Malonic ( $n = 1$ ), Succinic ( $n = 2$ ), Glutaric ( $n = 3$ ), Adipic ( $n = 4$ ) and Pimelic ( $n = 5$ ) acids.

Common names such as these can be trouble some to remember, so a catchy phrase, have been devised. For this group of compounds such phrase is “**O**h **M**y **S**uch **G**ood **A**pple **P**ie”.

Structure	Common name	IUPAC name
$\text{HCOOH}$	Formic acid	Methanoic acid
$\text{CH}_3\text{COOH}$	Acetic acid	Ethanoic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Propionic acid	Propanoic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Butyric acid	Butanoic acid
$(\text{CH}_3)_2\text{CHCOOH}$	Isobutyric acid	2-Methylpropanoic acid
$\text{HOOC} - \text{COOH}$	Oxalic acid	Ethanedioic acid
$\text{HOOC} - \text{CH}_2 - \text{COOH}$	Malonic acid	Propanedioic acid
$\text{HOOC} - (\text{CH}_2)_2 - \text{COOH}$	Succinic acid	Butanedioic acid
$\text{HOOC} - (\text{CH}_2)_3 - \text{COOH}$	Glutaric acid	Pentanedioic acid
$\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$	Adipic acid	Hexanedioic acid
$\text{HOOC} - \text{CH}_2 - \text{CH}(\text{COOH}) - \text{CH}_2 - \text{COOH}$	---	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzene carboxylic acid (Benzoic acid)
	Phenylacetic acid	2-phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

### Methods of Preparation of Carboxylic Acids:

#### a. From primary alcohols :

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ( $\text{KMnO}_4$ ) in neutral, acidic or alkaline media.

The acid is first obtained as its potassium salt, which on treatment with a mineral acid gives the carboxylic acid.

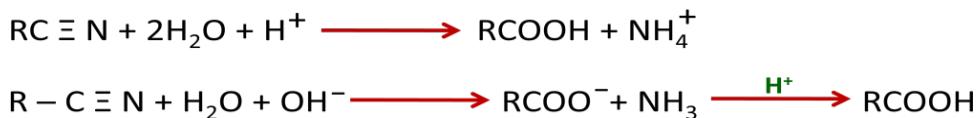


Oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  in acidic medium often gives some amount of esters. Hence the oxidation by  $\text{KMnO}_4$  is preferred.

Readily available aldehydes can also be used to obtain carboxylic acids, which may be oxidised even by milder oxidising agents.

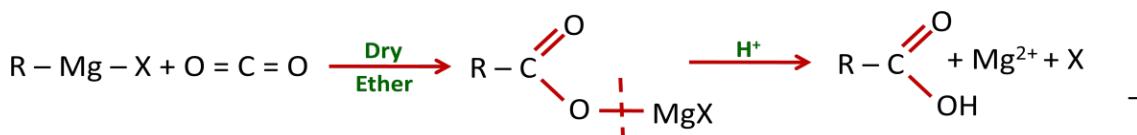
### b. From nitriles:

Hydrolysis of nitriles with aqueous acid or alkali gives carboxylic acids.



### c. From Grignard reagent:

Grignard reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on acidification with mineral acids.



### Physical properties:

#### a. Physical state:

1. The first three acids are colourless, pungent-smelling liquids. The acids from butyric to nonanoic are oily liquids. Butyric acid has odour of rancid butter. The acids higher than decanoic acid are odourless

solids.

## **2. Boiling points:**

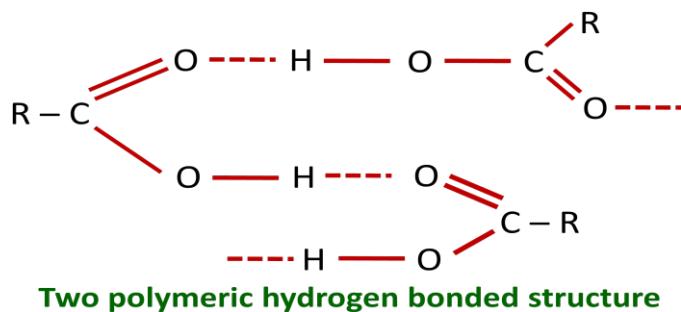
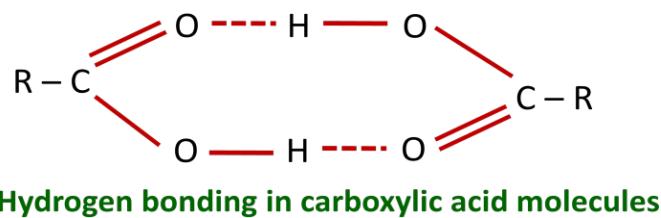
Organic acids have high boiling points. It is due to

- a. Intermolecular hydrogen bondings

- b. Strong van der Waals forces due to their polar nature

Lower members exist as

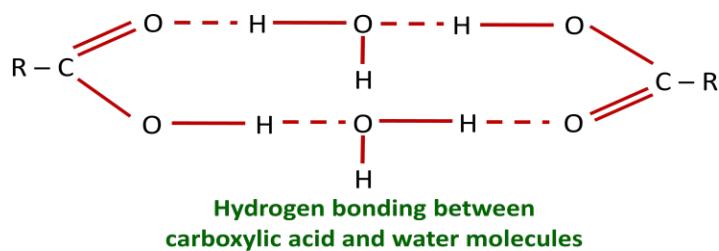
- a. Dimers in the aqueous solutions and vapour phase
- b. Polymers in the liquid phase



Higher boiling points of acids relative to alcohols are due to the higher degree and strength of hydrogen bonding in them (because of the presence of two oxygen atoms)

### 3. Solubility:

The first few members are highly soluble in water. This solubility is due to the hydrogen bonding between carboxylic acid and water molecules.



The solubility decreases with the increase in molecular mass.

Aromatic acids like benzoic acid are less soluble in water due to large number of C-atoms in them. Carboxylic acids are soluble in organic solvents like alcohol, ether and benzene.

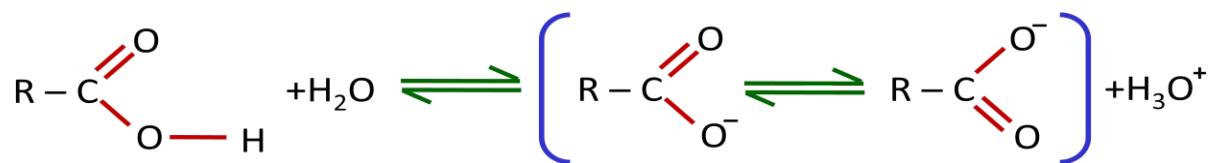
### **Chemical properties:**

The reactions of carboxylic acids are classified as follows

- a. Reactions involving cleavage of O – H bonds
- b. Reactions involving cleavage of C – OH bonds
- c. Reactions involving – COOH groups
- d. Substitution reaction in hydrocarbon part

### **Acidic nature of carboxylic acids :**

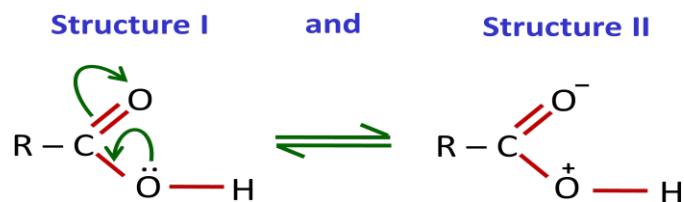
The aqueous solutions of carboxylic acids dissociate as follows:



Since they liberate hydrogen ions in solution, they are acidic. However they are weaker than mineral acids like HCl, HNO<sub>3</sub> etc. But stronger acids than alcohols and phenols.

Carboxylic compounds are the most acidic among all the organic compounds. This can be explained as follows:

Carboxylic acids as well as carboxylate ion both are stabilized by resonance. However, carboxylate ion is more stabilized by resonance because its contributing structures are exactly identical. The contributing structures of carboxylic acid involve charge separation.



Since carboxylate ion is more stabilized by resonance than carboxylic acid therefore equilibrium in above reaction lies very much in forward direction i.e., in favour of ionized form. Hence carboxylic acids behave as strong acids.

Carboxylic acids are stronger acids than phenols. It can be understood by comparing the hybrid structures of carboxylate ion and phenoxide ions. In carboxylate ion, the negative charge is equally distributed over two electronegative atoms (oxygen atoms) while in phenoxide ion, it is present only on one oxygen atom. Thus, carboxylate ion is more stabilized as compared to phenoxide ion. Hence, carboxylic acids ionize to the greater extent than phenols.

furnishing higher concentration of  $\text{H}^+$  ions. Therefore carboxylic acids behave as stronger acids than phenols.



### a. Reactions involving cleavage of O–H bonds:

All carboxylic acids release proton to form more stable carboxylate ion. These all reactions proves that acidity of carboxylic acids.

1. Carboxylic acids liberate hydrogen with active metals like Mg, Ca, Zn, Fe etc.,



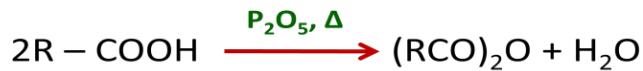
2. They also react with metal hydroxides, carbonates and bicarbonates



### b. Reactions involving cleavage of C –OH bonds:

1. Formation of anhydride (dehydration):

Carboxylic acids on heating with a phosphorus pentoxide to form acid anhydrides



## 2. Esterification (acid to ester):

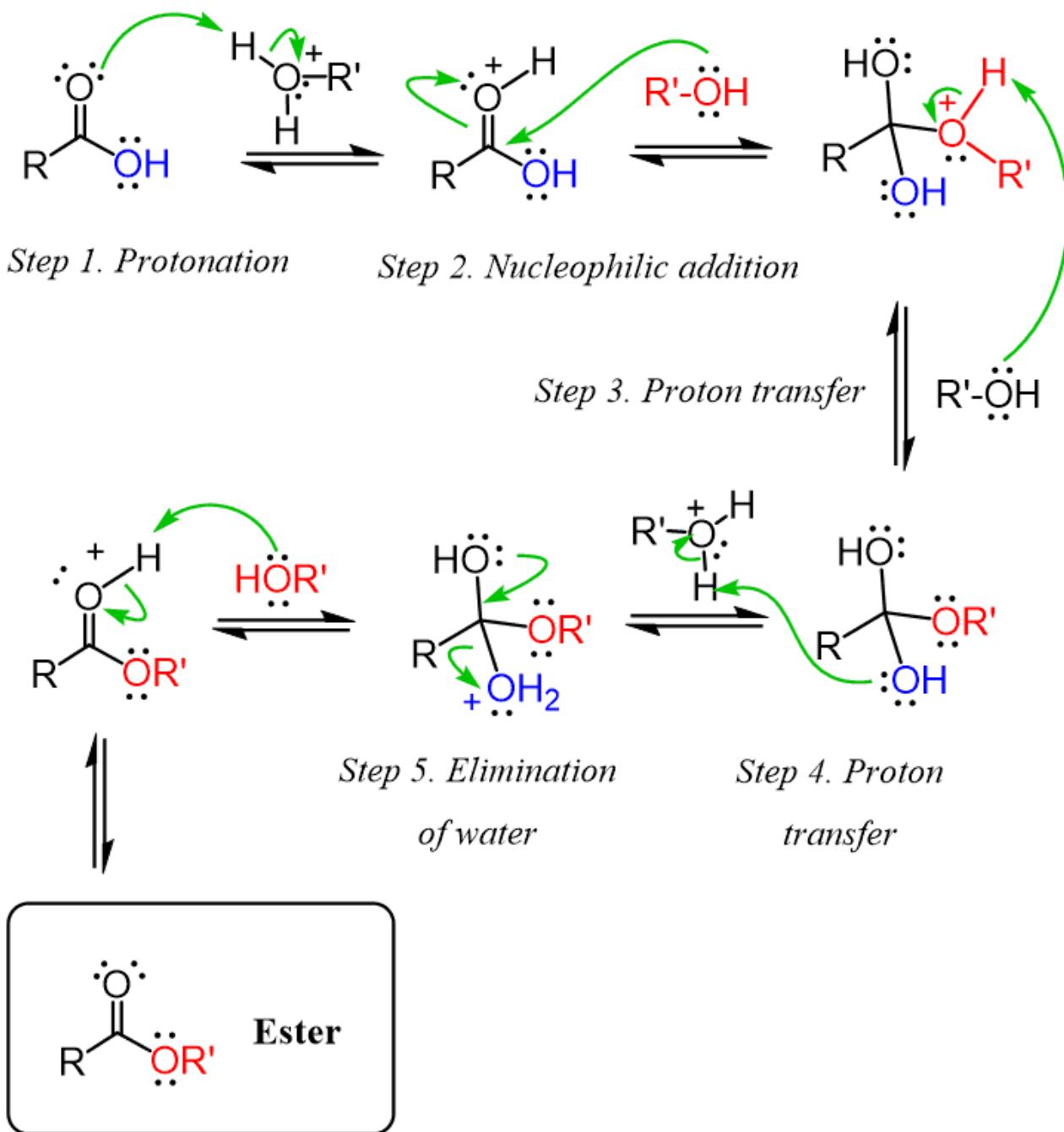
Carboxylic acids react with alcohols in the presence of few drops of conc.  $H_2SO_4$  to form esters (**see alcohols unit**)



When dry hydrogen chloride is used in this reaction, we called it **Fischer Esterification**.

# Mechanism :

## Fischer Esterification Mechanism



### 3. Action with $\text{SOCl}_2$ :

Carboxylic acids react with  $\text{SOCl}_2$  to form acid chlorides.



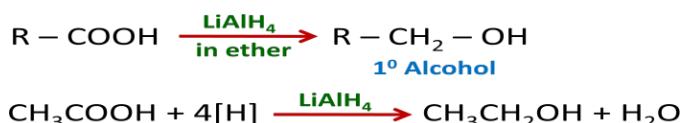
Example :



## C, Reaction involving -COOH group:

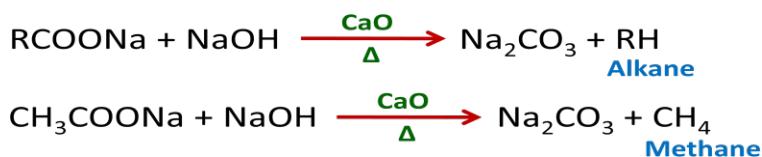
### 4. Reduction:

Acids are not easily reduced by catalytic hydrogenation or with sodium and ethanol. Strong reducing agent as lithium aluminium hydride reduces an acid into primary alcohol.



### 5. Decarboxylation:

Simple monocarboxylic acids do not lose carbon dioxide (decarboxylation) when heated alone. However, when sodium salt of the carboxylic acids are heated with soda lime ( $\text{NaOH} + \text{CaO}$ ), they yield hydrocarbons.

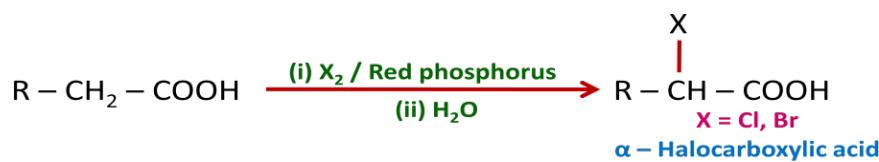


The reaction is known as Kolbe's electrolysis.

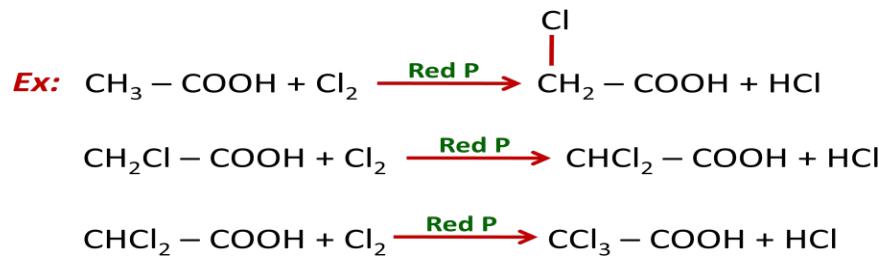
### c. Substitution reactions in hydrocarbon part:

#### 1. Halogenations:

When carboxylic acids react with chlorine or bromine in the presence of red phosphorous, the  $\alpha$ -hydrogen atoms are replaced by halogen atoms. It is called Hell-Volhard-Zelinsky (HVZ) reaction.



Acetic acid reacts with chlorine in presence of red phosphorus to form chloro acetic acid, dichloro acetic acid or trichloro acetic acid depending on the quantity of chlorine reacting.



**Review questions:**

**Example set:**

1. The IUPAC name of  $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \overset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{COOH}$  is

- a. 3-ethyl-2-methyl pentanoic acid
- b. 2 -ethyl-3-methyl pentanoic acid
- c. 3-ethyl-4-methyl pentanoic acid
- d. 2-methyl-3-ethyl pentanoic acid

**Solution:** c)

2. When \_\_\_\_\_ is treated with Grignard reagent, followed by hydrolysis with an acid, it forms carboxylic acid
- a.  $\text{CH}_2 = \text{CH}_2$
  - b.  $\text{CO}_2$
  - c.  $\text{CH}_3 - \text{CO} - \text{CH}_3$
  - d.  $\text{CH}_3\text{CHO}$

**Solution:** b)

3. Which compound is likely to have the highest boiling point
- a.  $\text{CH}_3\text{CH}_3$
  - b.  $\text{CH}_3\text{OCH}_3$
  - c.  $\text{CH}_3\text{CH}_2\text{OH}$
  - d.  $\text{CH}_3\text{COOH}$

**Solution:** d)

4. Acetic acid undergoes reduction with  $\text{LiAlH}_4$  to give finally \_
- a. Ethanol
  - b. Ethane
  - c. Ethanal
  - d. Ethyne

**Solution:** a)

5. Which of the following reagents will convert acetic acid into acetyl chloride
- a.  $\text{NaCl}$
  - b. Conc.  $\text{HCl} / \text{ZnCl}_2$
  - c.  $\text{SOCl}_2$
  - d.  $\text{HCl}$

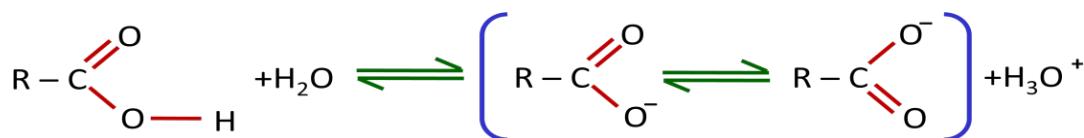
**Solution:** c)

6. Discuss about acidity of carboxylic acids

**Solution:**

## Acidic nature:

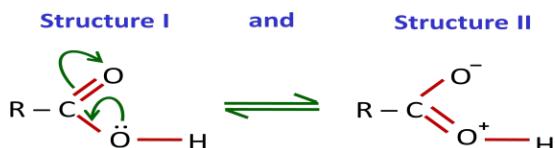
The aqueous solutions of carboxylic acids dissociate as follows:



Since they liberate hydrogen ions in solution, they are acidic. However they are weaker than mineral acids like HCl, HNO<sub>3</sub> etc., But stronger acids than alcohols and phenols.

Carboxylic compounds are most acidic among all the organic compounds. This can be explained as follows:

Carboxylic acids as well as carboxylate ion both are stabilized by resonance. However, carboxylate ion is more stabilized by resonance because its contributing structures are exactly identical. The contributing structures of carboxylic acid involve charge separation.



Since carboxylate ion is more stabilized by resonance than carboxylic acid therefore equilibrium in above reaction lies very much in forward direction *i.e.*, in favour of ionized form. Hence carboxylic acids behave as strong acids.

Carboxylic acids are stronger acids than phenols. It can be understood by comparing the hybrid structures of carboxylate ion and phenoxide ions. In carboxylate ion, the negative charge is equally distributed over two electronegative atoms (oxygen atoms) while in phenoxide ion, it is present only on one oxygen atom. Thus, carboxylate ion is more stabilized as compared to phenoxide ion. Hence, carboxylic acids ionize to the greater extent than phenols

furnishing higher concentration of  $H^+$  ions. Therefore carboxylic acids behave as stronger acids than phenols.



7. Write any two methods of preparation of carboxylic acids

**Solution:**

#### Methods of Preparation of Carboxylic Acids:

##### 1. From primary alcohols and aldehydes:

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ( $KMnO_4$ ) in neutral, acidic or alkaline media.

The acid is first obtained as its potassium salt, which on treatment with mineral acid gives the carboxylic acid.

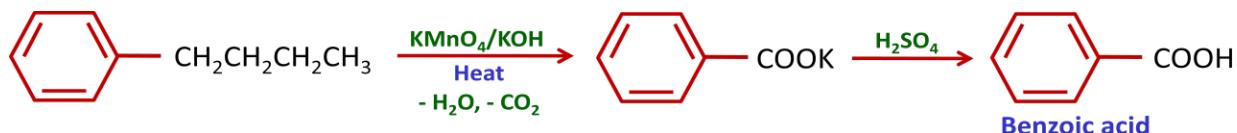


Oxidation with  $K_2Cr_2O_7$  or  $CrO_3$  in acidic medium often gives some amount of esters. Hence the oxidation by  $KMnO_4$  is preferred.

Readily available aldehydes can also be used to obtain carboxylic acids, which may be oxidised even by milder oxidising agents.

## 2. From alkyl benzenes and alkenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline  $\text{KMnO}_4$ . The  $-\text{COOH}$  group formed is always attached to the aromatic ring and position of  $-\text{COOH}$  group indicates the position of original side chain in the starting arene (alkyl benzene).



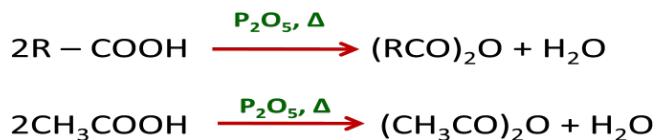
8. Write the reaction involving cleavage of C – OH bond in carboxylic acids

**Solution:**

### a. Reactions involving cleavage of C – OH bonds:

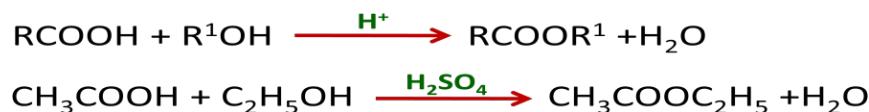
#### 1. Formation of anhydride (dehydration):

Acid on heating with a phosphorus pentoxide to form acid anhydrides



#### 2. Esterification (acid to ester):

Carboxylic acids react with alcohols in the presence of few drops of conc.  $\text{H}_2\text{SO}_4$  to form esters (see alcohols unit)



When dry hydrogen chloride is used in this reaction, we called it Fischer Esterification

### 3. Action with $\text{PCl}_3$ , $\text{PCl}_5$ or $\text{SOCl}_2$ [acid to acid chloride]:

Carboxylic acids react with  $\text{PCl}_3$ ,  $\text{PCl}_5$  or  $\text{SOCl}_2$  to form acid chlorides



The byproducts with thionyl chloride are gases whereas with  $\text{PCl}_5$  and  $\text{PCl}_3$ , we have phosphorous oxychloride (volatile liquid) and phosphorous acid (non-volatile) respectively. Thus, if the boiling point of the acid chloride is higher than the boiling point of thionyl chloride, then thionyl chloride is preferred because the resulting acid chloride can be separated easily from the excess of thionyl chloride by distillation.

### 4. Reaction with ammonia:

Carboxylic acids is heated with ammonia to form amides



#### Problem set:

1. Aliphatic carboxylic acids are isomeric with
  - a. Esters
  - b. Ethers
  - c. Ketones
  - d. Acid anhydride

**Solution:** a)

2. In  $\alpha$ -halogenation of aliphatic acids, the catalyst used is
  - a.  $P_4$
  - b. Zn
  - c.  $FeCl_3$
  - d. Al

**Solution:** a)

3. When ammonium formate is heated, it gives
  - a. Acetaldehyde
  - b. Acetic acid
  - c. Formamide
  - d. Formaldehyde

**Solution:** c)

4. Acetic acid reacts with methyl alcohol in the presence of an acid catalyst to give
  - a. Methyl formate
  - b. Ethyl formate
  - c. Methyl acetate
  - d. Ethyl acetate

**Solution:** c)

5. Butyric acid reacts with  $PCl_5$  to give
  - a.  $\alpha$ -chloro butyric acid
  - b. Butyryl chloride
  - c. 1-chlorobutane
  - d.  $\alpha, \alpha$ -dichloro butyric acid

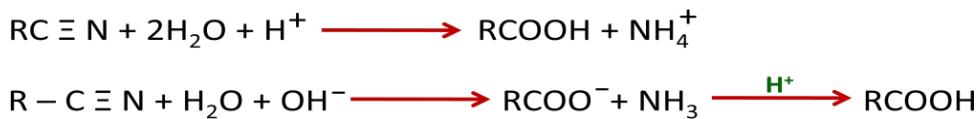
**Solution:** b)

6. How is acetic acid obtained using a
  - a. Nitriles
  - b. Grignard reagent

**Solution:**

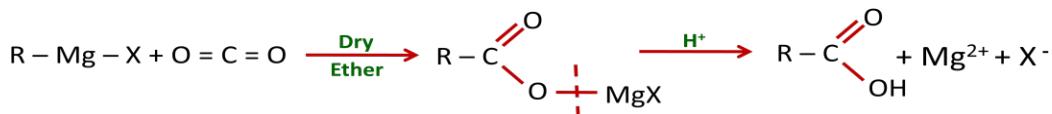
a. From nitriles:

Hydrolysis of nitriles with aqueous acid or alkali gives carboxylic acids.



b. From Grignard's reagent:

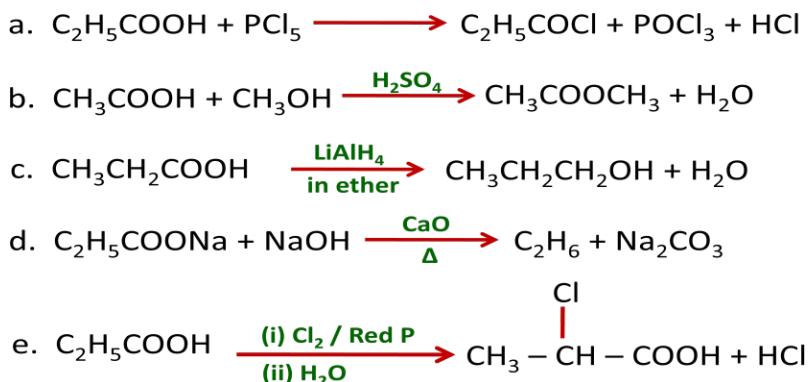
Grignards reagents react with carbon dioxide to form salts of carboxylic acids which give carboxylic acids on acidification with mineral acids.



7. Give the major organic product in the following reactions

- $\text{C}_2\text{H}_5\text{COOH} + \text{PCl}_5 \longrightarrow$
- $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \longrightarrow$
- $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{in ether}]{\text{LiAlH}_4} \longrightarrow$
- $\text{C}_2\text{H}_5\text{COONa} + \text{NaOH} \xrightarrow[\Delta]{\text{CaO}} \longrightarrow$
- $\text{C}_2\text{H}_5\text{COOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) Cl}_2 / \text{Red P}} \longrightarrow$

**Solution:**



8. Why boiling points of carboxylic acid are higher than those of alcohols or ethers of comparable molecular weights

**Solution:**

For example, acetic acid, n-propyl alcohol and ethyl methyl ether are having same molecular weights (60)

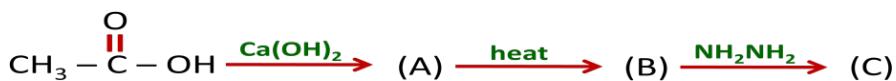
Acetic acid has more boiling point than n-propanol and ethyl methyl ether. It is due to intermolecular hydrogen bonding and also it exists as a dimer in acetic acid.

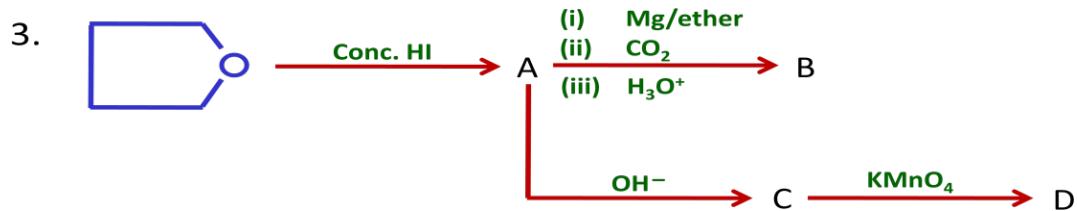


n-propanol has inter molecular hydrogen bonds only.

**Exercise questions:**

- How will you synthesize acetic acid from acetylene
- Identify (A), (B) and (C) in the following reaction sequence

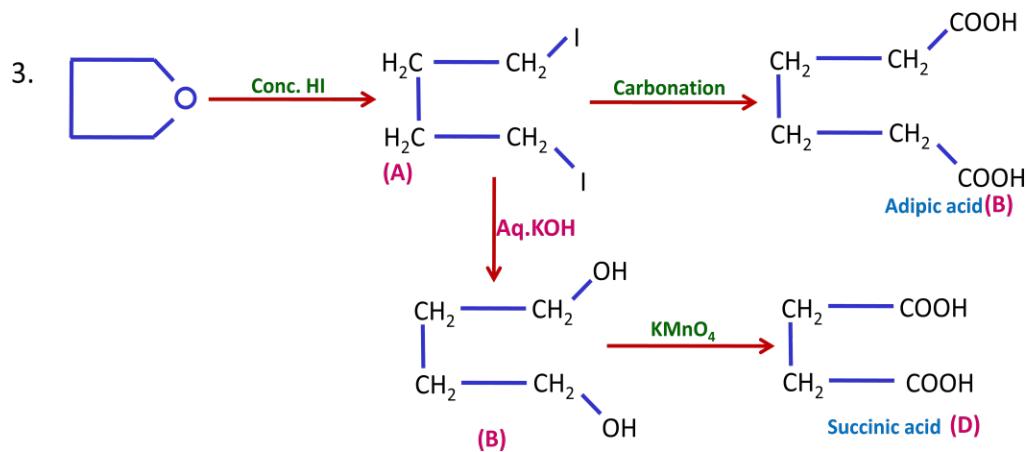
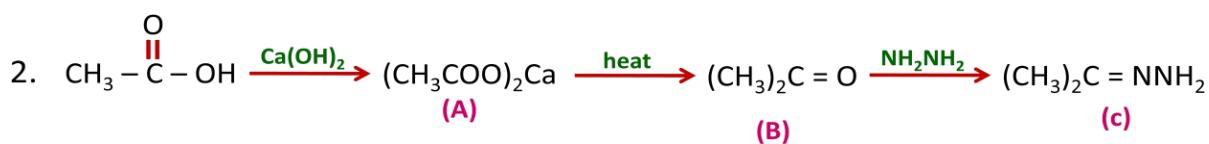
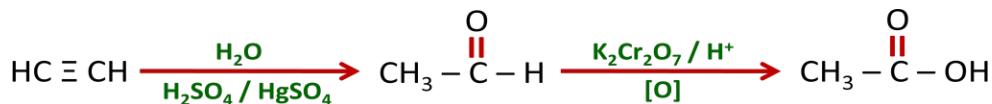




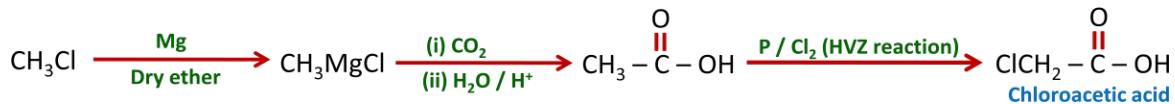
4. How will you synthesise chloroacetic acid from methyl chloride (in 4 steps)  
 5. Show how each of the following compounds can be converted to benzoic acid  
 a. Ethylbenzene  
 b. Acetophenone  
 c. Phenylethene (styrene)

### Solutions to exercise questions:

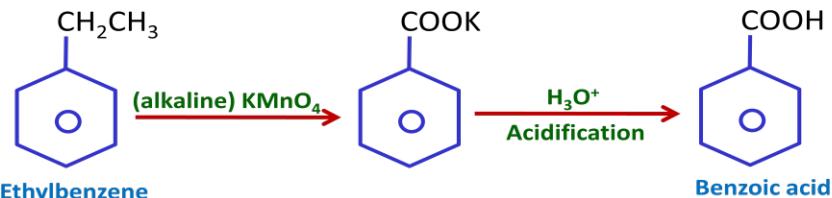
1. Following steps are involved



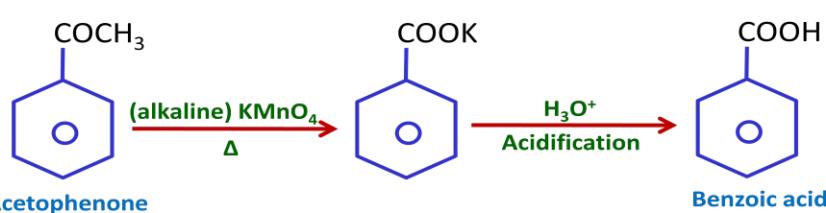
4. Following steps are involved



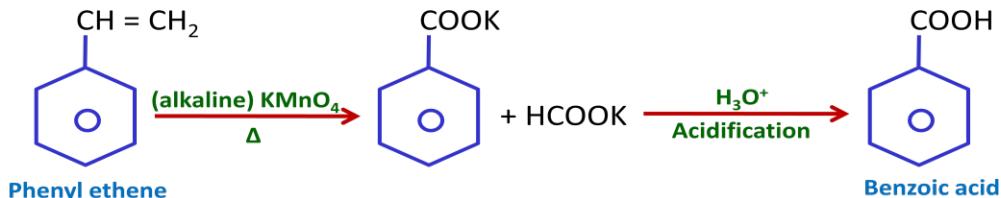
5. a.



b.



c.



### IIT Questions:

1. Which of the following orders of acid strength is correct?

- a. RCOOH > ROH > HOH > HC ≡ CH
- b. RCOOH > HOH > ROH > HC ≡ CH
- c. RCOOH > HOH > HC ≡ CH > ROH
- d. RCOOH > HC ≡ CH > HOH > ROH

2. Which of the following orders of base strength is correct?

- a. R<sup>-</sup> > NH<sub>2</sub><sup>-</sup> > HC ≡ C<sup>-</sup> > RCOO<sup>-</sup>
- b. R<sup>-</sup> > NH<sub>2</sub><sup>-</sup> > RCOO<sup>-</sup> > HC ≡ C<sup>-</sup>
- c. R<sup>-</sup> > RCOO<sup>-</sup> > NH<sub>2</sub><sup>-</sup> > HC ≡ C<sup>-</sup>
- d. HC ≡ C<sup>-</sup> > NH<sub>2</sub><sup>-</sup> > RCOO<sup>-</sup> > R<sup>-</sup>

3. Which of the following orders of acid strength is correct?

- a)  $\text{CH}_3\text{CH}_2\text{CHCOOH} < \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CH}_2\text{COOH} \end{array} \text{Cl} < \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{Cl} \end{array} < \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{Cl} \end{array}$
- b)  $\text{CH}_3\text{CH}_2\text{CHCOOH} > \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \end{array} \text{Cl} > \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{Cl} \end{array} > \begin{array}{c} \text{CH}_3\text{CHCH}_2\text{COOH} \\ | \\ \text{Cl} \end{array}$
- c)  $\text{CH}_3\text{CH}_2\text{CHCOOH} > \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \end{array} \text{Cl} > \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{Cl} \end{array} > \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{Cl} \end{array}$
- d)  $\text{CH}_3\text{CH}_2\text{CHCOOH} < \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{CH}_3\text{CHCH}_2\text{COOH} \end{array} \text{Cl} < \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{Cl} \end{array} < \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\ | \\ \text{Cl} \end{array}$

4. The relative order of esterification of acids is

- a.  $\text{RCH}_2\text{COOH} > \text{R}_2\text{CHCOOH} > \text{R}_3\text{CCOOH}$
- b.  $\text{RCH}_2\text{COOH} < \text{R}_2\text{CHCOOH} < \text{R}_3\text{CCOOH}$
- c.  $\text{RCH}_2\text{COOH} < \text{R}_3\text{CCOOH} < \text{R}_2\text{CHCOOH}$
- d.  $\text{R}_3\text{CCOOH} > \text{RCH}_2\text{COOH} > \text{R}_2\text{CHCOOH}$

5. Acetic acid differs from formic acid in that

- a. Acetic acid is stable to heat
- b. formic acid is stable to heat
- c. Acetic acid acts as a reducing agent
- d. Acetic acid shows positive test with tollens reagent

6. The Hell-Volhard-Zelinsky reaction is used in the synthesis of

- a. Aldehydes
- b.  $\alpha$ -haloacids
- c. acid halides
- d. ketones

7. Which of the following sequences is correct ?

- a.  $\text{pKa}(\text{p-O}_2\text{NC}_6\text{H}_4\text{COOH}) > \text{pKa}(\text{C}_6\text{H}_5\text{COOH}) > \text{pKa}(\text{p-HOC}_6\text{H}_4\text{COOH})$
- b.  $\text{pKa}(\text{p-O}_2\text{NC}_6\text{H}_4\text{COOH}) < \text{pKa}(\text{C}_6\text{H}_5\text{COOH}) < \text{pKa}(\text{p-HOC}_6\text{H}_4\text{COOH})$
- c.  $\text{pKa}(\text{p-O}_2\text{NC}_6\text{H}_4\text{COOH}) > \text{pKa}(\text{C}_6\text{H}_5\text{COOH}) < \text{pKa}(\text{p-HOC}_6\text{H}_4\text{COOH})$
- d.  $\text{pKa}(\text{p-O}_2\text{NC}_6\text{H}_4\text{COOH}) < \text{pKa}(\text{C}_6\text{H}_5\text{COOH}) > \text{pKa}(\text{p-HOC}_6\text{H}_4\text{COOH})$

8. Which of the following sequences of rates of alkaline hydrolysis of esters is correct?

- a.  $\text{CH}_3\text{CH}_2\text{COOCH}_3 < (\text{CH}_3)_2\text{CHCOOCH}_3 < (\text{CH}_3)_3\text{CCOOCH}_3$
- b.  $\text{CH}_3\text{CH}_2\text{COOCH}_3 > (\text{CH}_3)_2\text{CHCOOCH}_3 > (\text{CH}_3)_3\text{CCOOCH}_3$
- c.  $\text{CH}_3\text{CH}_2\text{COOCH}_3 > (\text{CH}_3)_2\text{CHCOOCH}_3 < (\text{CH}_3)_3\text{CCOOCH}_3$
- d.  $\text{CH}_3\text{CH}_2\text{COOCH}_3 < (\text{CH}_3)_2\text{CHCOOCH}_3 > (\text{CH}_3)_3\text{CCOOCH}_3$

9. When propionic acid is treated with aqueous sodium bicarbonate,  $\text{CO}_2$  is liberated. The C of  $\text{CO}_2$  comes from :

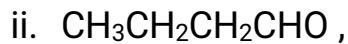
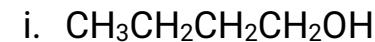
- a. Methyl group
- b. Carboxylic acid group
- c. Methylene group

d. Bicarbonate

10. Benzoyl chloride is prepared from benzoic acid by :

- a.  $\text{Cl}_2, h\nu$
- b.  $\text{SO}_2\text{Cl}_2$
- c.  $\text{SOCl}_2$
- d.  $\text{Cl}_2, \text{H}_2\text{O}$

11. Identify the correct order of boiling points of the following compounds :



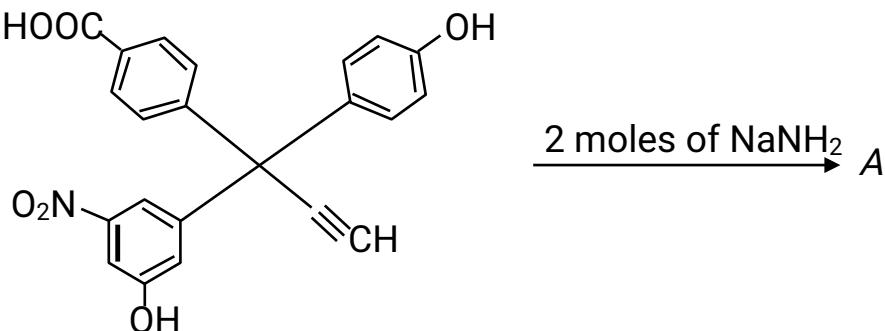
OH a. 1 > 2 > 3

b. 3 > 1 > 2

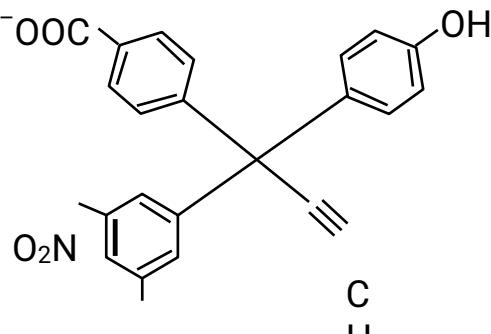
c. 1 > 3 > 2

d. 3 > 2 > 1

12.  $\text{HOOC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_3(\text{NO}_2)-\text{OH} + \text{CH}_3\text{C}_6\text{H}_4-\text{C}_6\text{H}_3(\text{NO}_2)-\text{CH}\equiv\text{C}$

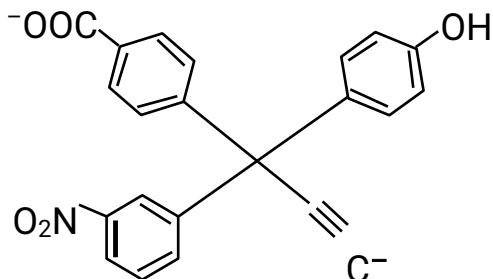


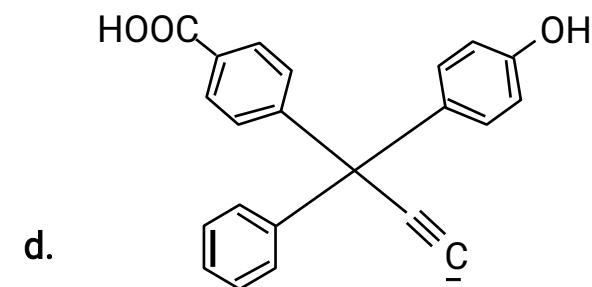
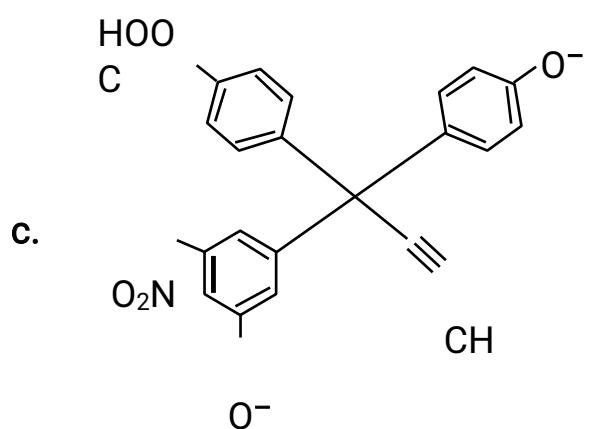
a.



O  
-

b.





13. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be :

14. Give reasons for the following in one or two sentences.

"Acetic acid be halogenated in the presence of P and Cl<sub>2</sub>, but formic acid cannot be halogenated in the same way."

15. Give reason in one or two sentences for the following :

"Formic acid is a stronger acid than acetic acid."

16. A liquid X, having a molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> is hydrolysed with water in the presence of an acid to give a carboxylic acid Y and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z.

17. How will you bring about the following conversions?

" Ethanoic acid to a mixture of methanoic acid and diphenyl ketone."

18. Arrange the following as stated :

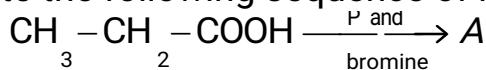
"Increasing order of acidic strength."

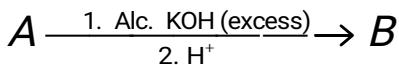
CICH<sub>2</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, CICH<sub>2</sub>CH<sub>2</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>CHCOOH, CH<sub>3</sub>COOH

19. Give reason for the following

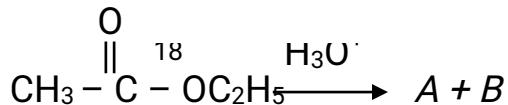
"In acylium ion the structure R – C ≡ O<sup>+</sup> is more stable than R – C<sup>+</sup>=O"

20. Complete the following sequence of reactions with appropriate structures :





21. Write the structures of the products A and B

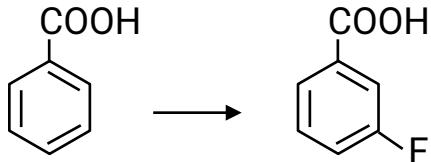


22. Five isomeric *para*-disubstituted aromatic compounds A to E with molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  were given for identification.

Based on the following observations, give structures of the compounds:

- i) Both A and B form a silver mirror with Tollen's reagent; also, B gives a positive test with  $\text{FeCl}_3$  solution.
- ii) C gives positive iodoform test.
- iii) D is readily extracted in aqueous  $\text{NaHCO}_3$  solution.
- iv) E on acid hydrolysis gives 1, 4 dihydroxy benzene.

23. Convert (in not more than 3 steps)



24. Compound A of molecular formula  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exists in keto form and predominantly in enolic form B. On oxidation with  $\text{KMnO}_4$ , A gives m-chlorobenzoic acid. Identify A and B.

### Solutions:

1. b

The order of acidic strength is  $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH}$

Electron releasing alkyl group R in ROH makes it lesser acidic than

2. a  $\text{H}_2\text{O}$

The base strength follows the reverse order as shown by the corresponding acids. The acids are RH, NH<sub>3</sub>, HC ≡ CH and RCOOH. Its order is

RCOOH > HC ≡ CH > NH<sub>3</sub> > RH. Hence, the correct order of the conjugate bases is



Nearer the chlorine to the -COOH group, stronger the acidity.

Hence, the correct order is



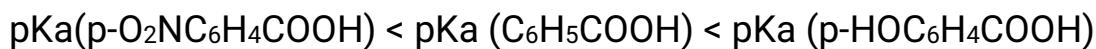
Increasing crowdedness near the site of esterification decreases the rate of esterification. Hence, the correct order is



6. b Acetic acid differs from formic acid in that acetic acid is stable to heat.

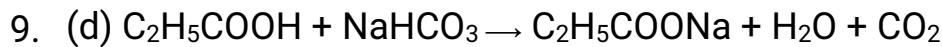
7. b The Hell-Volhard-Zelinsky reaction is used in the synthesis of α-haloacids.

Electron-releasing group makes benzoic acid a weaker acid while electron-attracting group makes it a stronger acid, lesser the value of pKa. Hence, the correct order is

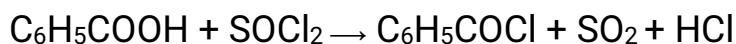


8. b

The correct order of alkaline hydrolysis is



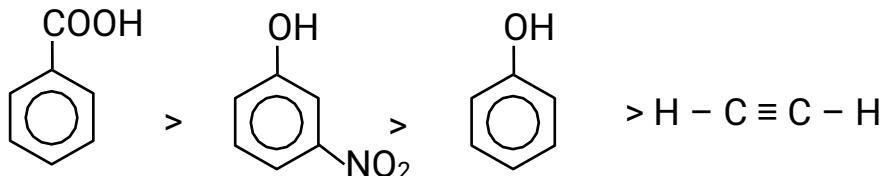
10.(c) SOCl<sub>2</sub> readily replaces -OH group of the acids by -Cl atom forming acid chloride.



Benzoic acid                    benzoyl chloride

11. (b) In these *C* forms dimer due to hydrogen bonds and compound *A*, form hydrogen bonds. Hence in these stronger hydrogen bond is in compound *C* than compound *A*. Compound *B* does not form hydrogen bond. Thus, they follow the following order of mol. wt.  $3 > 1 > 2$ . So they have same order in their boiling point.

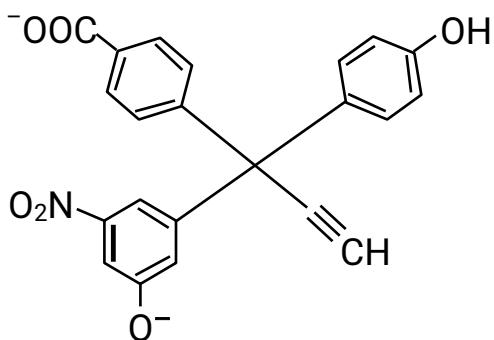
12. (a) The acidic strength of the attached groups is in the following order:



(Note: Due to attachment of electron attractive group acidic strength increases and carboxylic acids are more acidic than phenols.)

The two moles of  $\text{NH}^-$  ions will abstract two moles of a most acidic

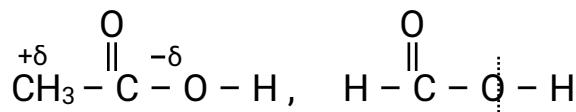
$^2$   
hydrogen out of the four moles of hydrogen present per mole of the given acidic compounds. Hence after abstraction of two moles of hydrogen the obtained product will be as shown:



13. When optically active acid reacts with racemic mixture of an alcohol, it forms two types of isomeric esters. In each, the configuration of the chiral center of acid will remain the same.  
So, the mixture will be optically active.

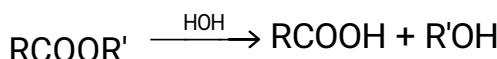
14. Because acetic acid has  $\alpha$ -hydrogen atoms which can replace by halogen but formic acid does not have  $\alpha$ -hydrogen.

15.

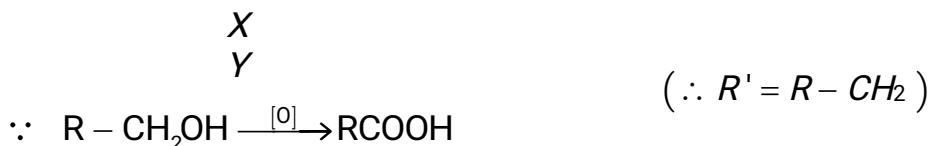
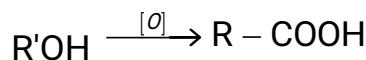
**Acetic acid + I effect**

Acetic acid is weaker acid than formic acid due to + I effect, Hence, formic acid is stronger acid than acetic acid.

16. Since  $X$  is hydrolysed to give an acid  $Y$  and an alcohol  $Z$  and thus,  $X$  is an ester  $R - COOR'$ .

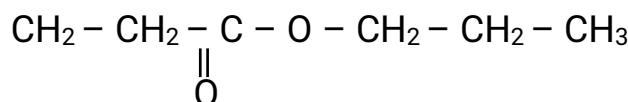


Oxidation of alcohol  $Z$  gives an acid  $Y$ , it shows that  $Z$  is a primary alcohol, i.e.,  $R - CH_2OH$



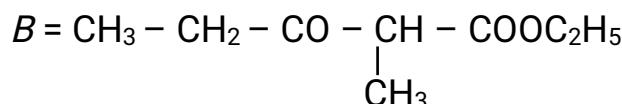
$$\text{So, } X = R - COOCH_2R$$

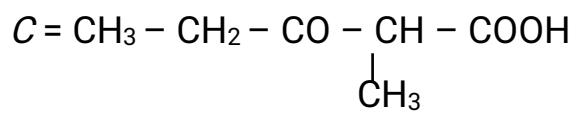
$\therefore X$  is

**Propyl propanoate**

$$\text{Hence, } A = \text{CH}_3 - \text{CH}_2 - \text{COOC}_2\text{H}_5$$

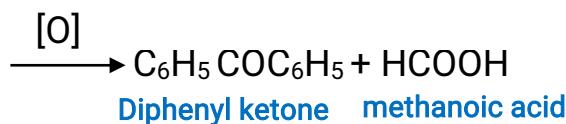
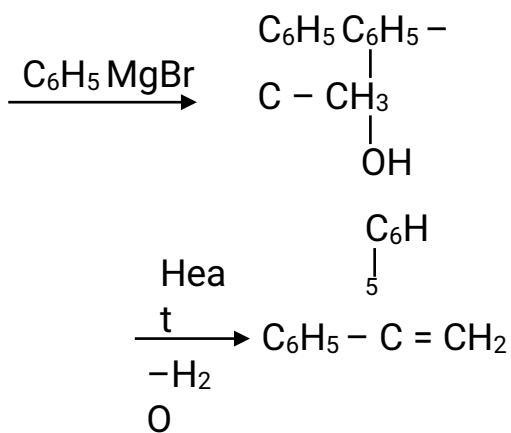
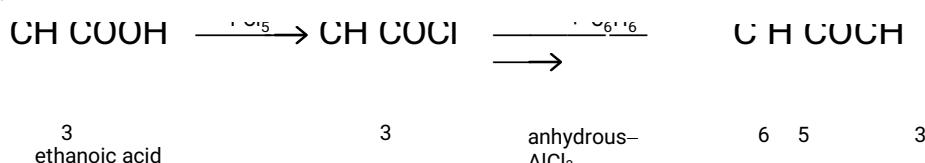
**Ethyl propanoate**

**Ethyl (2-methyl, 1,3-ketopentanoate)**

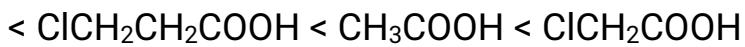
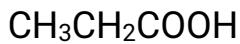


2-methyl, 3-keto, pentanoic acid

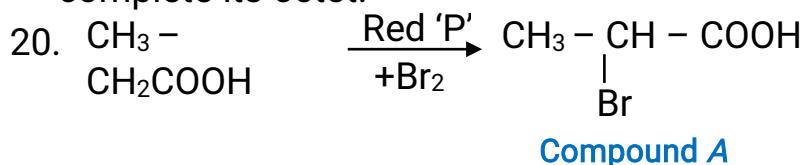
17.



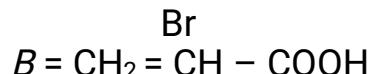
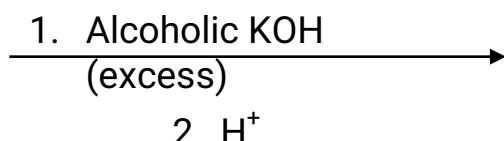
18. Increasing order of acid strength



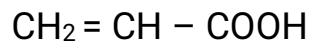
19. The structure  $R - C \equiv O^+$  is more stable because in it all elements have complete their octet, while in  $R - C^+ = O$ , C – atom does not have complete its octet.



(This bromination takes place on  $\alpha$ -carbon atom hence, in it  $\alpha$ -hydrogen is displaced.)

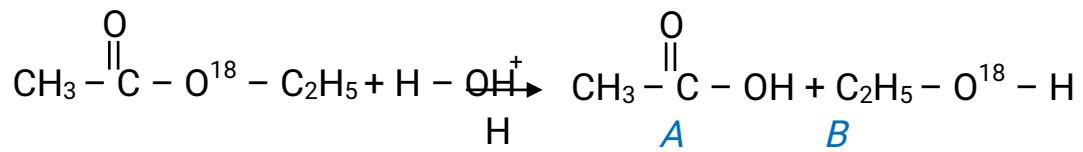


Thus Compound A =  $\text{CH}_3 - \underset{|}{\text{CH}} - \text{COOH}$



Compound *B*

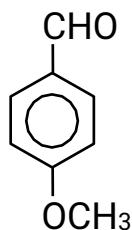
21.



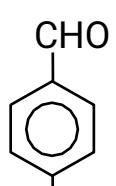
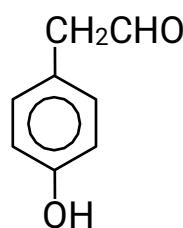
22. Five isomeric *p*-disubstituted aromatic compound *A* to *E* with molecular formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>, give following observations:

- i. Both compound *A* and *B* form a silver mirror with Tollen's reagent, thus they have aldehydic group in their structures.

**Compound 'A'**

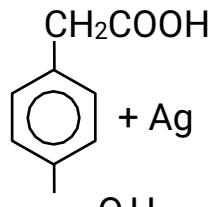
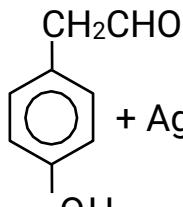
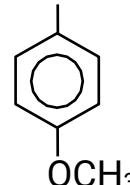


**Compound 'B'**



**Silver mirror**

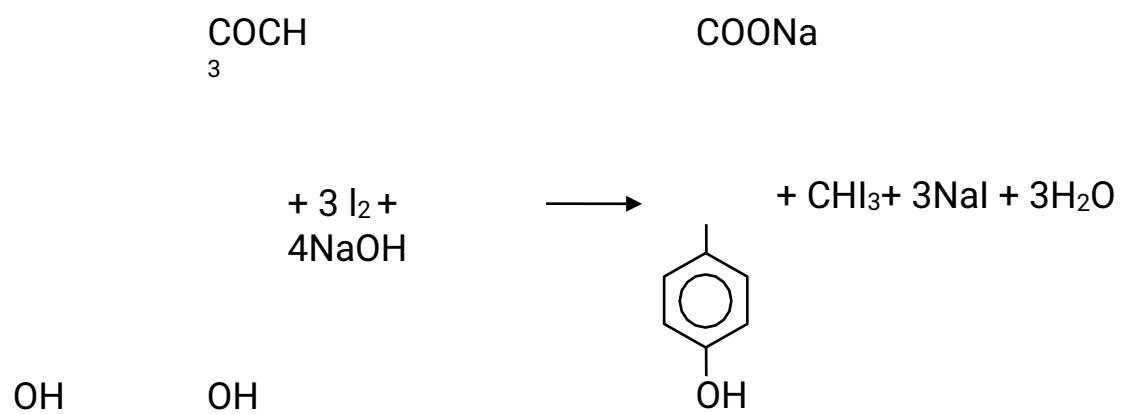
OCH<sub>3</sub>  
Tollen's  
reagent



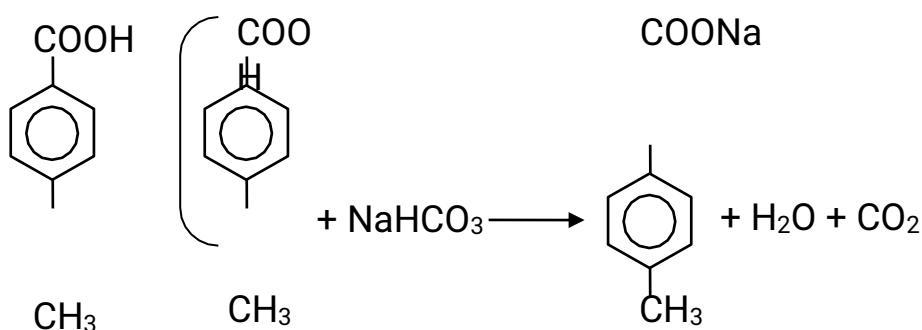
In these compound *B* gives positive test with FeCl<sub>3</sub> solution so it must have phenolic group in its structure. Hence, compound *A* is *p*-methoxy benzaldehyde and *B* is *p*-hydroxy phenyl acetaldehyde

- ii. Compound *C* gives positive iodoform test, so it must have CH<sub>3</sub>CO- group in its structure. Hence compound *C* is *p*-hydroxyphenyl methyl ketone



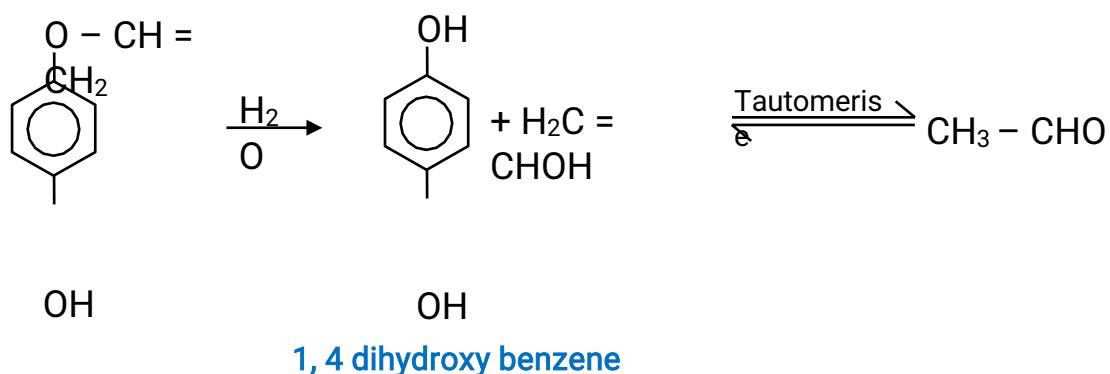


iii. Compound *D* is readily extracted in aqueous  $\text{NaHCO}_3$ , so it must have  $-\text{COOH}$  group in its structure.

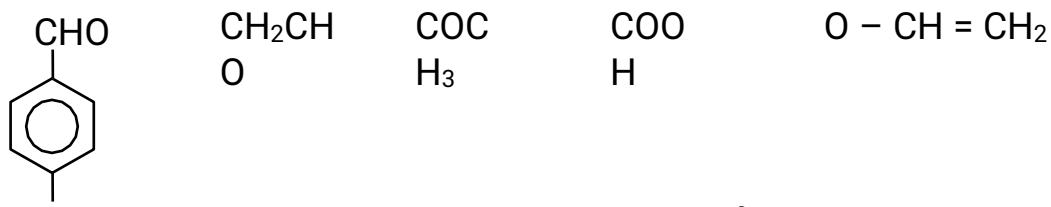


So, compound *D* is *p*-methyl benzoic acid

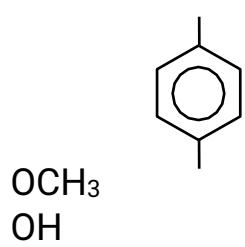
iv. Compound *E* on hydrolysis gives 1, 4-dihydroxy benzene,



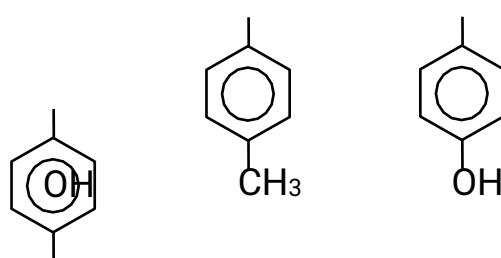
So compound *E* is *p*-hydroxylphenyl vinyl ether. Hence, compounds



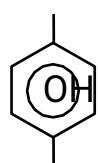
&



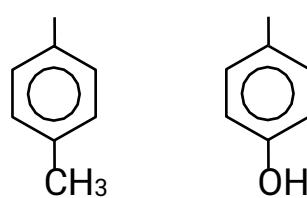
'A'



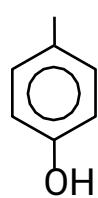
'B'



'C'

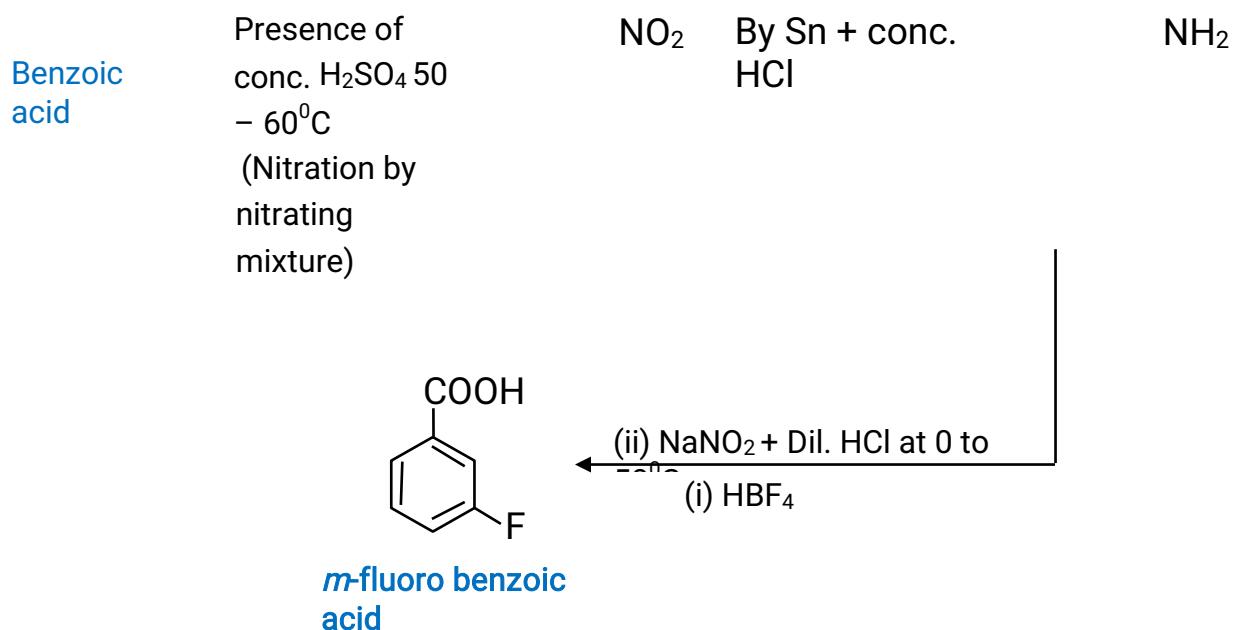
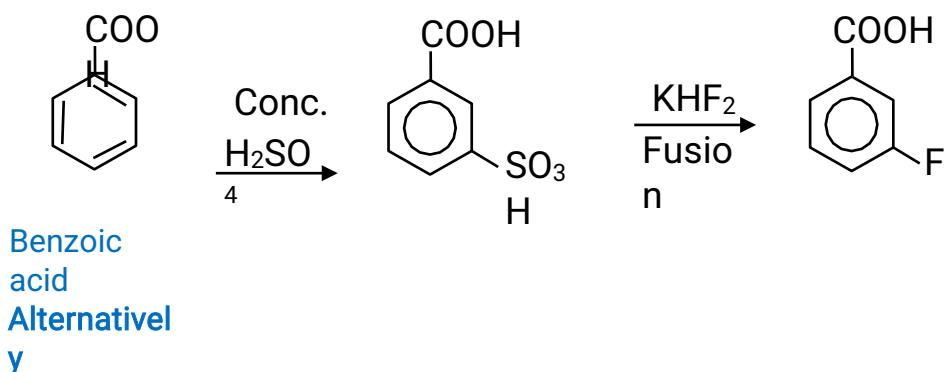


'D'

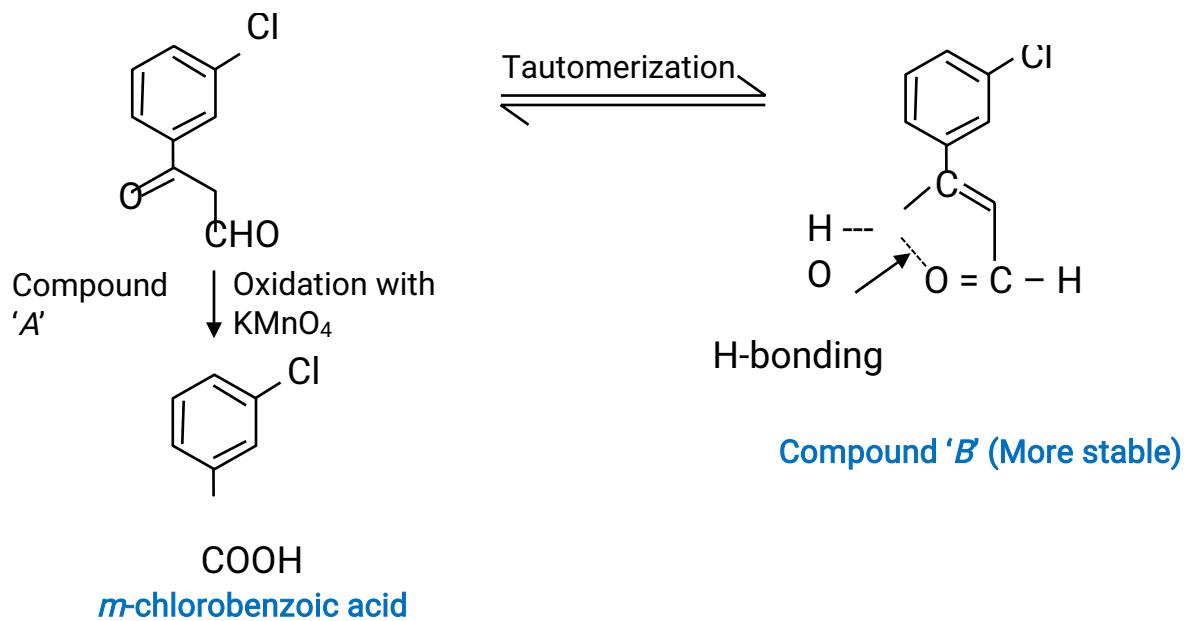


'E'

23.



24. (b) Compound A of molecular formula  $\text{C}_9\text{H}_7\text{O}_2\text{Cl}$  exists in keto form and predominantly in enolic form B. Hence, compound A must be carbonyl compound which has -hydrogen atom because it is enolised. Enolic form B is predominated due to H-bonding.



# Organic compounds containing Nitrogen

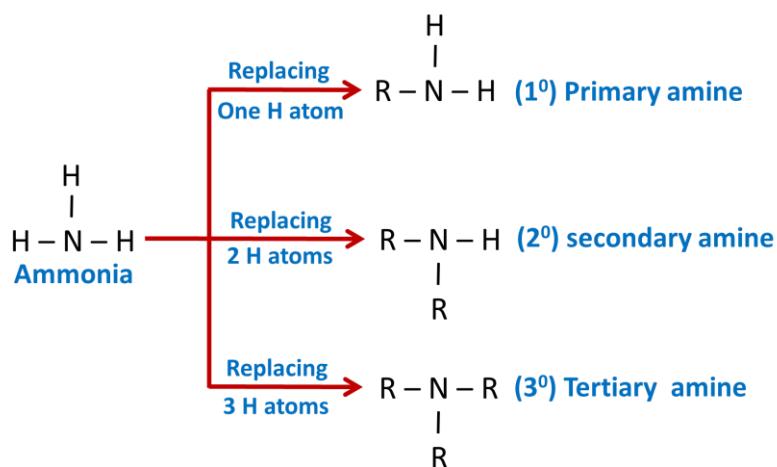
## Module 35.1: Nomenclature, classification preparation and physical properties of Amines

### Introduction:

Functional groups containing nitrogen are present in a variety of naturally occurring and man made organic compounds. These functional groups impart physico-chemical characteristics to these molecules. These groups are responsible for their unique chemical reactivity patterns and play crucial roles in the preparation of drugs, agrochemicals, dyes and molecules of life. There are many functional groups, which contain one or more nitrogen atoms. Some categories of compounds based on these functional groups include nitro compounds, amines, cyanides, isocyanides and diazo compounds.

### Classification:

Amines are regarded as the alkyl or aryl derivatives of ammonia. They are obtained by the replacement of one or more hydrogen atoms of ammonia by alkyl or aryl groups. They are classified into primary, secondary or tertiary amines depending upon whether two or three H atoms of ammonia have been replaced by alkyl or aryl groups.



## Nomenclature of Aliphatic Amines:

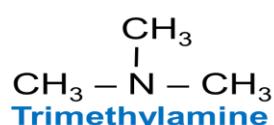
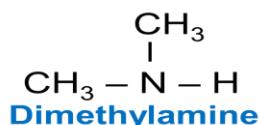
### Trivial method:

The following rules are applied in naming amines

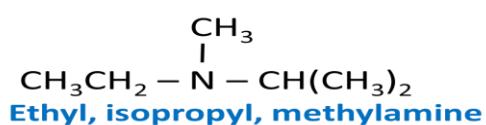
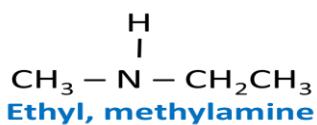
1. Amines are named by naming the alkyl groups attached to the nitrogen atom followed by the ending –amine. Notice that the names are written as one word.



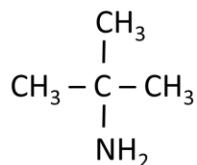
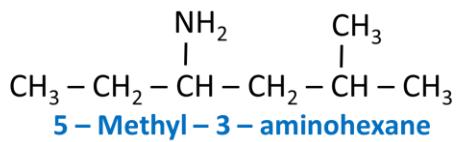
2. When two or three identical alkyl groups are attached to the nitrogen atom, the prefix di- or tri- is added to the name of the amine.



3. When two or three different alkyl groups are attached to the nitrogen atom, they are named in alphabetical order and the name is terminated as amine.

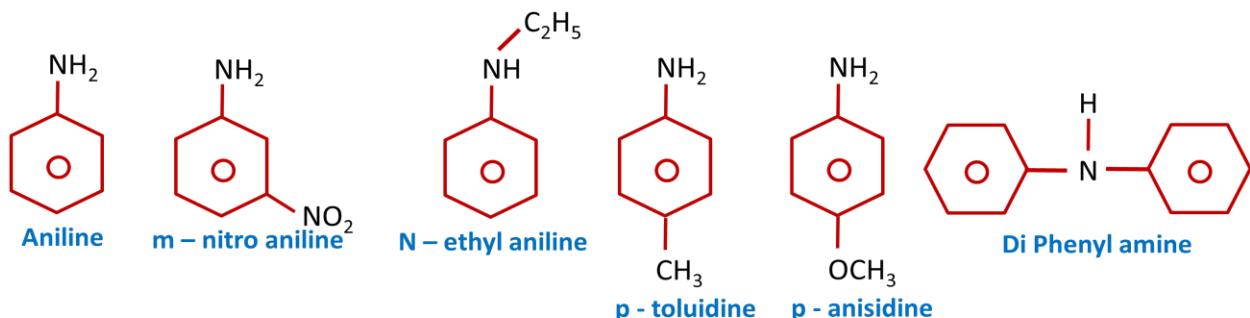


4. In the IUPAC system, the amines are considered to be amino derivatives of corresponding alkanes. Therefore, they are called aminoalkanes or alkanamines. These names are obtained either by adding a prefix amino before the name of parent alkane or by replacing 'e' from the name of the parent alkane with suffix amine.

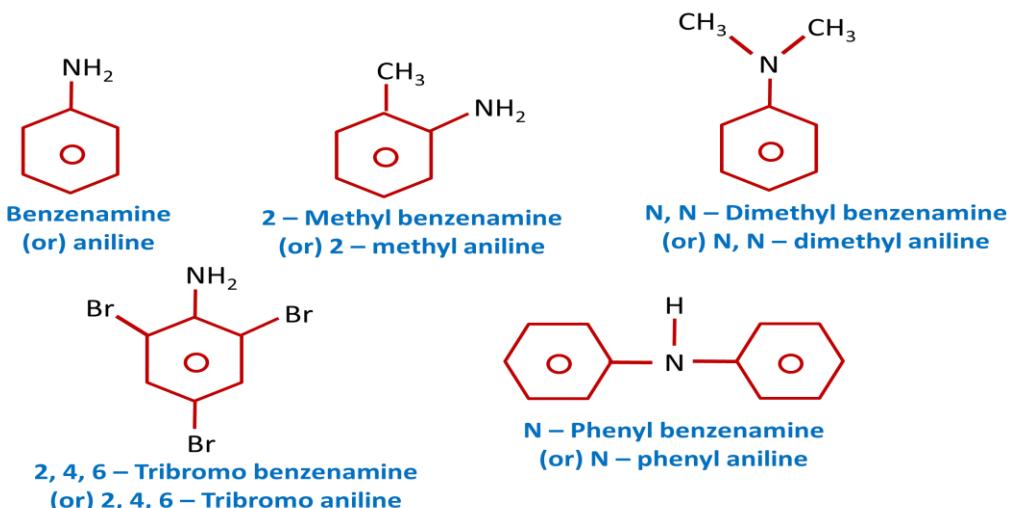


## Nomenclature of Aromatic Amines:

Aromatic amines in the common system are named by adding the suffix, amine to the name of aryl group. They are named as derivatives of the parent member aniline. But in some cases other names o/m/p - toluidine for o/m/p methylaniline and o/m/p - anisidine for o/m/p methoxy anilines are assigned. N-phenyl derivative of aniline is called diphenyl amine.

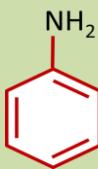
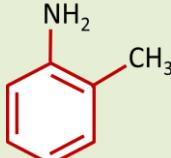
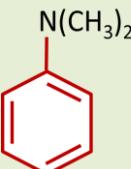


In the IUPAC system, the simplest aromatic amine is called benzenamine. Other amines are named as derivatives of benzene amines.



## Nomenclature of some alkylamines and arylamines

Amine	Common name	IUPAC name
$\text{CH}_3 - \text{CH}_2 - \text{NH}_2$	Ethylamine	Ethanamine
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	n-Propylamine	Propan-1-amine

$\text{CH}_3 - \underset{\text{NH}_2}{\underset{ }{\text{CH}}} - \text{CH}_3$	Isopropylamine	Propan – 2 – amine
$\text{CH}_3 - \underset{\text{H}}{\underset{ }{\text{N}}} - \text{CH}_2 - \text{CH}_3$	Ethylmethylamine	N – Methylmethanamine
$\text{CH}_3 - \underset{\text{CH}_3}{\underset{ }{\text{N}}} - \text{CH}_3$	Trimethylamine	N, N – Dimethylmethanamine
$\text{C}_2\text{H}_5 - \underset{\text{C}_2\text{H}_5}{\underset{ }{\text{N}}} - \overset{1}{\text{CH}_2} - \overset{2}{\text{CH}_2} - \overset{3}{\text{CH}_2} - \overset{4}{\text{CH}_3}$	N, N – Diethylbutylamine	N, N – Diethylbutan – 1 – amine
$\text{NH}_2 - \overset{1}{\text{CH}_2} - \overset{2}{\text{CH}} = \overset{3}{\text{CH}_2}$	Allylamine	Prop -2 – en -1 – amine
$\text{NH}_2 - (\text{CH}_2)_6 - \text{NH}_2$	Hexamethylenediamine	Hexane – 1, 6 – diamine
	Aniline	Aniline or Benzenamine
	o – Toluidine	2 – Aminotoluene
	p - Bromoaniline	4 – Bromobenzenamine or 4 - Bromoaniline
	N, N - Dimethylaniline	N, N - Dimethylbenzenamine

## Preparation of amines:

### 1. Ammonolysis of Alkyl halides:

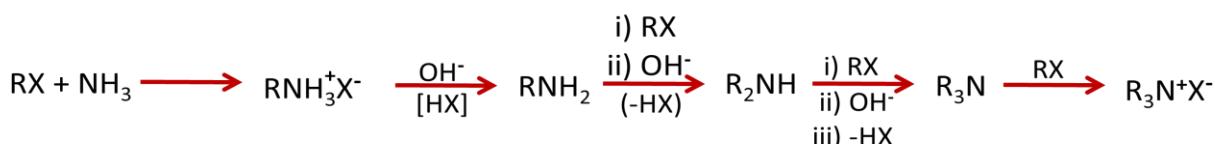
An alkyl halide or a benzyl halide reacts with ammonia to form a mixture of primary secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.

**Example:**



If alkyl halide is in excess, the primary amine formed, further reacts with alkyl halide to form secondary amine, tertiary amine and finally quaternary ammonium salt.

The reaction is a typical example of nucleophilic substitution reaction. Here the ammonia molecules in the first step and the amine molecules in the subsequent steps act as nucleophiles.



Using a large excess of alkyl halide, in the presence of a base which will consume HX formed, quaternary ammonium salt is the only product.

The above method is known as Hofmann's ammonolysis method. The reactivity of the various halides decreases in the following order.



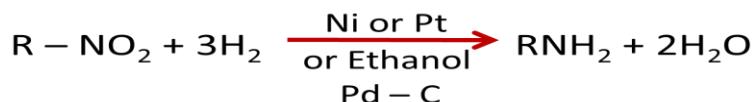
The disadvantage of this method is that ammonolysis does not give a single amine but a mixture of all the possible amines. Also this method is not suitable for preparing aryl amines because of the low reactivity of aryl halides towards nucleophilic substitutions.

## 2. Reduction of Nitro Compounds:

Nitro compounds are reduced to amines either by catalytic hydrogenation or chemically by using a metal and acid.

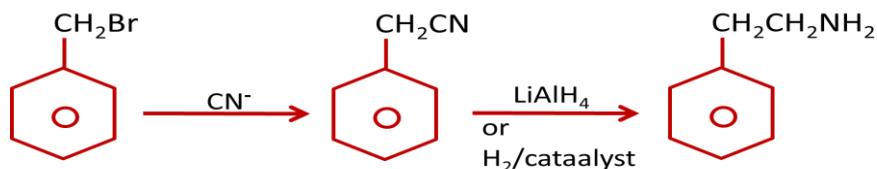


Or



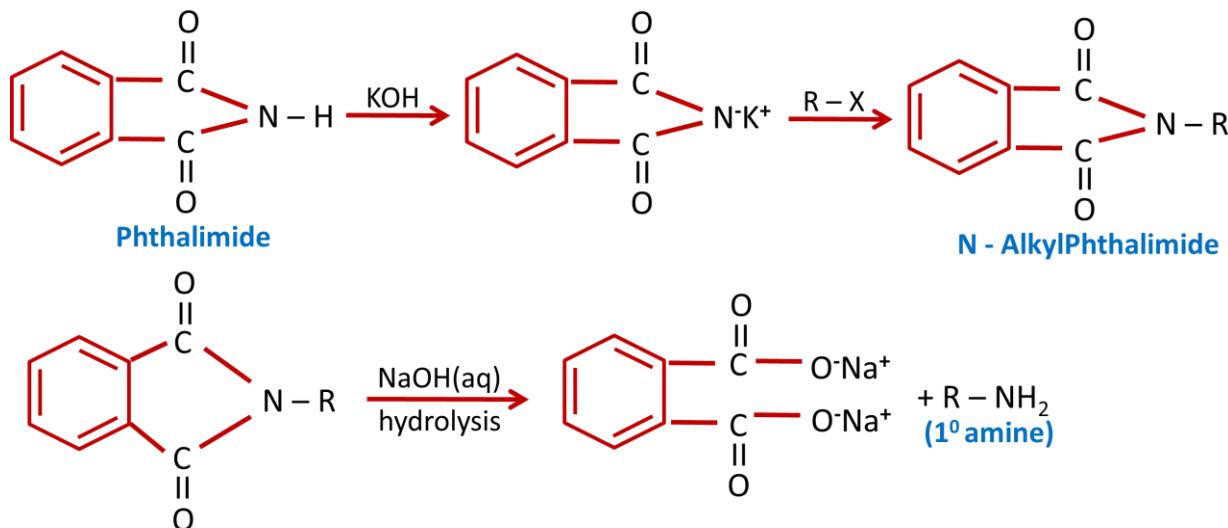
## 3. Reduction of Nitriles:

Alkyl nitriles, on reduction with  $\text{LiAlH}_4$  or Catalytic hydrogenation, form primary amines which have one more carbon than the alkyl halide used. This reaction is used for ascent of amines homologous series.



## 4. Gabriel Synthesis:

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Secondary and tertiary amines cannot be prepared by Gabriel synthesis. Also aniline cannot be prepared by this method as aryl halides do not undergo nucleophilic substitution under ordinary condition.

### 5. Hofmann bromamide degradation reaction:

Acid amides on reaction with bromine in the presence of alkalis at about 343 K give primary amines.



The amine formed by this method has one carbon atom less than the parent compound. (i.e. amide) ( $-CONH_2$  changes to  $-NH_2$ )

### Physical Properties:

### Physical state and odor:

Lower members of aliphatic amines are gases while higher members are liquids. Among, aryl amines, lower members are liquids and higher members are solids.

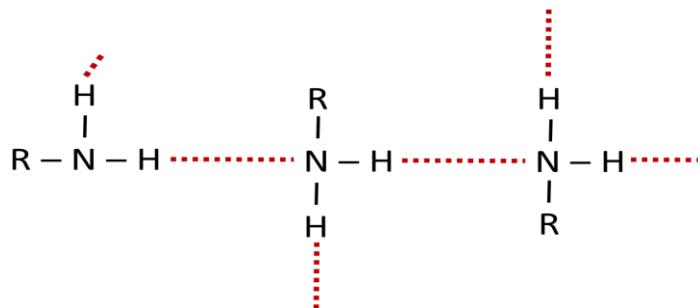
Methyl amine and ethyl amine have ammonical smell but higher amines have fishy smell.

Most of the aromatic amines are colorless in pure form. However, they become colored on keeping due to oxidation in air. Aromatic amines are generally toxic. They are easily absorbed through the skin.

### **Boiling point:**

Amines are polar compounds and have higher boiling points than non-polar compounds such as hydrocarbons of same molecular mass.

All amines can form hydrogen bonds as proton acceptors by coordination with the lone pair of electrons on the -N atom. But only primary and secondary amines can donate proton in hydrogen bonding. The 1° and 2° amines because of intermolecular hydrogen bonding have higher boiling points than tertiary amines.



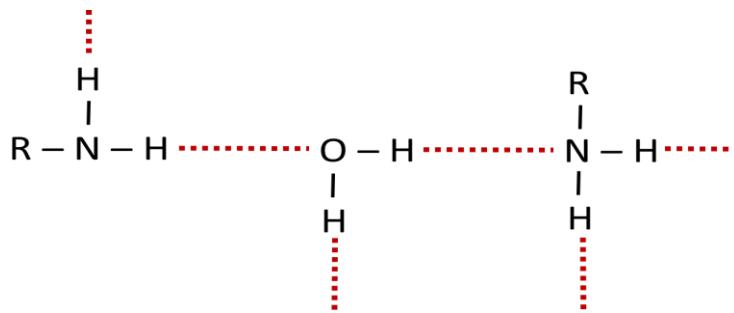
However amines have lower boiling points than those of corresponding alcohols or carboxylic acids. This is due to the reason that O - H bond is more polar than N-H bond and hence hydrogen bonds in alcohols and carboxylic acids are stronger than hydrogen bonds in amines.

### **Solubility:**

Smaller amines are soluble in water but as the hydrophobic part (*i.e.* hydrocarbon part) of the amine becomes larger than six carbons, their solubility in water decreases and still larger amines are essentially insoluble in water.

As the hydrogen bonds in amines are weaker than those in alcohols, the solubility of amines in water is less than that of alcohols of similar molecular weights.

The solubility of lower aliphatic amines in water is due to their capability to form hydrogen bonds with water molecules



Amines are soluble in organic solvents like ether, benzene, alcohol etc.

### Example Set:

1. Which of the following compounds is a secondary amine?

- (a)  $\text{CH}_3 - \overset{\text{NH}_2}{\underset{|}{\text{CH}}} - \text{CH}_3$
- (b)  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
- (c)  $\text{CH}_3\text{CH}_2\text{NHCH}_3$
- (d)  $(\text{CH}_3)_3\text{N}$

**Solution:** c)

2. A sample of pure amine molecules is found to possess no intermolecular H – bonding. This sample is most likely to be a
- a.  $1^0$  amine
  - b.  $2^0$  amine
  - c.  $3^0$  amine
  - d. All of these

**Solution:** c)

3. Which of the following amines is not soluble in water?
- a. Methylamine
  - b. Dimethylamine
  - c. Trimethylamine
  - d. None

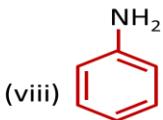
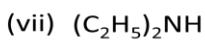
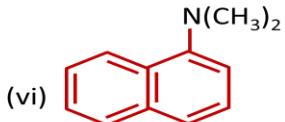
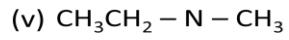
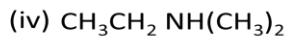
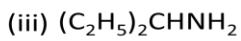
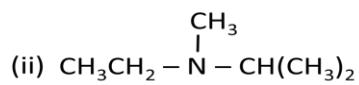
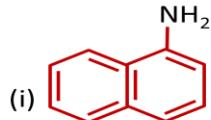
**Solution:** d)

4. Acetamide reacts with  $\text{Br}_2/\text{NaOH}$  to give

- a. Methylamine
- b.  $\alpha$  – Bromo acetamide
- c. Ethyl amine
- d. Acetyl bromide

**Solution:** a)

5. Classify the following amines as primary, secondary or tertiary

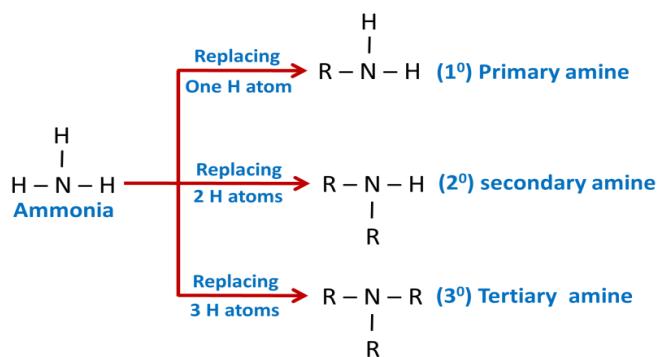


**Solution:**

- (i) Primary
- (ii) Tertiary
- (iii) Primary
- (iv) Tertiary
- (v) Secondary
- (vi) Tertiary
- (vii) Secondary
- (viii) Primary

6. Discuss about the classification of primary, secondary and tertiary amines

### Solution:



7. How do you prepare  $1^\circ$  – amines from
- Alkyl halides
  - Nitro compounds

### Solution:

#### a. Ammonolysis of Alkyl halides:

An alkyl halide or a benzyl halide reacts with ammonia to form a mixture of primary secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.

#### Example:

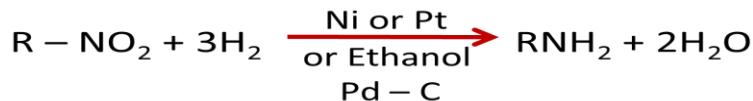


#### b. Reduction of Nitro Compounds:

Nitro compounds are reduced to amines either by catalytic hydrogenation or chemically by using a metal and acid.



Or



8. Write any three important physical properties of amines

**Solution: Physical Properties**

Lower members of aliphatic amines are gases while higher members are liquids. Among, aryl amines, lower members are liquids and higher members are solids

**Problem Set:**

1. Consider a  $1^0$ ,  $2^0$  and  $3^0$  amine, all of equivalent molecular weight. Which amine is most likely to have the lowest boiling point?
  - a.  $1^0$  amine
  - b.  $2^0$  amine
  - c.  $3^0$  amine
  - d. All have the same

**Solution: c)**

2. Acetonitrile ( $\text{CH}_3\text{CN}$ ) undergoes reduction with  $\text{LiAlH}_4$  to form
  - a. Methylamine
  - b. Dethylamine
  - c. Ethylamine
  - d. Trimethylamine

**Solution: c)**

3. Reduction of an azide will give an
  - a. Acid
  - b. Amide
  - c. Amine
  - d. Alcohol

**Solution: c)**

4. Alkyl halides react with the ammonia in the presence of a base to form

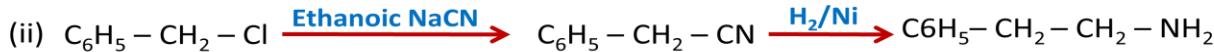
- a. Primary amines
- b. Nitrated alkyl halides
- c. Amides
- d. Nitro compounds

**Solution:** a)

5. Write the chemical equations for the following conversions

- (i)  $\text{CH}_3 - \text{CH}_2 - \text{Cl}$  into  $\text{CH}_3\text{CH}_2\text{NH}_2$  (in 1 step)
- (ii)  $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{Cl}$  into  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 - \text{NH}_2$  (in 2 steps)

**Solution:**

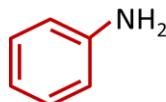


6. Write the structures and IUPAC names of the product formed when

- (i) Butanamide is treated for Hoffmann bromamide reaction
- (ii) The amine produced by the Hoffmann degradation of benzamide

**Solution:**

- (i) Propanamine  
 $\text{CH}_3\text{CH}_2\text{CH}_2 - \text{NH}_2$
- (ii) Benzamide is an aromatic amide containing seven carbon atoms. Hence, the amine formed from benzamide is aromatic primary amine containing six carbon atoms.



Aniline or benzenamine

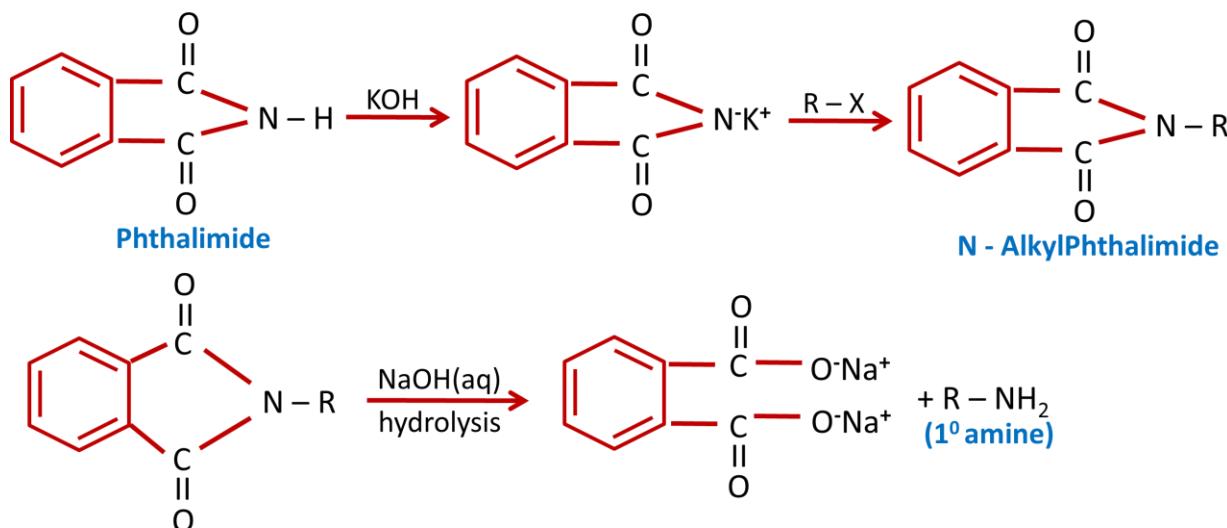
7. Write short notes on the following:

- a. Gabriel phthalimide synthesis
- b. Hoffmann's bromamide reaction

**Solution:**

**a. Gabriel Synthesis:**

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Secondary and tertiary amines cannot be prepared by Gabriel synthesis. Also aniline cannot be prepared by this method as aryl halides do not undergo nucleophilic substitution under ordinary condition.

### b. Hofmann bromamide degradation reaction:

Acid amides on reaction with bromine in the presence of alkalis at about 343 K give primary amines.



The amine formed by this method

### Exercise Questions:

- Acetamide is treated separately with the following reagents. Which one of these would give methylamine?
  - $\text{PCl}_5$
  - $\text{NaOH} + \text{Br}_2$

- c. Soda lime
- d. In hot conc.  $\text{H}_2\text{SO}_4$

**Solution:** b

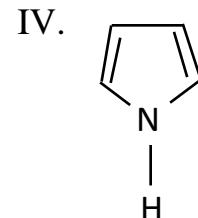
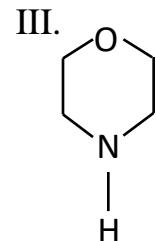
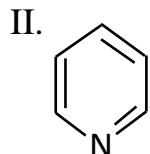
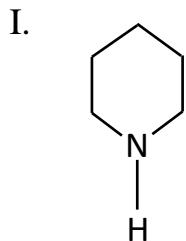
2. Amongst the following, the most basic compound is
- a. Benzylamine
  - b. Aniline
  - c. acetanilide
  - d. p - nitroaniline

**Solution:** a

3. Butanenitrile may be prepared by heating
- a. Propyl alcohol with KCN
  - b. Butyl alcohol with KCN
  - c. Butyl chloride with KCN
  - d. Propyl chloride with KCN

**Solution:** d

4. In the following compounds:



The order of basicity is

- a. IV > I > III > II
- b. III > I > IV > II
- c. II > I > III > IV
- d. I > III > II > IV

**Solution:** d

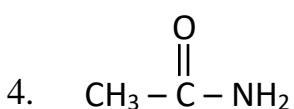
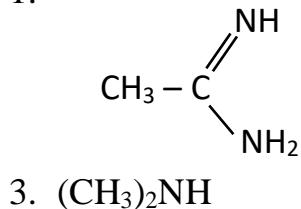
5. Among the following, the strongest base is
- a.  $\text{C}_6\text{H}_5\text{NH}_2$
  - b. p -  $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$

- c.  $m - NO_2.C_6H_4NH_2$
- d.  $C_6H_5CH_2NH_2$

**Solution:** d

6. The correct order of basicity of the following compound is

- 1.  $CH_3 - CH_2 - NH_2$



- a.  $2 > 1 > 3 > 4$
- b.  $1 > 3 > 2 > 4$
- c.  $3 > 1 > 2 > 4$
- d.  $1 > 2 > 3 > 4$

**Solution:** b

7. Compound ‘A’ (molecular formula  $C_3H_8O$ ) is treated with acidified potassium dichromate to form a product ‘B’ (molecular formula  $C_3H_6O$ ). ‘B’ forms a shining silver mirror on warming with ammonical silver nitrate. ‘B’ when treated with an aqueous solution of  $H_2NCONHNH_2.HCl$  and sodium acetate gives a product ‘C’. Identify the structure of ‘C’.

- a.  $CH_3CH_2CH_2 = NNHCONH_2$

- b.  $CH_3 - C - NNHCONH_2$



- c.  $CH_3 - C - NCONHNH_2$



- d.  $CH_3CH_2CH = NCONHNH_2$

**Solution:** a

8. Benzamide on reaction with  $POCl_3$  gives

- a. aniline

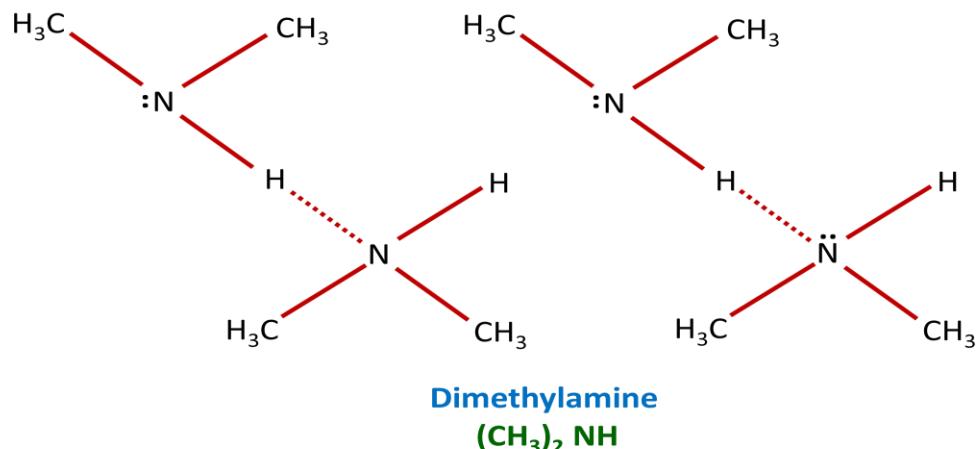
- b. chlorobenzene
- c. benzylamine
- d. benzonitrile

**Solution:** d

9. Explain the fact that trimethylamine boils at lower temperature than that of dimethylamine.

**Solution:**

Even though dimethylamine has a lower molecular weight than trimethylamine, it boils at a higher temperature



Liquid dimethylamine forms hydrogen bonds that must be broken in the boiling process. Since extra energy must be added to break these bonds, dimethylamine has a higher boiling point than trimethylamine which does not form hydrogen bonds

10. Identify (A), (B) and (C) in the following reaction sequence:



**Solution:**

$$\begin{aligned} A &= CH_3CH_2Cl \\ B &= CH_3CH_2CN \\ C &= CH_3CH_2CH_2NH_2 \end{aligned}$$

**11.** How will you synthesize 1, 4-diaminobutane from ethylene?

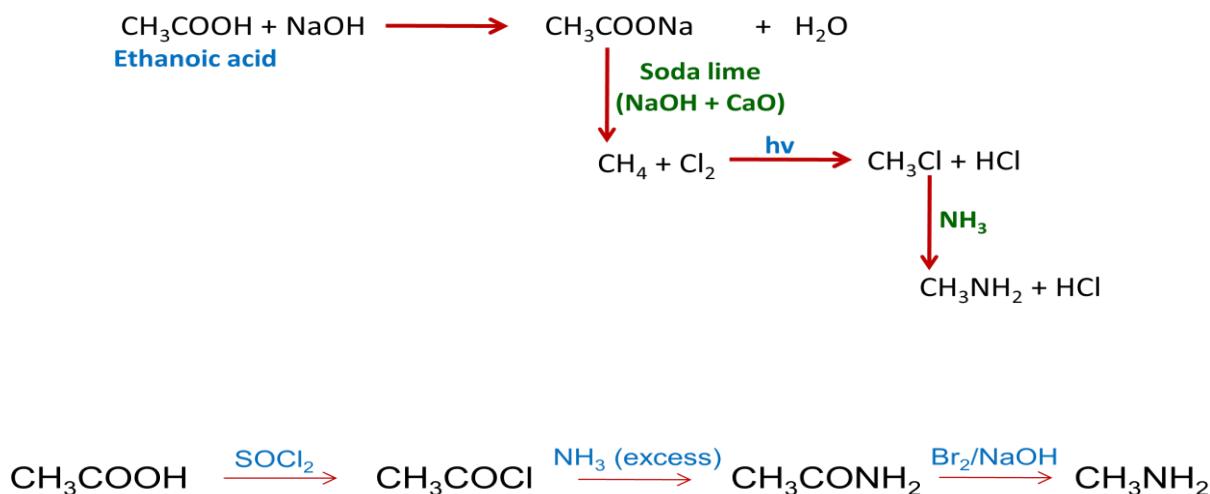
**Solution:**

Following steps are involved



**12.** How will you convert ethanoic acid into methanamine. Give two different methods.

**Solution:**

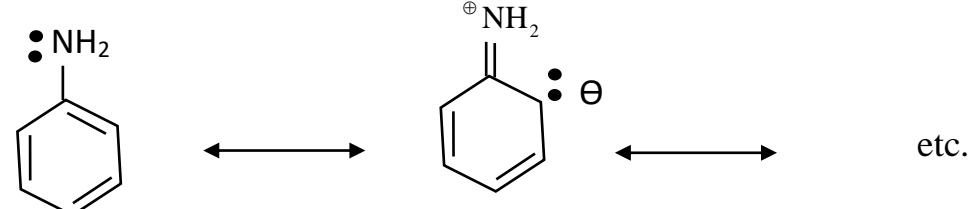


**13.** Give reasons for the following

- Cyclohexylamine is a stronger base than aniline
- Dimethylamine is a stronger base than trimethylamine

**Solution:**

i.



Resonating  
structures of  
aniline

whereas cyclohexylamine has does not resonance structures.

- ii. Two factors operate in deciding the basicity of alky amines.
- Inductive effect and
  - Solvation effect
- a. **Inductive effect.** The alkyl group being electron relating increases the charge density on Nitrogen this inturn increases the basicity of amines. The expected order of basicity is  $3^0 > 2^0 > 1^0$
- b. **Solvation effect.** Because of the positive charge carried by the conjugate acid of an amine, it is stabilized by the hydrogen bonding with the solvent water. The larger the number of hydrogen attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity  $1^0 > 2^0 > 3^0$ .

The inductive and solvent effects predict the opposite trend in the basicity of alkyl amines. In going from  $R_2NH$  to  $R_3N$  the solvation effect plays a more dominating role as compared to the inductive effect making  $R_2NH$  more basic than  $R_3N$ .

**14.** Arrange the following:

- p – toluidine, N, N – dimethyl – p – toluidine, p – nitroaniline, aniline in increasing basicity.
- Methylamine , dimethylamine, aniline, N – methylamine in increasing order of base strength.

**Solution:**

- Presence of + I group increases the basicity whereas presence of – I group decreases the basicity.  
 $N, N - \text{dimethyl} - p - \text{toluidine} < p - \text{nitroaniline} < \text{aniline} < p - \text{toluidine}$ .

Presence of + I group like alkyl group in the benzene nucleus of aniline increases the basicity.

The effect is more when the alkyl group is in o – and – p = position than in m – position.

Presence of – I group like – NO<sub>2</sub> group in the benzene nucleus of aniline decreases the basicity.

The effect is much more in o – and p – position than in m – position.

ii. Aniline < N – methylamine < methylaniline < dimethylaniline.

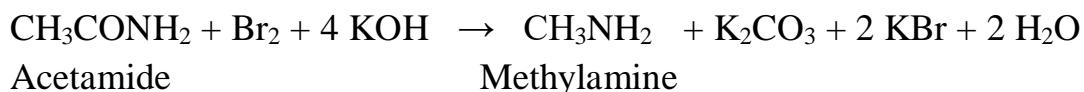
The ease with which the lone pair of electron (unshared) on the N – atom co – ordinates with a proton determines the relative basic strength of amines. Further C<sub>6</sub>H<sub>5</sub> is an electron attracting group. Hence aniline is least basic.

**15.** Write balanced equations for the following reaction:

Acetamide is reacted with bromine in their presence of potassium hydroxide.

**Solution:**

**Hoffmann degradation reaction.**



# Organic compounds containing nitrogen

## Module – 35.2: Chemical Properties of Amines & Aniline

### Chemical Properties of Amines

#### Basicity of amines

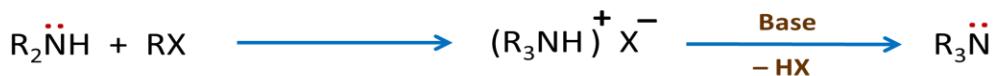
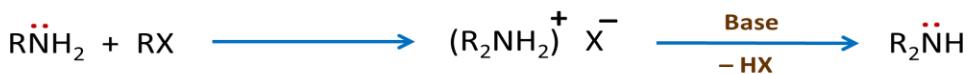
The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. Amines are **nucleophilic reagents** as the lone pair of electrons can be donated to electron seeking reagents so amines are lewis bases.

Except the amines containing tertiary butyl group, all lower aliphatic amines are stronger bases than ammonia because of + I (inductive) effect. The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or Lewis acids and making the amine more basic. Thus, it is expected that the basic nature of amines should be in the order **tertiary > secondary > primary > NH<sub>3</sub>**, but the observed order in the case of methylamine is found to be as **secondary > primary > tertiary > NH<sub>3</sub>**; This anomalous behavior of tertiary amines is **due to steric factors**, i.e., crowding of nitrogen atom from all sides by the alkyl groups makes the approach and bonding by a proton or an electrophile relatively difficult. The maximum steric strain results in tertiary amines. The electrons are there but the path is blocked, resulting in its reduced basicity.

#### 1) Alkylation:

An alkyl halide can react with a primary or secondary amine which acts as a nucleophile. On undergoing nucleophilic substitution, a 1° – amine is converted to a 2° – amine and a 2° – amine in quaternary amine compound to a 3° – amine. The 2° – amine being a more powerful nucleophile again reacts with an alkyl halide to form a tertiary amine.

Ultimately the tertiary amine reacts with alkyl halides to form a quaternary ammonium salt.



Aromatic amines also react in a similar manner.

At every stage a molecule of HX is eliminated. The strong acid generated may protonate the amine making unshared pair of electrons unavailable for nucleophilic attack and thus may stop the reaction before completion. In order to prevent this, a base such as a carbonate is added to neutralize the acid produced.

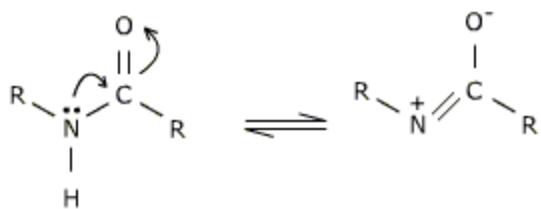
## 2) Acylation:

Aliphatic and aromatic primary and secondary amines undergo acylation through nucleophilic substitution with acid derivatives such as acid halides or anhydrides to form amides.



This reaction generates an acid which reacts with the amine to form salt. Thus the amine loses its nucleophilic character and the reaction will not proceed to completion. A base is added to remove the acid and facilitate the reaction.

Unlike in the case of alkylation reaction, the amide formed here does not react further with the organic halide because the amide is not a strong electrophile and a poor nucleophile due to its nitrogen unshared pair of electrons on nitrogen being in conjugation with carbonyl group.



Tertiary amines do not react with acid derivatives because they cannot lose a proton to stabilise the product. So for the acylation of an amine, it should have nucleophilic character and also a H-atom should be present on nitrogen.

Aliphatic and aromatic primary and secondary amines react with  $C_6H_5SO_2Cl$  (Benzene sulphonyl chloride) to form secondary and tertiary sulphonamides. Secondary sulphonamides ( $pK_a \sim 10$ ) are as acidic as phenol and are freely soluble in aqueous KOH. They can be recovered from the solution by acidification. Tertiary sulphonamide lacking H-atom on nitrogen is insoluble in aqueous KOH. This is used to differentiate the different types of amines as well as to separate them from one another.

### 3) Reaction with Hinsberg's Reagent: ( Distinguishing amines )

Primary and secondary amines combine with Hinsberg's Reagent (benzene sulphonyl chloride) to form sulphonamides.



It reacts with an alkali to form a soluble sodium salt.

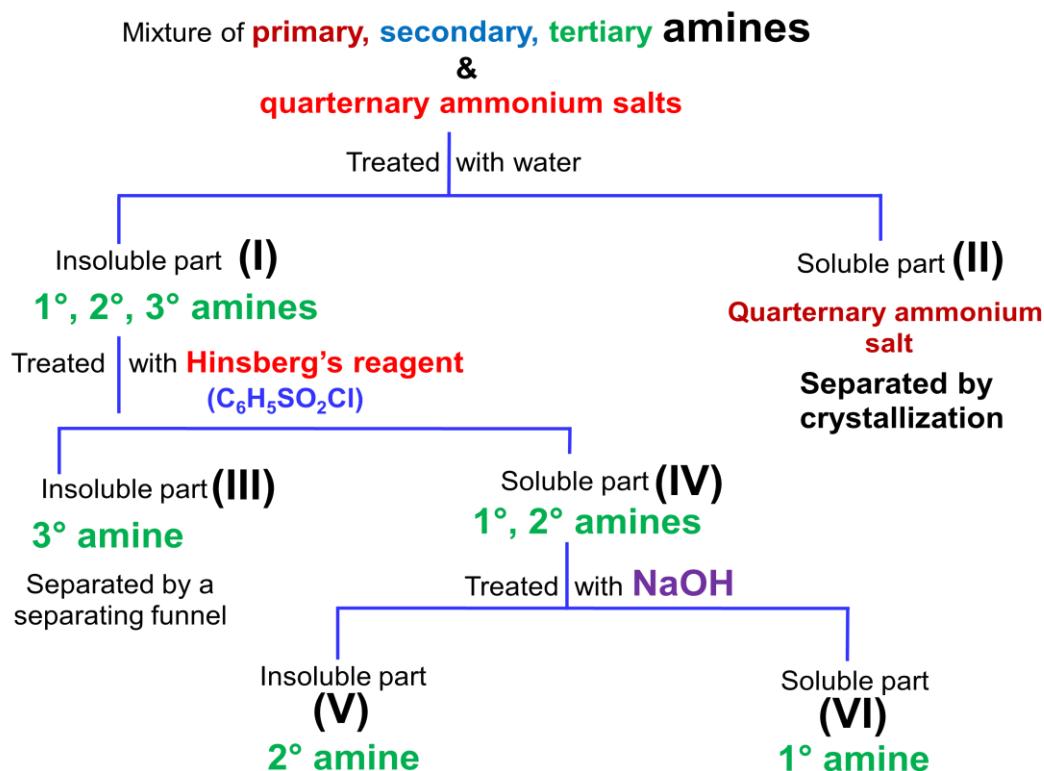


The product formed by the action of secondary amine on benzene sulphonyl chloride does not dissolve in an alkali. This is because there is no hydrogen atom attached to the N atom in the product. It is insoluble in alkali.



Tertiary amines do not react with  $C_6H_5SO_2Cl$ .

Hence Hinsberg's reagent is used for separation of primary, secondary and tertiary amines.



#### 4) Carbylamine reaction (Isocyanide test):

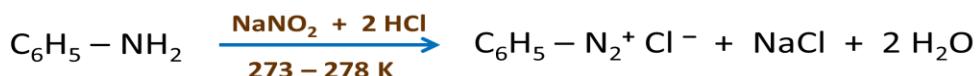
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines only.



## 5) Reaction with nitrous acid: (Diazotization reaction)

The reaction of converting aromatic primary amine to diazonium salt is called **diazotisation**.

Aniline (or any aromatic 1<sup>0</sup> – amine) react with nitrous acid at low temperatures (273-278 K) to form diazonium salts. These are a very important class of compounds used for synthesis of a variety of aromatic compounds



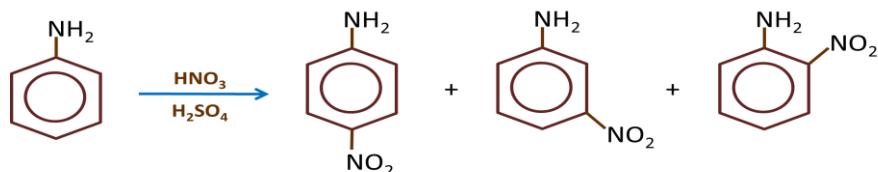
### Electrophilic Substitution Reactions:

All amino groups -NH<sub>2</sub>, -NHR, -NR<sub>2</sub> are most powerful activating groups in aromatic electrophilic substitution reactions and are ortho and para directing.

Aniline gets instantaneously brominated at the entire three o, p – positions (all o-, p-, positions) to give a white precipitate in aqueous solutions with Bromine water.



Nitration of aniline gives unexpectedly high percentage yield of m-nitro aniline.



This is due to the fact that aniline gets protonated to form a – N<sup>+</sup>H<sub>3</sub> group which is meta directing and ring deactivating group. Thus to carryout nitration, aromatic

amines are converted to amides first, then they are nitrated. After nitration the products are hydrolyzed back to amino compounds.

## Aniline

### Methods of preparation:

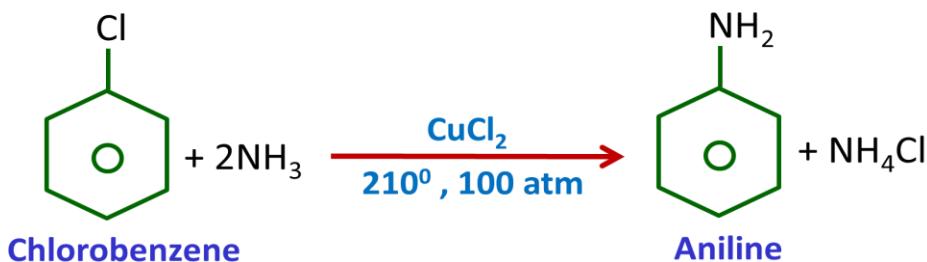
#### 1. Reduction of nitro compounds:

This is a very convenient and most widely used method of preparing aniline



#### 2. Ammonolysis of aryl chlorides:

Aniline is prepared by treating chlorobenzene with ammonia in the presence of copper salts at high temperature and pressure



### Physical properties:

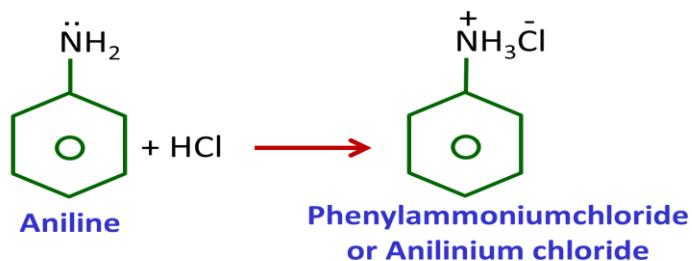
1. Aniline when pure is colorless oil, BP  $184.4^\circ \text{C}$ , density 1.002 at  $20^\circ \text{C}$ .
2. It becomes pale yellow, and then rapidly darkens on exposure to air owing to oxidation

3. It has a faint characteristic odour
4. It is sparingly soluble in water but dissolves readily in ethanol, diethyl ether and chloroform

### Chemical properties:

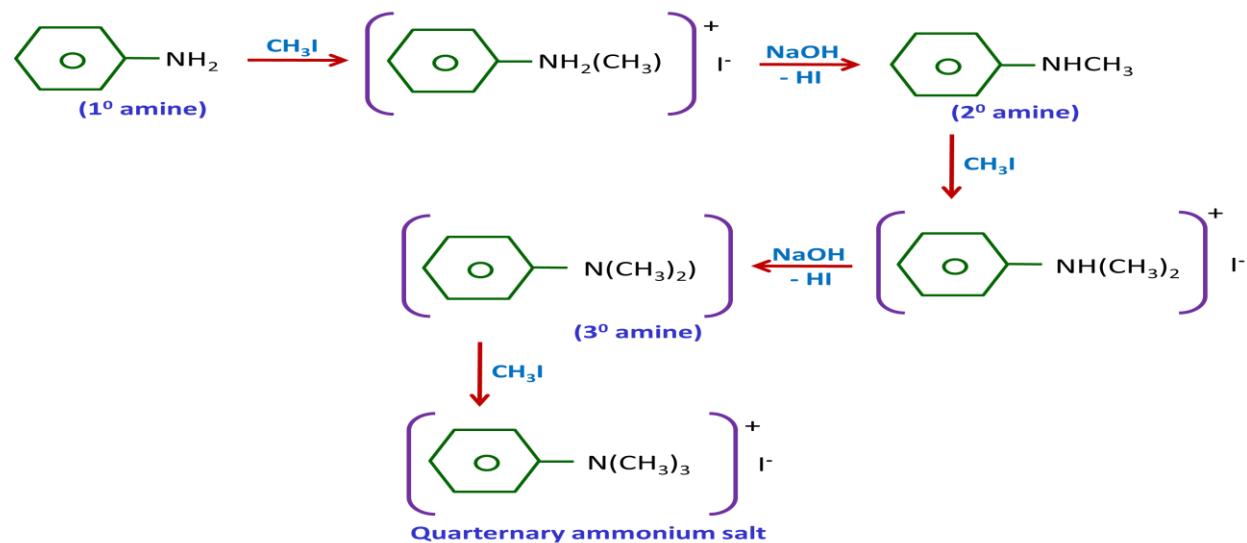
#### 1. Reaction with strong acids to form salts:

Aniline is a weak base ( $K_b = 4.2 \times 10^{-10}$ ) and forms salts with mineral acids



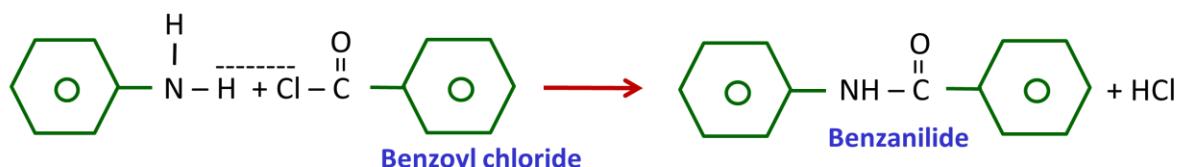
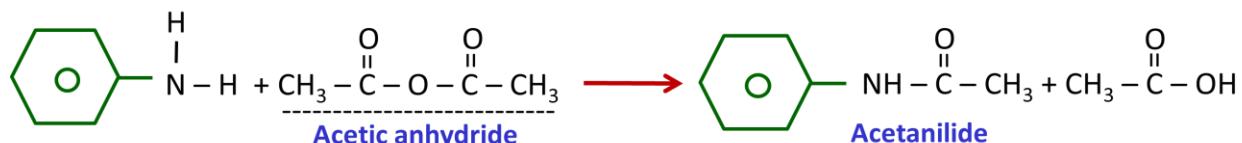
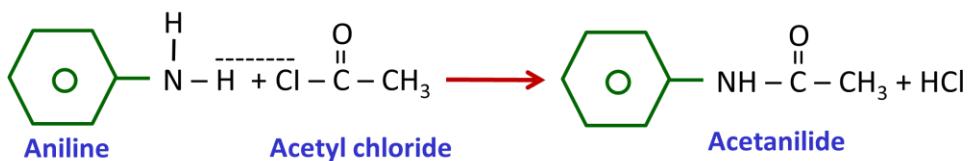
#### 2. Reaction with alkylhalides (alkylation reaction):

Aniline reacts with alkyl halides to form 2° amine. The 2° amines can further react with an alkyl halide to form 3° amines and finally quaternary ammonium salts. The salt can be treated with aqueous NaOH to regenerate free 2° amine



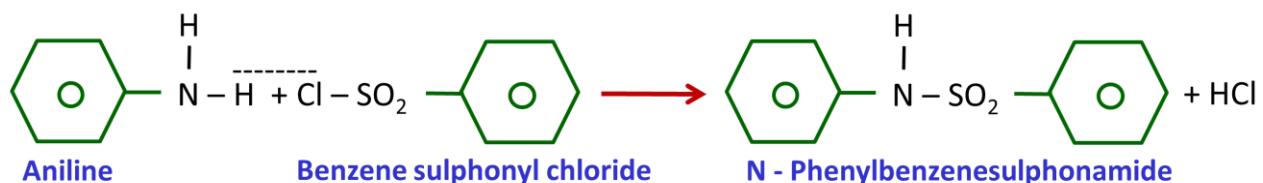
#### Reaction with acid chlorides (acylation reaction):

Aniline reacts with acid chloride (or acid anhydrides) to form the corresponding amides called anilides



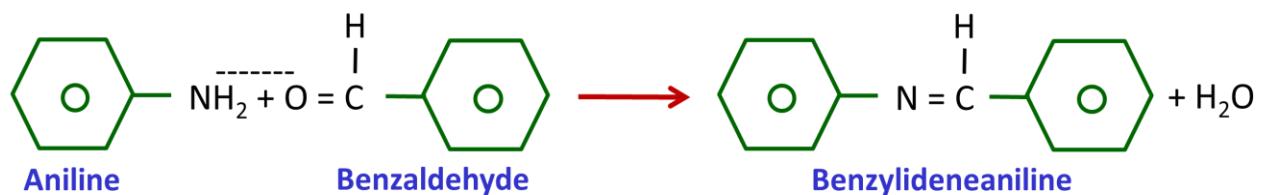
### 3. Reaction with benzenesulphonyl chloride (or Hinsberg reagent):

Aniline reacts with benzenesulphonyl chloride to form N – phenylbenzenesulphonamide



### 4. Reaction with benzaldehyde:

Aniline condenses with benzaldehyde to give benzylideneaniline (a Schiff's base)



### 5. Carbylamine reaction:

Aniline reacts with chloroform and alcoholic KOH to give phenyl isocyanide (phenyl carbylamine) which has an offensive smell. It can be identified by its smell.



### 6. Reaction with nitrous acid:

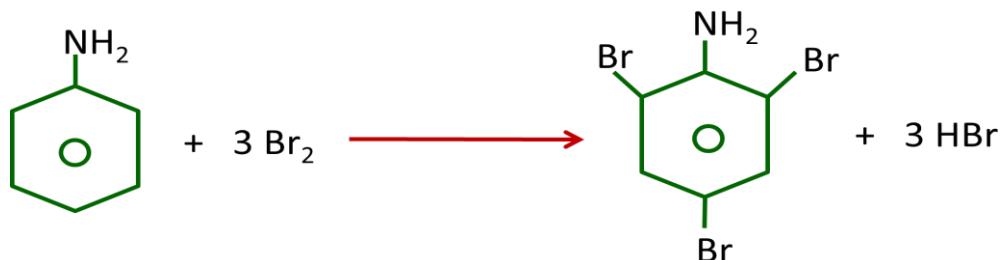
Aniline reacts with nitrous acid (from  $\text{NaNO}_2 + \text{HCl}$ ) in the presence of HCl at  $0 - 5^{\circ}\text{C}$  to give benzenediazonium chloride



### 7.) Electrophilic Substitution Reactions:

All the types of amino groups  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$  are most powerful ring activating groups in aromatic electrophilic substitution reactions and are ortho and para directing.

Aniline gets instantaneously brominated at all of the three o, p – positions (all o -, p-, positions) to give a white precipitate in aqueous solutions with Bromine water. This is a test for identifying aniline.



**Uses:**

Aniline is used

1. For preparation of dyes and intermediates in dyes industry
2. For manufacture of antioxidants and vulcanization in rubber industry
3. For synthesis of drugs, notably sulpha drugs
4. For making isocyanates required for polyurethane plastics used for insulation

**Review Questions:**

**Examples Set:**

1. Hinsberg reagent is
  - a. Acetyl chloride
  - b. Benzoyl chloride
  - c. Benzene sulphonyl chloride
  - d. Sulphonyl chloride

**Solution:** c)

2. Which of the following is the stronger base?
  - a. Methyl amine
  - b. Dimethyl amine
  - c. Trimethyl amine
  - d. Ammonia

**Solution:** b)

3. Reaction of an aliphatic primary amine with nitrous acid in warm conditions may lead to the formation of
  - a. A nitrile
  - b. An alcohol
  - c. A secondary amine
  - d. An iso cyanide

**Solution:** b)

4. Which of the following reactants will evolve nitrogen with a mixture of  $\text{NaNO}_2$  and  $\text{HCl}$  on warming?
  - a. Primary amines
  - b. Secondary amines
  - c. Tertiary amines
  - d. 2 & 3

**Solution:** a)

5. Primary and secondary amines are distinguished by
  - a.  $\text{Br}_2/\text{KOH}$
  - b.  $\text{H}_2\text{SO}_4$
  - c.  $\text{HClO}_4$
  - d.  $\text{HNO}_2$

**Solution:** d)

6. Aniline is prepared by
  - a. The reaction of benzene with ammonia
  - b. The reduction of nitrobenzene with  $\text{Sn}/\text{HCl}$

- c. The hydrogenation of nitrobenzene
- d. Both b) and c)

**Solution:** d)

7. When ammonia is heated with an alkyl halide, in the presence of base, which of the following is formed first?
- a. Primary amines
  - b. Amides
  - c. Nitrated alkyl halides
  - d. Quaternary ammonium salts

**Solution:** a)

8. Aniline reacts with nitrous acid at low temperature to give
- a. a N- nitrosoamine
  - b. a nitrile
  - c. a diazonium salt
  - d. Toluene

**Solution:** c)

9. When aniline is heated with chloroform and alcoholic KOH, the product is
- a. Benzonitrile
  - b. p – Chloroaniline
  - c. Phenylisocyanide
  - d. m – Chloroaniline

**Solution:** c)

10. Benzamide reacts with  $\text{Br}_2$  and KOH to give
- a. Benzene
  - b. Benzylamine
  - c. Aniline
  - d. Benzonitrile

**Solution:** c)

11.What happens when an amine under goes

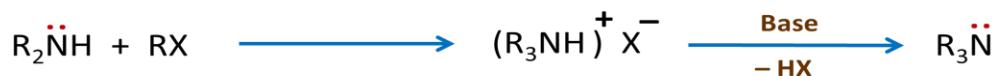
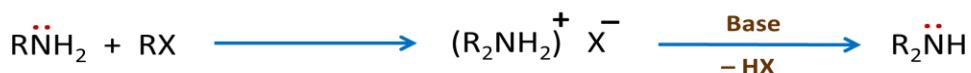
- a. Alkylation
- b. Acylation

**Solution:**

**a. Alkylation:**

An alkyl halide can react with a primary or secondary amine which acts as a nucleophile. On undergoing nucleophilic substitution, a  $1^\circ$  – amine is converted to a  $2^\circ$  – amine and a  $2^\circ$  – amine in quaternary amine compound to a  $3^\circ$  – amine. The  $2^\circ$  – amine being a more powerful nucleophile again reacts with an alkyl halide to form a tertiary amine.

Ultimately the tertiary amine reacts with alkyl halides to form a quarternary ammonium salt.



**b. Acylation:**

Aliphatic and aromatic primary and secondary amines undergo acylation through nucleophilic substitution with acid derivatives such as acid halides or anhydrides to form amides.





12. Give the reaction of an amine with Hinsberg's reagent. What is the use of the reaction?

**Solution:**

**Reaction with Hinsberg's Reagent:**

Primary and secondary amines combine with Hinsberg's Reagent (benzene sulphonyl chloride) to form sulphonamides.



It reacts with an alkali to form a soluble sodium salt.



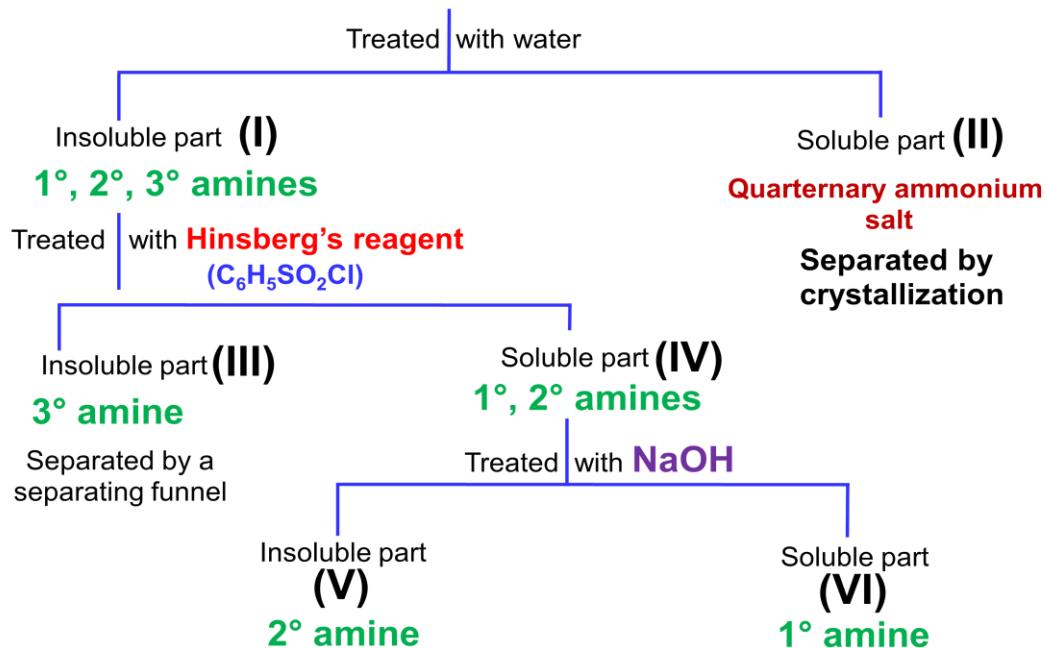
The product formed by the action of secondary amine on benzene sulphonyl chloride does not dissolve in an alkali. This is because there is no hydrogen atom attached to the N atom in the product. It is insoluble in alkali.



Tertiary amines do not react with  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ .

Hence Hinsberg's reagent is used for separation of primary, secondary and tertiary amines.

**Mixture of primary, secondary, tertiary amines  
&  
quaternary ammonium salts**



13. How do you identify primary, secondary and tertiary amines? Give the reactions.

**Solution:**

**Distinction between primary, secondary and tertiary amines:**

Test	Primary amine	Secondary amine	Tertiary amine
Action of $\text{CHCl}_3$ and alcoholic $\text{KOH}$ . (Carbylamine test)	Bad smelling carbylamine (Isocyanide) is formed.	No action.	No action.
Action of $\text{CS}_2$ and $\text{HgCl}_2$ . (Mustard oil test)	Alkyl isothiocyanate is formed which has pungent smell like mustard oil.	No action.	No action

Action of nitrous acid.	Alcohol is formed with evolution of nitrogen.	(Liebermann's test). Forms nitrosoamine which gives green colour with phenol and conc. $H_2SO_4$	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.
Action of acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No action.
Action of Hinsberg's reagent.	Monoalkyl sulphonamide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
Action of methyl iodide.	3 molecules (moles) of $CH_3I$ to form quaternary salt with one mole of primary amine.	2 moles of $CH_3I$ to form quaternary salt with one mole of secondary amine.	One mole of $CH_3I$ to form quaternary salt with one mole of tertiary amine.

14. How is aniline prepared in laboratory method?

**Solution:**

**Methods of preparation:**

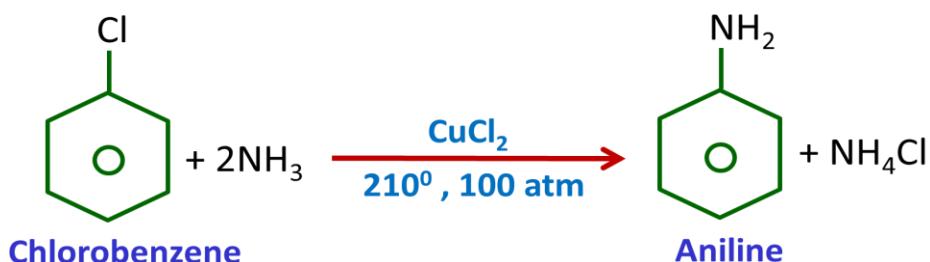
**Reduction of nitro compounds:**

This is a very convenient and most widely used method of preparing aniline



**Ammonolysis of aryl chlorides:**

Aniline is prepared by treating chlorobenzene with ammonia in the presence of copper salts at high temperature and pressure



### Physical properties:

15. What happens when aniline is treated with nitrous acid ( $\text{NaNO}_2 + \text{HCl}$ ) at  $0 - 5^\circ \text{C}$

### Solution:

#### Reaction with nitrous acid:

Aniline reacts with nitrous acid (from  $\text{NaNO}_2 + \text{HCl}$ ) in the presence of HCl at  $0 - 5^\circ \text{C}$  to give benzenediazonium chloride



### Problem Set:

1.  $\text{C}_2\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3 \text{ KOH} \rightarrow \text{X} + 3\text{Y} + 3 \text{ H}_2\text{O}$       compounds X and Y are
  - a.  $\text{CH}_3\text{CN}$  and  $\text{KCl}$
  - b.  $\text{CH}_3\text{NC}$  and  $\text{KClO}$
  - c.  $\text{C}_2\text{H}_5\text{CN}$  and  $\text{KClO}_3$
  - d.  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{KCl}$

**Solution:** d)

2. When tertiary amine is treated with acetyl chloride
- An acyl chloride is formed
  - Alkyl ammonium is formed
  - Ammonia is liberated
  - No reaction takes place

**Solution:** d)

3. Aniline on treatment with nitrating mixture yields mainly
- $\text{o}$  – nitro aniline
  - $\text{p}$  – nitro aniline
  - $\text{m}$  – nitro aniline
  - All the above.

**Solution:** c)

4. When an alcoholic solution of aniline is warmed with chloroform the product is \_\_\_\_\_
- Benzyl amine
  - Cyanobenzene
  - Benzanilide
  - phenyl isocyanide

**Solution:** d)

5. Aniline reacts with bromine water to form
- Bromobenzene
  - $\text{m}$  – Bromoaniline
  - $2, 4, 6$  – Tribromoaniline
  - $\text{o}$  – and  $\text{p}$  – Bromoaniline

**Solution:** c)

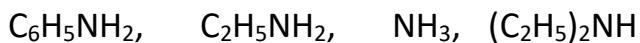
6. Aniline reacts with acetic anhydride to give
- $\text{N}$  – Methylaniline
  - $\text{p}$  – Aminoacetophenone
  - Acetanilide
  - $\text{m}$  – Aminoacetophenone

**Solution:** c)

7. Which of the following reagents does not react with aniline?
- Acetyl chloride
  - Acetic anhydride
  - Ammonia
  - Nitrous acid

**Solution:** c)

8. Arrange the following in decreasing order of their basic strength.



**Solution:**



9. Complete the following acid – base reactions and name the products

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow$
- $(\text{C}_2\text{H}_5)_3\text{N} + \text{HCl} \rightarrow$

**Solution:**

- $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+ \text{Cl}^-$
- $(\text{C}_2\text{H}_5)_3\text{N} + \text{HCl} \rightarrow (\text{C}_2\text{H}_5)_3\text{NH}_3^+ \text{Cl}^-$

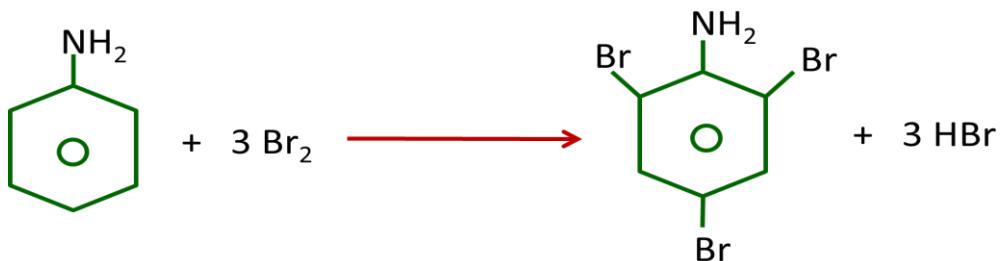
10. Write short notes on electrophilic substitution of aniline

**Solution:**

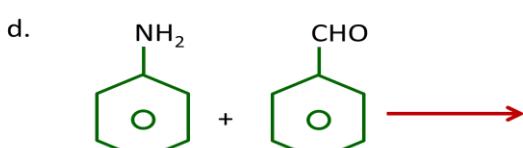
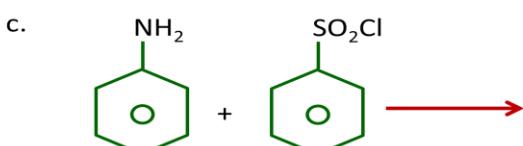
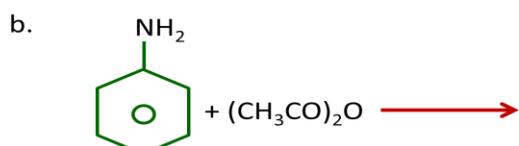
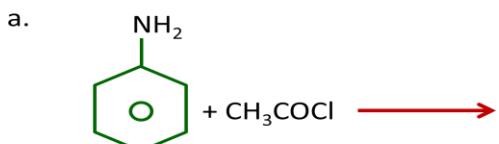
### Electrophilic Substitution Reactions:

All the types of amino groups  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$  are most powerful ring activating groups in aromatic electrophilic substitution reactions and are ortho and para directing. This is a test for identifying aniline.

Aniline gets instantaneously brominated at all of the three o, p – positions (all o -, p-, positions) to give a white precipitate in aqueous solutions with Bromine water.

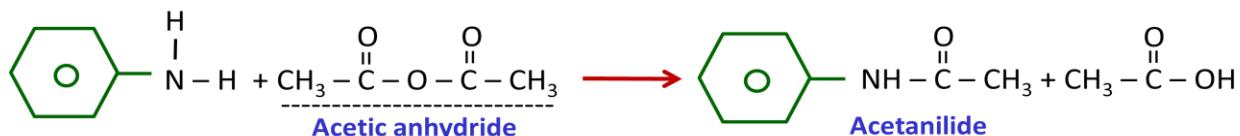
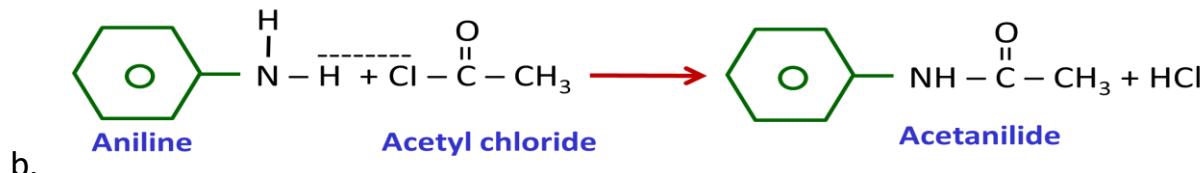


11. Complete the following reactions. Write the structures of the products.

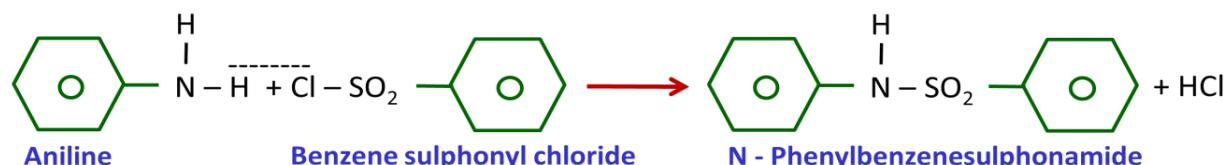


**Solution:**

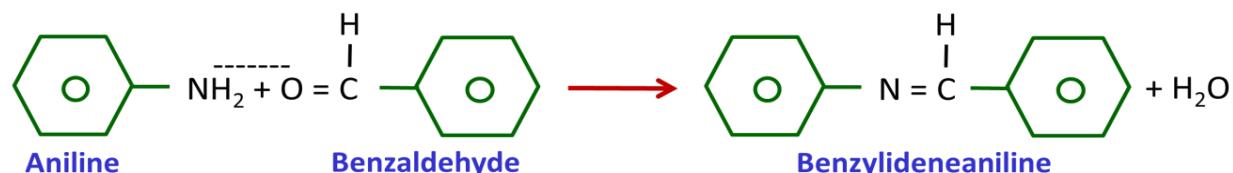
a.



c.



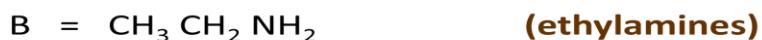
d.

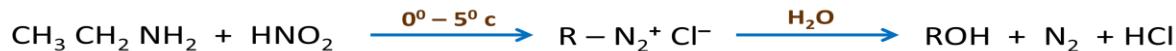


### Exercise questions:

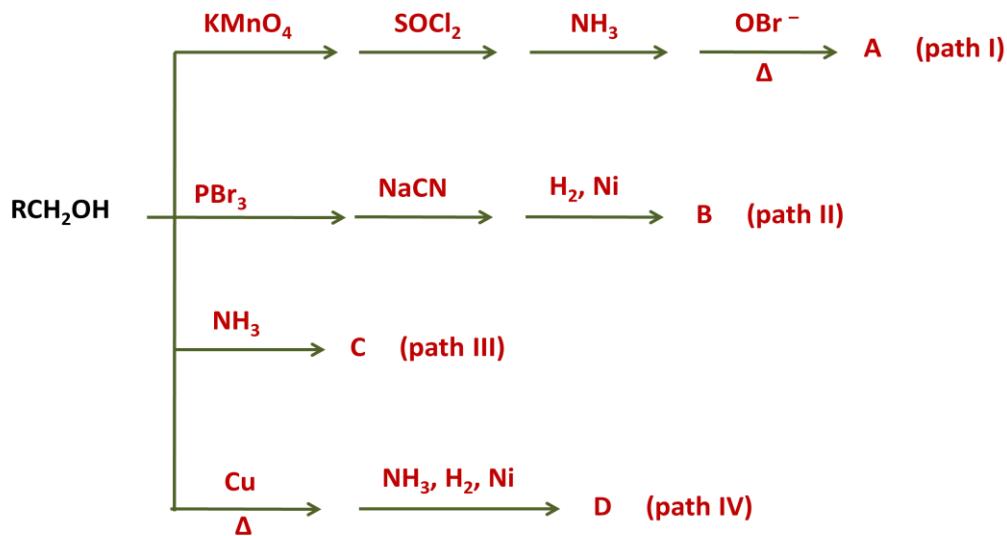
1. Compound (A), with molecular formula C<sub>3</sub>H<sub>7</sub>NO, reacts with bromine in the presence of NaOH to give (B). Compound (B) reacts with nitrous acid to form ethyl alcohol on warming with H<sub>2</sub>O and nitrogen. identify (A) and (B) show the reactions involved

### Solution:

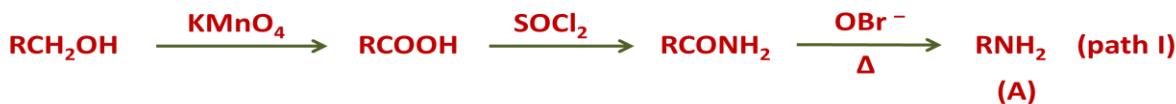




2.  $\text{RCH}_2\text{OH}$  can be converted into  $1^\circ$  amines by following methods. What is the type (upgraded or degraded or same)  $1^\circ$  amine obtained?



**Solution:**



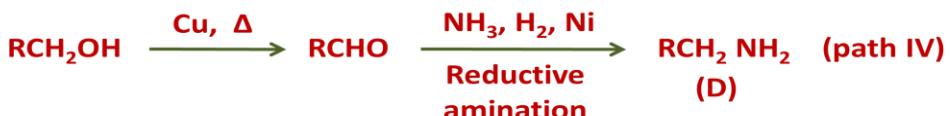
A is  $1^\circ$  amine with one carbon less (degraded)



B is  $1^\circ$  amine with one carbon less (upgraded)

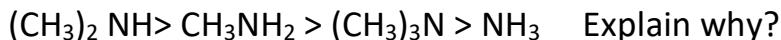


C is  $1^\circ$  amine with same number of carbon atoms



D is  $1^\circ$  amine with same number of carbon atoms

3. In aqueous solution the order of basicity is in order

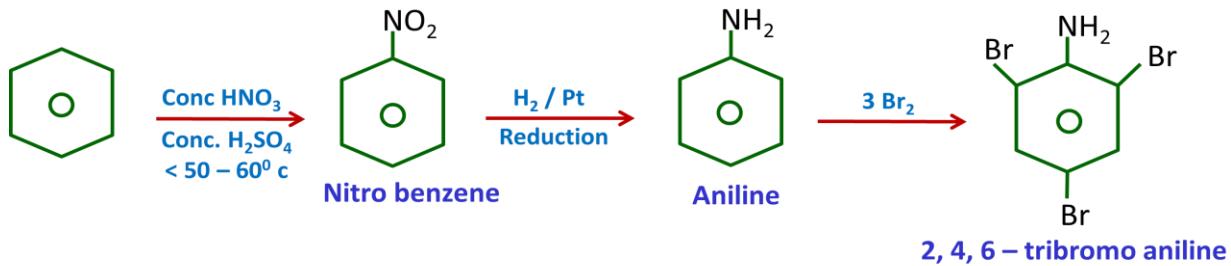


**Solution:**

In aqueous solution the aminium ions formed from secondary and primary amines are stabilized by hydration through hydrogen bonding much more effectively than are the aminium ions formed from tertiary amines.  $(\text{CH}_3)_3\text{NH}^+$  ion (the aminium ion formed from tertiary amine) has only one hydrogen to use in hydrogen bonding to water molecules (as compared to aminium ions of primary and secondary amines which have three and two hydrogens respectively) and poorer salvation of this aminium ion more than counteracts the electron-releasing effect of the three methyl groups and makes the tertiary amine less basic than primary and secondary amines in aqueous solution. However, it is the electron-releasing tendency of the three methyl group that make it tertiary amine more basic than ammonia.

4. How will you synthesize 2, 4, 6 – tribromo aniline from benzene?

**Solution:**



5. How will you synthesize p – toluidine (p – methylaniline) from benzene?

**Solution:**



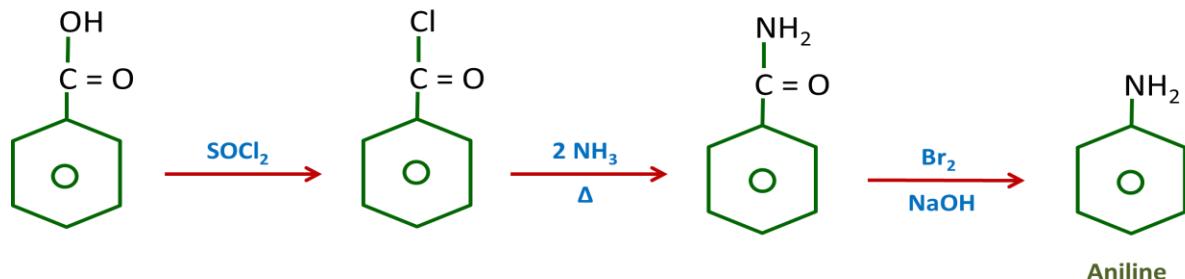
6. Give the preparation of the following compounds from benzoic acid

a. Aniline

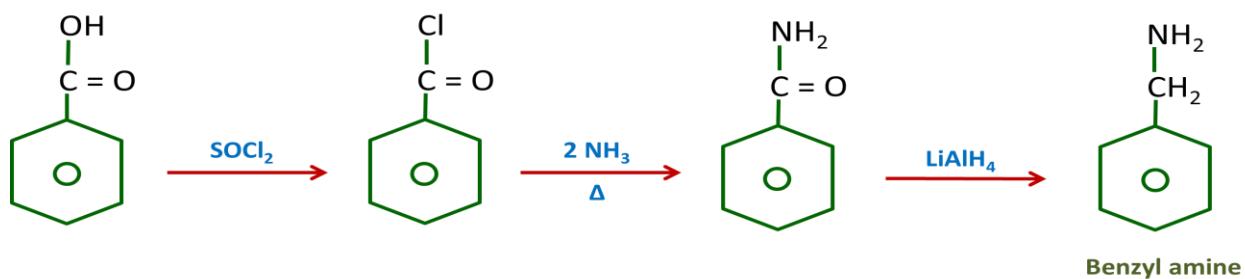
b. Benzyl amine

**Solution:**

a.

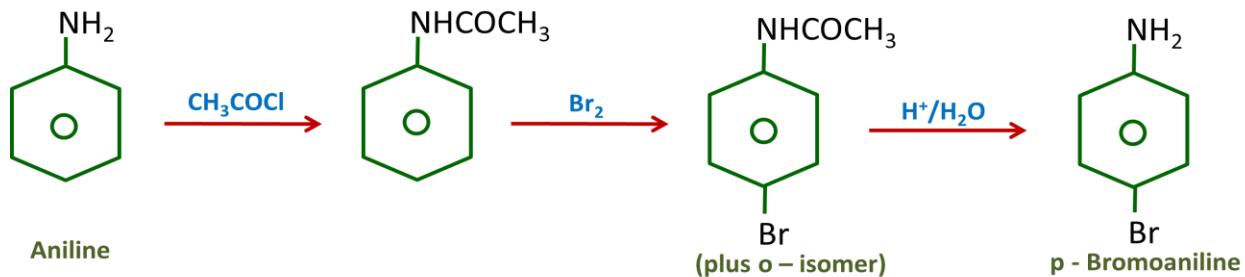


b.



7. How will you synthesise p – bromoaniline from aniline

**Solution:**



## 25.1 General Principles of Metallurgy

A few elements like ‘Carbon, silver, gold and noble gases occur in free state, while others are present in combined form in the earth’s crust. Most of the metals occur as their minerals. For obtaining a particular metal, first we look for **minerals**; they are naturally occurring chemical substances in the earth’s crust obtained by mining.

**“The branch of science deals with the different methods of extracting the metal from its natural sources and then converting them into useful materials to the mankind is known as metallurgy.”**

Out of many minerals in which a metal may be found, only a few are able to be used as sources of that metal. Such minerals are known as **Ores**.

### A. Occurrence:

Metals occur mostly as their oxides, carbonates, sulphides, chlorides. The principal ores of aluminium, iron, copper and zinc have been given in the table given below.

Metal	Ores	Composition
Al	Bauxite Cryolite kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ $\text{Na}_3\text{AlF}_6$ $[\text{Al}(\text{OH})_4\text{Si}_2\text{O}_5]$
Fe	Haematite Magnetite Siderite Iron pyrites	$\text{Fe}_2\text{O}_3$ $\text{Fe}_3\text{O}_4$ $\text{FeCO}_3$ $\text{FeS}_2$
Cu	Malachite Azurite Cuprite Copper glance Copper pyrites	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ $\text{Cu}_2\text{O}$ $\text{Cu}_2\text{S}$ $\text{CuS} \cdot \text{Fe}_2\text{S}_3$
Zn	Zinc blende or sphalerite Calamine Zincite	$\text{ZnS}$ $\text{ZnCO}_3$ $\text{ZnO}$

## B. Principle of Extraction:

The minerals available in nature contain various types of impurities. Some impurities are combined with the minerals either physically or chemically. So depending on the nature of the impurities, different types of treatment of the ore are adopted. Some of these treatments are described here.

### a. Ore Concentration

**“Removal of the unwanted materials (e.g., sand, clay, stones etc.,) from the ore is known as Concentration, dressing or benefaction.**

The impurities of certain types can be eliminated from the ore in the molten state only. Most of the impurities in the ores do not melt easily at the temperature of the normal industrial furnaces. Therefore “an outside substance, added to the ore to lower its melting point, is known as flux.”

“Flux combines with the **gangue** (i.e. impurities in the ore) chemically and forms easily fusible products, called **Slag**.” Since this entire process is costly, the gangue is removed first by other cheap physical methods. Some of the common methods of ore dressing are described here.

Flux + gangue = slag

#### (i) Hand picking:

In this method sand and small stones are removed. Lumps of the ore are broken to small pieces. The sand and mud adhering to the ore are washed by a stream of water. Then the pieces of the ore are dropped on a rotating roller belt and the stones are weeded out.

**Ex:** The sand and stones, from the Haematite are removed by hand.

#### (ii) Hydraulic washing:

This is based on the differences in gravities of the ore and the gangue particles. It is therefore a type of gravity separation. In one such process an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and heavier ores are left behind.

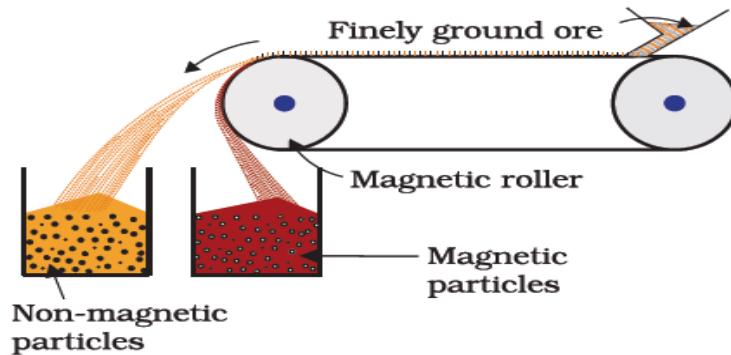
**Example:** Cassiterite ( $\text{SnO}_2$ ) is concentrated by this method. Wilfley's tables are specially made tables for washing of ores.



### (iii) Magnetic separation:

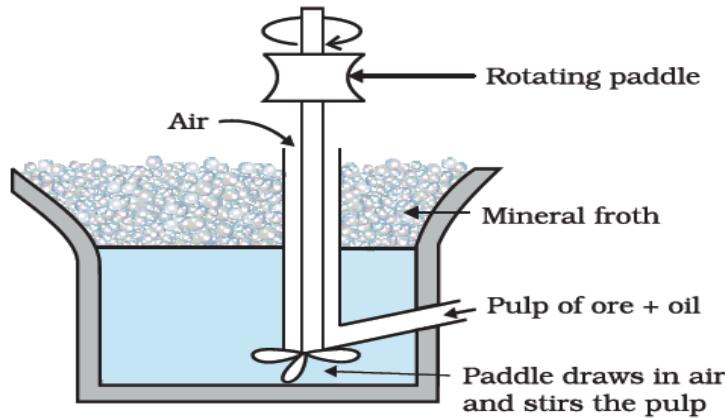
This is based on differences in magnetic properties of the ore components. If either of the ore or the gangue is magnetic substance, then such separations are carried out. In this process, the finely powdered ore is dropped on a belt moving on two strong electro magnetic rollers. The magnetic and the non – magnetic substances form two separate heaps.

**Ex:** Haematite and magnetite have magnetic ore particles where as cassiterite and wolframites have a magnetic impurity.



### (iv) Froth Floatation method:

This method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilizers are added. Collectors (e.g., pine oil, fatty acids, xanthates etc.,) enhance non – wettability of the mineral particles and froth stabilizers (e.g., cresols, aniline) stabilize the froth.



The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

#### (v) Liquification:

This method is useful for such ores which contain fusible mineral particles and high melting gangue. This method is used with stibnite, an antimony mineral. It is taken in a fireclay pots with perforated bottom and heated to around  $500 - 600^{\circ}\text{C}$ . Only the mineral part of the ore melts and flows out leaving the gangue behind.

#### b. Oxidation:

Some sulphides and halide ores are oxidized to obtain non – metals. The most commonly used oxidizing agent in the metallurgy is  $\text{O}_2$  gas.

#### (i) Oxidation of sulphide ore:

On roasting at high temperatures, the sulphides change to oxides.

#### **Example**



### c. Reduction:

Some oxides and halide ores are reduced to obtain the metals. The commonly used reducing agents in the metallurgy are

- (i) Coke      (ii) CO      (iii) water gas      (iv) H<sub>2</sub>gas      (v) Al – metal

The selection of the reductant depends on the chemical activity of the metal. The following are some examples.

#### (i) Reduction of oxides:

(a) Zinc and tin are obtained by reduction with coke



(b) Fe<sub>2</sub>O<sub>3</sub> is reduced by CO to get Fe



(c) NiO is reduced by water gas



(d) Molybdenum and Tungsten oxides are reduced with H<sub>2</sub>



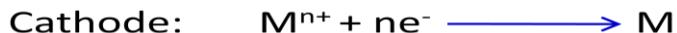
(e) Metals like Al, Mg or Ca are also used for the reduction. When Al is used as a reducing agent, the process is referred as Goldschmidt's Alumino Thermic process or simply Gold Schmidt Thermite process.



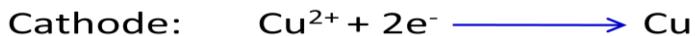
These reactions require about  $600^{\circ}\text{C}$ . This is provided by the exothermic nature of the reduction. During these reactions the temperatures increase up to  $2500^{\circ}\text{C}$  to  $3000^{\circ}\text{C}$ . So the metal is obtained in molten state.

#### d. Electrolytic method – refining:

Zn, Cu, Ag, Au etc., impure metals are refined by this method. In this method, the impure metal is made the anode and the pure metal is made the cathode. An acidified solution of the metal salt or a molten metal salt is made the electrolyte. On passing electricity pure metal is deposited on the cathode. The impurities settle to the bottom at the anode. This is known as anode mud.



**Example:** Cu is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. Acidified  $\text{CuSO}_4$  solution is used as an electrolyte.



Impurities from the blister copper deposit as anode mud. Zinc may also be refined in this way.

#### Assignment questions:

1. Write a note on ore dressing in metallurgy?
2. Write in brief about the methods of refining of metals
3. Describe magnetic separation method for concentration of an ore. Explain with a suitable example
4. Write short notes on each of the following in connection with the metallurgy
  - a. Liquification
  - b. Oxidation
  - c. Reduction

5. Discuss froth floatation process

**Example set:**

1. Which one of the following is gangue?
  - a. Waste materials present in the ore to be removed during concentration
  - b. Waste materials left after concentration
  - c. Waste materials left after purification of the metal
  - d. All the above.

**Solution:** a)

2. Which of the following methods are used for the concentration of Cassiterite?
  - a. Hand picking
  - b. Hydraulic washing
  - c. Magnetic separation
  - d. Froth floatation process

**Solution:** b)

3. Which of the following will use when an ore of tin has impurity of Iron (II) tungstate?
  - a. Froth floatation method
  - b. Hand picking
  - c. Magnetic separation
  - d. Liquification

**Solution:** c)

4. The reagent used to facilitate froth floatation process is called
  - a. Depressant
  - b. Activator
  - c. Flux
  - d. Both a and b

**Solution:** d)

5. Why haematite is concentrated by electromagnetic separation method?

**Solution:**

- (1) Haematite is magnetic ore particles.
  - (2) In this process, either the ore or the gangue is capable of being attracted by a magnetic field, and then such separations are carried out.
  - (3) That's why haematite is concentrated by electro magnetic separation method.
6. Why magnetite is concentrated by electromagnetic method?

**Solution:**

- (1) Magnetite is magnetic ore particles.
  - (2) In this process, either the ore or the gangue is capable of being attracted by a magnetic field, and then such separations are carried out.
  - (3) That's why magnetite is concentrated by electro magnetic separation method.
7. How is nickel oxide reduced to the metal?

**Solution:**

Nickel oxide is reduced by water gas at  $60^{\circ}$  -  $80^{\circ}\text{C}$ .



**Problem set:**

1. Identify the process in which ore is heated in the presence of the oxygen
  - a. Calcination
  - b. Smelting
  - c. Reduction
  - d. Roasting

**Solution:** d)

2. A mineral from which the metal can be extracted economically is known as
  - a. Ore
  - b. Slag

- c. Gangue
- d. Pyrites

**Solution:** a)

- 3. The electrolytic reduction technique is used in the extraction of
  - a. High electro positive elements
  - b. High electro negative elements
  - c. Metalloids
  - d. Non – metals.

**Solution:** a)

- 4. The common method of extraction of methods form oxide ores involves.
  - a. Reduction with C
  - b. Electrolytic method
  - c. Roasting
  - d. Both a and b

**Solution:** a)

- 5. Write two equations that use the principle of thermite process?

**Solution:**



- 6. Write the reduction equations for the conversion of metal oxides to metals?

**Solution:**

**Reduction of oxides:**

- (a) Zinc and tin are obtained by reduction with coke



(b)  $\text{Fe}_2\text{O}_3$  is reduced by CO to get Fe



(c) NiO is reduced by water gas



(d) Molybdenum and Tungsten oxides are reduced with  $\text{H}_2$



(e) Metals like Al, Mg or Ca are also used for the reduction. When Al is used as a reducing agent, the process is referred as Goldschmidt's Alumino Thermic process or simply Gold Schmidt Thermite process.



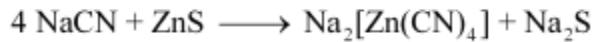
These reactions require about  $600^\circ\text{C}$ . This is provided by the exothermic nature of the reduction. During these reactions the temperatures increase up to  $2500^\circ\text{C}$  to  $3000^\circ\text{C}$ . So the metal is obtained in molten state.

### Exercise questions:

1. Which of the ores mentioned in the Table given can be concentrated by magnetic separation method?
2. What is the role of depressant in froth floatation process?
3. Which is a better reducing agent at 673 K? C and CO why?
4. Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?

### Solutions to exercise questions:

- When the ore or the gangue and not both can be attracted by the magnetic field, then the ore can be concentrated by this process of magnetic separation. Among the ores mentioned in table 6.1, the ores of iron such as haematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), siderite ( $\text{FeCO}_3$ ), and iron pyrites ( $\text{FeS}_2$ ) can be separated by the process of magnetic separation.
- In the froth floatation process, the role of the depressants is to separate two sulphide ores by selectively preventing one ore from forming froth. For example, to separate two sulphide ores ( $\text{ZnS}$  and  $\text{PbS}$ ),  $\text{NaCN}$  is used as a depressant which selectively allows  $\text{PbS}$  to come with froth, but prevents  $\text{ZnS}$  from coming to froth. This happens because  $\text{NaCN}$  reacts with  $\text{ZnS}$  to form  $\text{Na}_2[\text{Zn}(\text{CN})_4]$ .



- At 673 K, the value of  $\Delta G_{(\text{CO},\text{CO}_2)}$  is less than that of  $\Delta G_{(\text{C},\text{CO})}$ . Therefore, CO can be reduced more easily to  $\text{CO}_2$  than C to CO. Hence, CO is a better reducing agent than C at 673 K.
- In electrolytic refining of copper, the common elements present in anode mud are selenium, tellurium, silver, gold, platinum, and antimony. These elements are very less reactive and are not affected during the purification process. Hence, they settle down below the anode as anode mud.

## Module - 25.2

### Occurrence and Principles of extraction of Fe

#### A. Occurrence:

Iron is the second most abundant metal after Al and fourth most abundant element in the earth's crust. The earth's core is believed to consist mainly of iron and nickel, and the occurrence of iron meteorites suggests that it is abundant also in the solar system. It mostly occurs in the combined state.

**The major iron ores are given here under**

Name of the mineral	Formula
Haematite (Reddish brown coloured)	$\text{Fe}_2\text{O}_3$
Magnetite (Magnetic oxide)	$\text{Fe}_3\text{O}_4$
Limonite (Hydrated oxide)	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Siderite (Spathic iron ore)	$\text{FeCO}_3$
Iron pyrites	$\text{FeS}_2$
Copper pyrites	$\text{CuFeS}_2$

#### B. Principles of extraction of Fe:

The chemistry of iron can be studied under three sections depending upon the type of iron required. The sections are

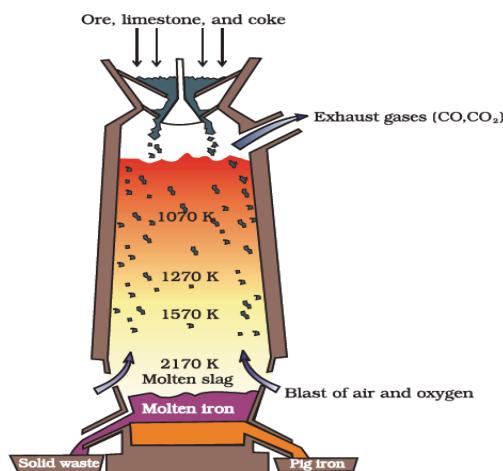
- a. Manufacture of cast iron
- b. Manufacture of wrought iron and
- c. Manufacture of steel.

#### a. Manufacture of cast iron:

Iron is extracted from its oxides in a blast furnace. This is an almost cylindrical furnace, lined inside with fire bricks. It is charged from the top with an iron ore (8 parts), desulphurised coke (4 parts) and lime stone (1 part) and is mixed in 8:4:1 parts by weight. Air is blown from the bottom. The coke burns producing heat and CO. The temperature range in the furnace is  $300^{\circ}\text{-}1600^{\circ}\text{C}$ . Various

reactions take place in the blast furnace at different temperature and different zones.

S.No	Temperature range	Name of zone	Changes occurring in the zone	Chemical reaction
1	400 <sup>0</sup> -700 <sup>0</sup> C	Zone of reduction	Spongy iron is formed iron oxide is reduced	$\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$ $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
	800 <sup>0</sup> -1000 <sup>0</sup> C	Zone of slag formation.	CO <sub>2</sub> is reduced to CO. Limestone decomposes to lime and CO <sub>2</sub> . Lime combines with SiO <sub>2</sub> to form the slag, CaSiO <sub>3</sub> .	$\text{CO}_2 + \text{C} \rightarrow 2\text{CO} -163\text{kJ}$ $\Delta$ $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
	1200 <sup>0</sup> -1300 <sup>0</sup> C	Zone of fusion	Coke burns to CO <sub>2</sub> . Porous iron melts. Any iron oxide remaining is completely reduced to Fe.	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
	Above 1400 <sup>0</sup> C		Molten iron collects in the bottom of the hearth. Slag floats on iron molten.	

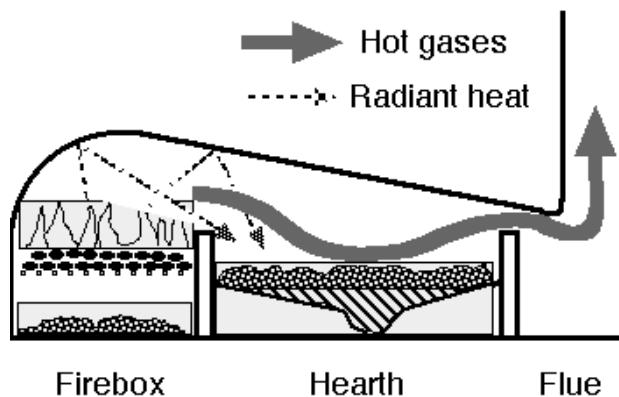


Blast furnace – Manufacture of cast iron

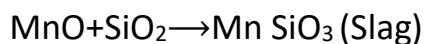
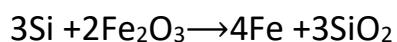
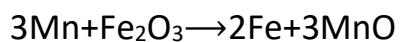
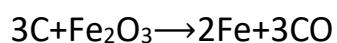
The iron obtained is known as Pig iron". The pig iron is melted and poured into moulds. The solid iron obtained by cooling pig iron is called as "cast iron" It contains nearly 4% C.

### b. Manufacture of wrought iron:

Wrought iron is the purest form of iron containing about 0.2 % C. It is prepared by heating cast iron in a reverberatory furnace. The furnace is given a basic lining of iron oxide. The impurities and the carbon present in cast iron combine with the lining. The impurities form a slag and carbon is oxidized to CO and escapes. It burns with a blue flame. The flames are known as "puddler's candles". Hence the process is known as puddling process.



Carbon and various impurities present combine with lining and form slag.



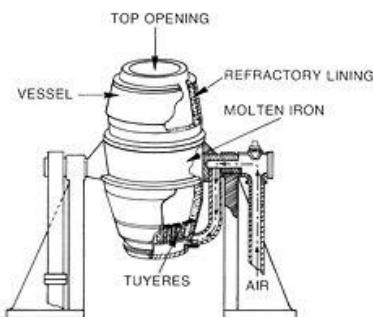
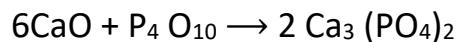
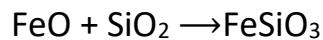
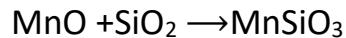
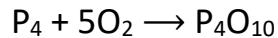
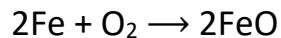
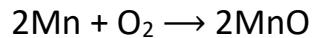
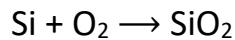
### c. Manufacture of steel:

Steel contains a lower percentage of carbon and other impurities than the pig iron. It is prepared by blowing air through molten pig iron taken in Bessemer converter.

### Bessemer converter process:

The Bessemer converter is a pear shaped furnace. It is constructed with steel. It is lined with silica or lime depending on the proportions of impurities (P, Si, Mn and C) present in the iron (P, Si, Mn and C). It is mounted on trunnions so that it can be tilted as one desires. Air is forced through the inlets at the bottom.

Carbon and various other impurities present combine with oxygen and form slag.



The basic slag containing  $\text{Ca}_3(\text{PO}_4)_2$  is known as Thomas slag. It is used as phosphatic fertilizer the CO burns with a blue flame. As soon as the CO is completely burnt out, the Bessemer converter is tilted to take some more substances in to it. A calculated amount of carbon is added in the form of

spiegeleisen (an alloy of iron with 15-20% Mn; 60% C and the rest iron). Manganese reduces the loss of iron. Also the ferromanganese unites with O<sub>2</sub> caught in the steel after Bessemerization process.

**Example set:**

1. Hematite is \_\_\_\_\_

- a. Fe<sub>3</sub>O<sub>4</sub>
- b. Fe<sub>2</sub>O<sub>3</sub>
- c. FeCO<sub>3</sub>
- d. 2Fe<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O

**Solution:** b)

2. Pig iron is also called \_\_\_\_\_

- a. Cast Iron
- b. Graft Iron
- c. Steel
- d. Stainless steel

**Solution:** a)

3. Which of the following is the least pure form of Iron?

- a. Bessemer Iron
- b. Steel
- c. Pig Iron
- d. Wrought Iron

**Solution:** c)

4. Which of the following is prepared by puddling process?

- a. Pig Iron
- b. Wrought Iron
- c. Steel
- d. All the above

**Solution:** b)

5. Write any three minerals of Fe?

**Solution:**

Haematite (Reddish brown coloured)       $\text{Fe}_2\text{O}_3$

Magnetite (Magnetic oxide)       $\text{Fe}_3\text{O}_4$

Limonite (Hydrated oxide)       $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

6. Describe a method for the manufacture of Pig iron from the ore.

**Solution:**

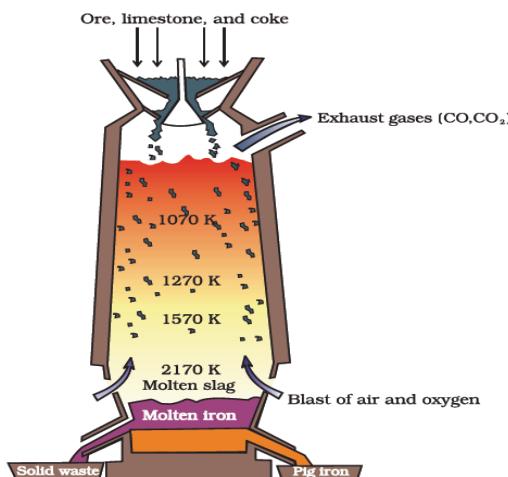
**a. Manufacture of cast iron**

Iron is extracted from its oxides in a blast furnace. This is an almost cylindrical furnace, lined inside with fire bricks. It is charged from the top with an iron ore (8 parts), desulphurised coke (4 parts) and lime stone (1 part) and is mixed in 8:4:1 parts by weight. Air is blown from the bottom. The coke burns producing heat and CO. The temperature range in the furnace is  $300^{\circ}\text{C}$ - $1600^{\circ}\text{C}$ . Various reactions take place in the blast furnace at different temperature and different tones.

The iron obtained is known as "Pig iron". The pig iron is melted and poured into moulds. The solid iron obtained by cooling pig iron is called as "cast iron". It contains nearly 4% C.

S.No	Temperature range	Name of zone	Changes occurring in the zone	Chemical reaction
1	$400^{\circ}\text{C}$ - $700^{\circ}\text{C}$	Zone of reduction	Spongy iron is formed iron oxide is reduced	$\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$ $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
	$800^{\circ}\text{C}$ - $1000^{\circ}\text{C}$	Zone of slag formation.	$\text{CO}_2$ is reduced to CO. Limestone decomposes to lime and $\text{CO}_2$ . Lime combines with $\text{SiO}_2$ to form the slag, $\text{CaSiO}_3$ .	$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ -163kJ $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$ $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$

	$1200^{\circ}\text{C}$ - $1300^{\circ}\text{C}$	Zone of fusion	Coke burns to $\text{CO}_2$ . Porous iron melts. Any iron oxide remaining is completely reduced to Fe.	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
	Above $1400^{\circ}\text{C}$		Molten iron collects in the bottom of the hearth. Slag floats on iron molten.	



### Blast furnace – Manufacture of cast iron

#### Assignment questions:

1. Compare “Bessemer process” and “open – hearth process” for the preparation of steel
2. Draw a neat diagram of Blast furnace. Indicate the temperature zones and their names in it
3. Draw a neat diagram of a reverberatory furnace and label it neatly

#### Example set:

1. Spiegeleisen used in steel making is a form of \_\_\_\_\_
  - a. Ferro – vanadium
  - b. Ferro – chromium

- c. Ferro – silicon
- d. Ferro - manganese

**Solution:** d)

- 2. In which one of the following smelting is carried out
  - a. Blast furnace
  - b. Open hearth furnace
  - c. Bessemer converter
  - d. All of these

**Solution:** a)

- 3. The hottest part of the blast furnace is
  - a. Hearth
  - b. Tuyers
  - c. Outlet for gases
  - d. Entrance for charge

**Solution:** a)

- 4. Which of the following process involves the smelting process
  - a.  $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$
  - b.  $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$
  - c.  $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
  - d.  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}$

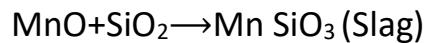
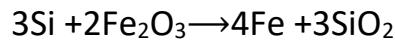
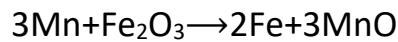
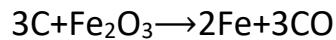
**Solution:** c)

- 5. The important oxide ore of iron is
  - a. Siderite
  - b. Haematite
  - c. Pyrites
  - d. Bauxite

**Solution:** b)

6. Write the equations for the chemical reactions that take place in the manufacture of wrought iron.

**Solution:**



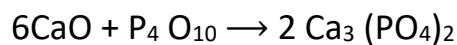
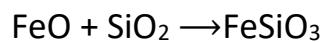
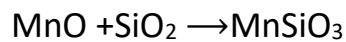
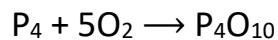
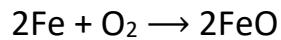
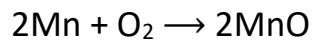
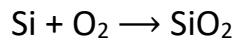
7. Describe a method to convert cast – iron into steel of high quality.

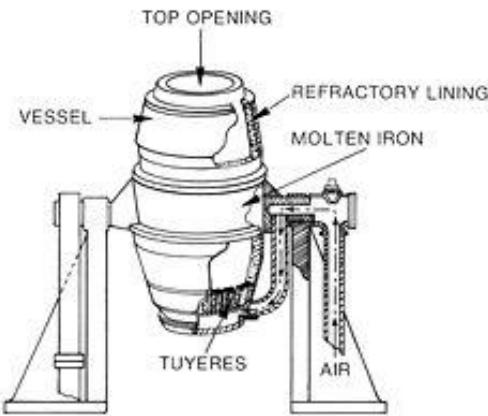
**Solution:**

### Bessemer converter process

The Bessemer converter is a pear shaped furnace. It is constructed with steel. It is lined with silica or lime depending on the proportions of impurities (P, Si, Mn and C) present in the iron. It is mounted on trunnions so that it can be tilted as one desires. Air is forced through small holes at the bottom.

Carbon and various other impurities present combine with oxygen and form slag.





The basic slag containing  $\text{Ca}_3(\text{PO}_4)_2$  is known as Thomas slag. It is used as phosphatic fertilizer. The CO burns with a blue flame. As soon as the CO is completely burnt out, the Bessemer converter is tilted to take some more substances in to it. A calculated amount of carbon is added in the form of spiegeleisen (an alloy of iron with 15-20% Mn; 60% C and the rest iron). Manganese reduces the loss of iron. Also the ferromanganese unites with  $\text{O}_2$  caught in the steel after Bessemerization process.

#### **Exercise questions:**

1. Differentiate between “minerals” and “ores”.
2. How is ‘cast iron’ different from ‘pig iron’?
3. a. What is name and formula of slag formed from  $\text{P}_2\text{O}_5$  impurity in the metallurgy of iron  
b. In what form carbon is present in white cast iron?  
c. Which molten metals are found in the core of earth?
4. What is the chemical formula of fool’s gold
5. Give the names of two metals for which Bessemerisation is used

#### **Solutions to exercise questions:**

1. Minerals are naturally occurring chemical substances containing metals. They are found in the Earth’s crust and are obtained by mining.

Ores are rocks and minerals viable to be used as a source of metal.

For example, there are many minerals containing zinc, but zinc cannot be extracted profitably (conveniently and economically) from all these minerals.

Zinc can be obtained from zinc blende ( $\text{ZnS}$ ), calamine ( $\text{ZnCO}_3$ ), Zincite ( $\text{ZnO}$ ) etc.

Thus, these minerals are called ores of zinc.

2. The iron obtained from blast furnaces is known as pig iron. It contains around 4% carbon and many impurities such as S, P, Si, Mn in smaller amounts.

Cast iron is obtained by melting pig iron and coke using a hot air blast. It contains a lower amount of carbon (3%) than pig iron. Unlike pig iron, cast iron is extremely hard and brittle.

3. a. Thomas slag  $\text{Ca}_3(\text{PO}_4)_2$   
b. Cementite  $\text{Fe}_3\text{C}$   
c. Nickel and iron
4.  $\text{FeS}_2$
5. Fe and Cu

## Module 25.3

### Occurrence and principles of extraction of Cu

#### Copper (Cu):

##### A. Occurrence:

Copper is a chemical element with symbol “Cu” comes from Latin word “cuprum” and atomic number 29. It occurs in the combined state mostly. The important minerals of copper are given below

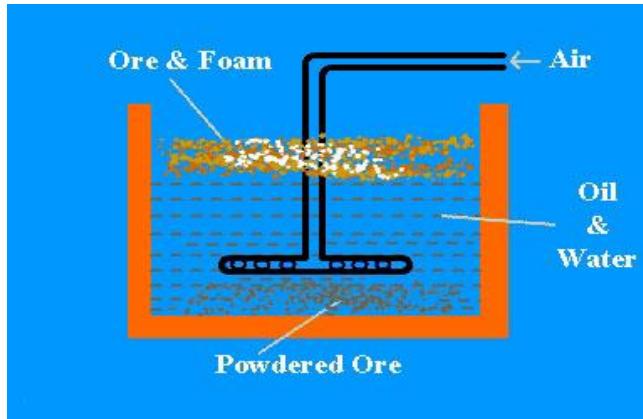
Name of the mineral	formula
Cuprite	$\text{Cu}_2\text{O}$
Chalcocite or copper glance	$\text{Cu}_2\text{S}$
Copper pyrite or chalcopyrite	$\text{CuFeS}_2$
Malachite green	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Azurite blue	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

##### B. Extraction of copper from sulphide ore:

Copper pyrites is the main source of copper metal. From it copper metal is obtained by smelting process. Following steps are involved in the extraction of copper by smelting process.

###### a. Concentration:

The finely crushed ore is concentrated by Froth-Floatation process. The finely crushed ore is suspended in water containing a little amount of pine oil. A blast of air is passed through the suspension. The particles get wetted by the oil and float as a froth which is skimmed. The gangue sinks to the bottom. The froth is separated and about 95% concentrated ore is obtained.



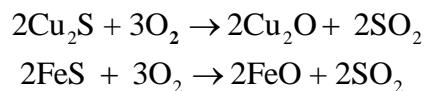
### b. Roasting:

The concentrated ore is then roasted in a furnace in a current of air. Sulphur is oxidized to  $\text{SO}_2$  and impurities of arsenic and antimony are removed as volatile oxides.

The following reaction takes place.

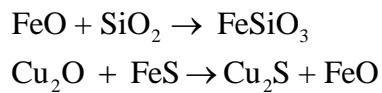


Cuprous sulphide and ferrous sulphide are further oxidized into their oxides.



### c. Smelting:

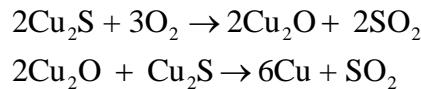
The roasted ore is mixed with coke and silica ( $\text{SiO}_2$ ) and is introduced into a blast furnace. The hot air blast converts  $\text{FeO}$  into ferrous silicate ( $\text{FeSiO}_3$ ).



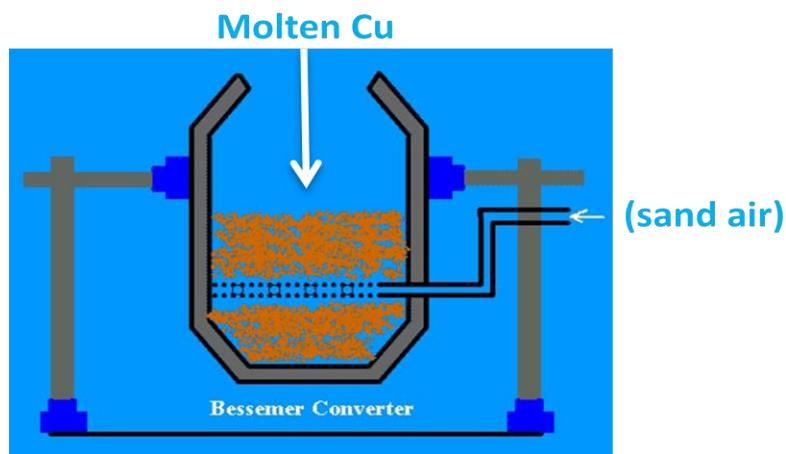
The product of the blast furnace consists mostly of  $\text{Cu}_2\text{S}$  and a little of ferrous sulphide. This product is known as "**Matte**". It is collected from the outlet at the bottom of the furnace.

#### d. Bessemerization process:

Copper metal is extracted from molten matte through bessemerization. The matte is introduced in to Bessemer converter which is upheld by tuyers. The air is blown through the molten matte. Blast of air converts  $\text{Cu}_2\text{S}$  partly into  $\text{Cu}_2\text{O}$  which reacts with remaining  $\text{Cu}_2\text{S}$  to give molten copper.

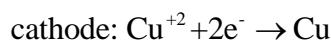
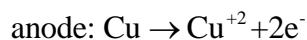


The copper so obtained is called "Blister copper" (98% pure) because, as it solidifies,  $\text{SO}_2$  escapes out producing blisters on its surface.

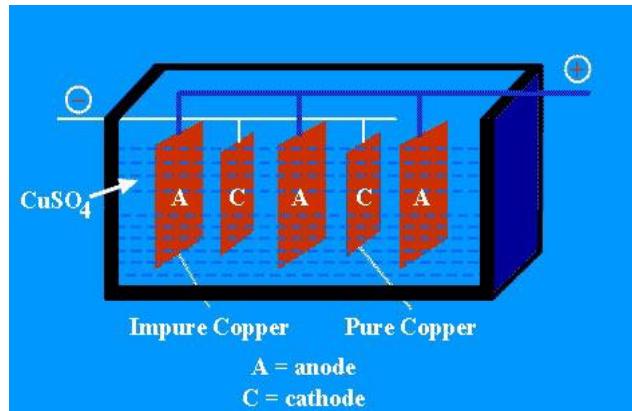


#### e. Refining of copper:

Blister copper is refined by electrolysis. Blocks of blister copper (impure copper) are used as anodes and thin sheets of pure copper act as cathodes. The cathode plates are coated with graphite in order to remove deposited copper. The electrolyte is copper sulphate ( $\text{CuSO}_4$ ) mixed with a little amount of  $\text{H}_2\text{SO}_4$  to increase the electrical conductivity. Optimum potential difference is 1.3 volt for this electrolytic process. During electrolysis, pure copper is deposited on the cathode plates and impurities which are soluble fall to the bottom of the cell as anode mud.



This electrically refined copper is 100% pure.



### Uses:

It is used as thermal conductor, an electrical conductor, a building material and a constituent of various metal alloys.

### Assignment questions:

1. Write an essay on the Belgain process for the extraction of Zinc metal?
2. Write the short notes on concentration of Zinc ores.
3. How is copper pyrites concentrated?

### Example set:

1. What is symbol of copper?
  - a. Cd
  - b. Cu
  - c. Cr
  - d. Co

### Solution: b)

2. Which of the following is Sulphide mineral of copper
  - a. Cuprite
  - b. Azurite
  - c. Malachite

d. Chalcocite

**Solution:** d)

3. Froth floatation method is used to increase the concentration of
- a. Chalcopyrites
  - b. Bauxite
  - c. Haematite
  - d. Calamine

**Solution:** a)

4. Blister copper is \_\_\_\_\_ % pure
- a. 20
  - b. 40
  - c. 80
  - d. 98

**Solution:** d)

5. In the electrolysis of  $\text{CuSO}_4$ ,  $\text{H}_2\text{SO}_4$  is added to \_\_\_\_\_
- a. Increase the conductivity
  - b. Decrease the conductivity
  - c. Remove impurities from  $\text{CuSO}_4$
  - d. Both b and c

**Solution:** a)

6. The most commonly method used for the reduction of the zinc oxide
- a. Baeyer's process
  - b. Hall's process
  - c. Serpek's process
  - d. Belgain process

**Solution:** d)

7. The Zinc obtained by electrolytic refining \_\_\_\_\_ % pure
- a. 80

- b. 90
- c. 99.99%
- d. 70

**Solution:** c)

8. Write the name of any three minerals of Cu with their formulae.

**Solution:**

Cuprite ( $\text{Cu}_2\text{O}$ ); Covellite ( $\text{CuS}$ ); Chalocite or copper glance ( $\text{Cu}_2\text{S}$ ).

9. What is the primary product of Bessemerization of matte?

**Solution:**

Copper metal is extracted from molten matte through bessemerization. The matte is introduced in to Bessemer converter which is upheld by tuyers. The air is blown through the molten matte. Blast of air converts  $\text{Cu}_2\text{S}$  partly into  $\text{Cu}_2\text{O}$  which reacts with remaining  $\text{Cu}_2\text{S}$  to give molten copper.

10. Write the names of minerals with the following formulae.

- a.  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
- b.  $\text{Zn}_2\text{SiO}_4$
- c.  $\text{ZnCO}_3$

**Solution:**

$\text{ZnO} \cdot \text{Fe}_2\text{O}_3$  - Franklinite

$\text{Zn}_2\text{SiO}_4$  - willemite

$\text{ZnCO}_3$  – Calamine

**Problem set:**

1. Heating pyrites in air to remove sulphur is known as \_\_\_\_\_
  - a. calcination
  - b. fluxing

- c. smelting
- d. roasting

**Solution:** d)

2. In smelting, the roasted ore is mixed with coke and \_\_\_\_\_
- a. sulphur
  - b. silica
  - c. copper
  - d. zinc

**Solution:** b)

3. Which of the following is sulphide ore of zinc
- a. Zinc blende
  - b. Zincite
  - c. Calamine
  - d. Willemite

**Solution:** a)

4. Froth floatation method may be used to increase the concentrion of ----
- a. Hemiatite
  - b. Bauxite
  - c. Calmanie
  - d. Zinc blende

**Solution:** d)

5. Heating pyrites in air to remove sulphur is known as
- a. Calcination
  - b. Fluxing
  - c. Roasting
  - d. Smelting

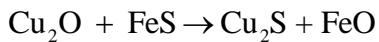
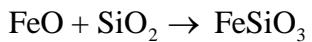
**Solution:** c)

6. Describe the smelting of copper ore.

**Solution:**

**Smelting:**

The roasted ore is mixed with coke and silica ( $\text{SiO}_2$ ) and is introduced into a blast furnace. The hot air blast converts  $\text{FeO}$  into ferrous silicate ( $\text{FeSiO}_3$ ).



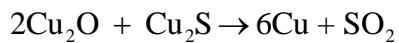
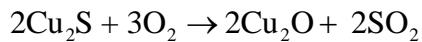
The product of the blast furnace consists mostly of  $\text{Cu}_2\text{S}$  and a little of ferrous sulphide. This product is known as "**Matte**". It is collected from the outlet at the bottom of the furnace.

7. Write an essay how copper matte is treated to get pure copper.

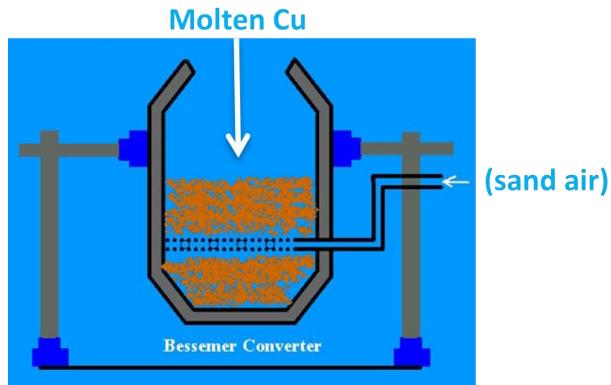
**Solution:**

**BESSEMERIZATION:**

Copper metal is extracted from molten matte through bessemerization. The matte is introduced into Bessemer converter which is upheld by tuyers. Air is blown through the molten matte. Blast of air converts  $\text{Cu}_2\text{S}$  partly into  $\text{Cu}_2\text{O}$  which reacts with the remaining  $\text{Cu}_2\text{S}$  to give molten copper.



The copper so obtained is called "Blister copper" (98% pure) because, as it solidifies,  $\text{SO}_2$  escapes out producing blisters on its surface.

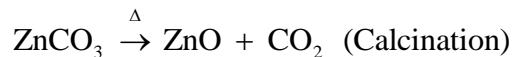


### Exercise questions:

1. Write only the chemical reactions that take place in the metallurgy of Zinc.
2. Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?
3. State the role of silica in the metallurgy of copper.
4. Copper *matte* is put in silica lined converter. Give an explanation.
5. Why is zinc not extracted from zinc oxide through reduction with CO?

### Solution to exercise questions:

1.



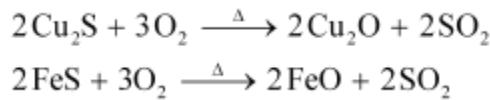
2. Cu – pyrites, when reduced with H<sub>2</sub>, gives H<sub>2</sub>S; it gives CS<sub>2</sub> on reduction with C gives CS<sub>2</sub>. The Gibbs free energy of formation ( $\Delta_f G$ ) of Cu<sub>2</sub>S is less than that of H<sub>2</sub>S and CS<sub>2</sub>. Therefore, H<sub>2</sub> and C cannot reduce Cu<sub>2</sub>S to Cu.

On the other hand, the Gibbs free energy of formation of Cu<sub>2</sub>O is greater than that of CO. Hence, C can reduce Cu<sub>2</sub>O to Cu.

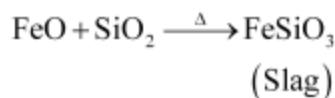


Hence, the extraction of copper from its pyrites ore is difficult than from its oxide ore through reduction.

- During the roasting of pyrites ore, a mixture of FeO and Cu<sub>2</sub>O is obtained.

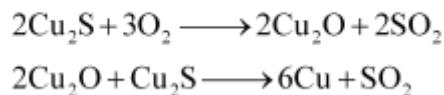
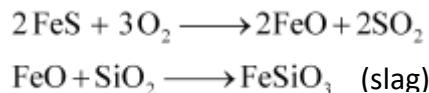


The role of silica in the metallurgy of copper is to remove the iron oxide obtained during the process of roasting as 'slag'. If the sulphide ore of copper contains iron, then silica (SiO<sub>2</sub>) is added as flux before roasting. Then, FeO combines with silica to form iron silicate, FeSiO<sub>3</sub> (slag).



- Copper *matte* contains Cu<sub>2</sub>S and FeS. Copper *matte* is put in a silica-lined converter to remove the remaining FeO in the *matte* as slag (FeSiO<sub>3</sub>). Also, some silica is added to the silica-lined converter. When a hot air blast is blown, As a result, the remaining FeS is changed to FeO and FeO is converted to iron silicate (FeSiO<sub>3</sub>) and Cu<sub>2</sub>S is converted into metallic copper.

The reaction are represented as



- The standard Gibbs free energy of formation of ZnO from Zn is lower than that of CO<sub>2</sub> from CO. Therefore, CO cannot reduce ZnO to Zn. Hence, Zn is not extracted from ZnO through reduction using CO.

## Module – 25.4

### Process of molten electrolysis of Al

#### Aluminium:

##### (a) Occurrence:

In the earth's crust, aluminium is the most abundant (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon). It is never found in the elemental state. The important minerals of Al are given below.

Name of the mineral	Formula
Corundum	$\text{Al}_2\text{O}_3$
Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Cryolite	$\text{Na}_3\text{AlF}_6$

##### (b) Extraction:

For the purpose of extraction of Al, bauxite is by far the important source. From bauxite Al is obtained by electrolysis. For this purpose pure bauxite is necessary. The following steps are used in extraction of aluminum.

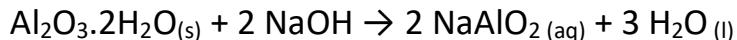
- (i) Purification of Bauxite(or) Ore concentration
- (ii) Electrolytic reduction of alumina
- (iii) Refining of aluminium.

##### (i) Purification of Bauxite:

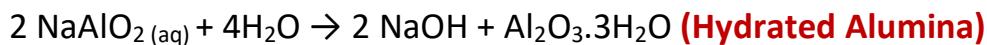
Bauxite containing iron oxide as impurity is known as **red bauxite**; it is purified either by **Baeyer's process** and by **Hall's process** where as bauxite containing silica as impurity is known as **white bauxite** and is purified by **Serpek's process**.

## 1. Baeyer's Process:

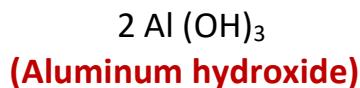
Crushed bauxite is treated with moderately concentrated sodium hydroxide solution, under pressure (about 35 atm) at 423 K for a few hours in a furnace called autoclave. Alumina reacts with NaOH and forms sodium meta aluminate and the impurities present in that solution are left behind and are removed by filtration.



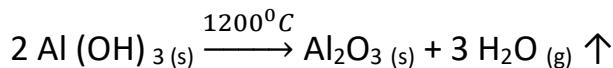
The filtered sodium meta Aluminate is diluted with water, then hydrated aluminum oxide is precipitated as aluminum hydroxide.



or

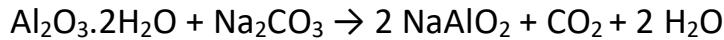


The precipitate thus obtained is calcined at  $1050^{\circ}\text{C}$ ; the aluminum hydroxide decomposes to alumina, giving of water vapour in the process.

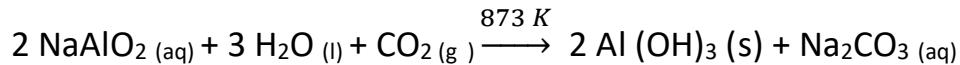


## 2. Hall's Process:

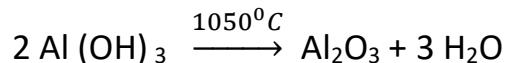
In Hall's process when red bauxite is treated with sodium carbonate aluminum oxide converts into soluble sodium Meta aluminate.



The extracted sodium meta – Aluminate is separated by filtration, then the solution heated at  $500^{\circ}\text{C}$  by passing  $\text{CO}_2$  to get pure anhydrous aluminum hydroxide.

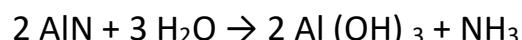
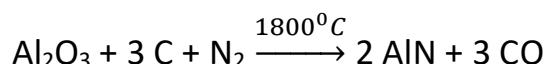


The aluminium hydroxide obtained in this process on heating at  $1050^{\circ}\text{C}$  gives Alumina.

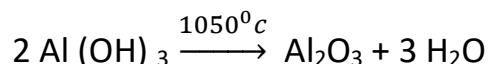


### 3. Serpek's process:

In this process, most of the silica of the bauxite is volatilized. Powdered bauxite and coke are mixed and heated in an atmosphere of nitrogen at  $1800^0\text{C}$  to get dehydrated alumina.



The Aluminium hydroxide thus obtained is heated to  $1050^0\text{C}$ . The Aluminium hydroxide decomposes to Alumina.

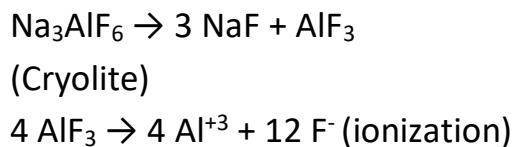


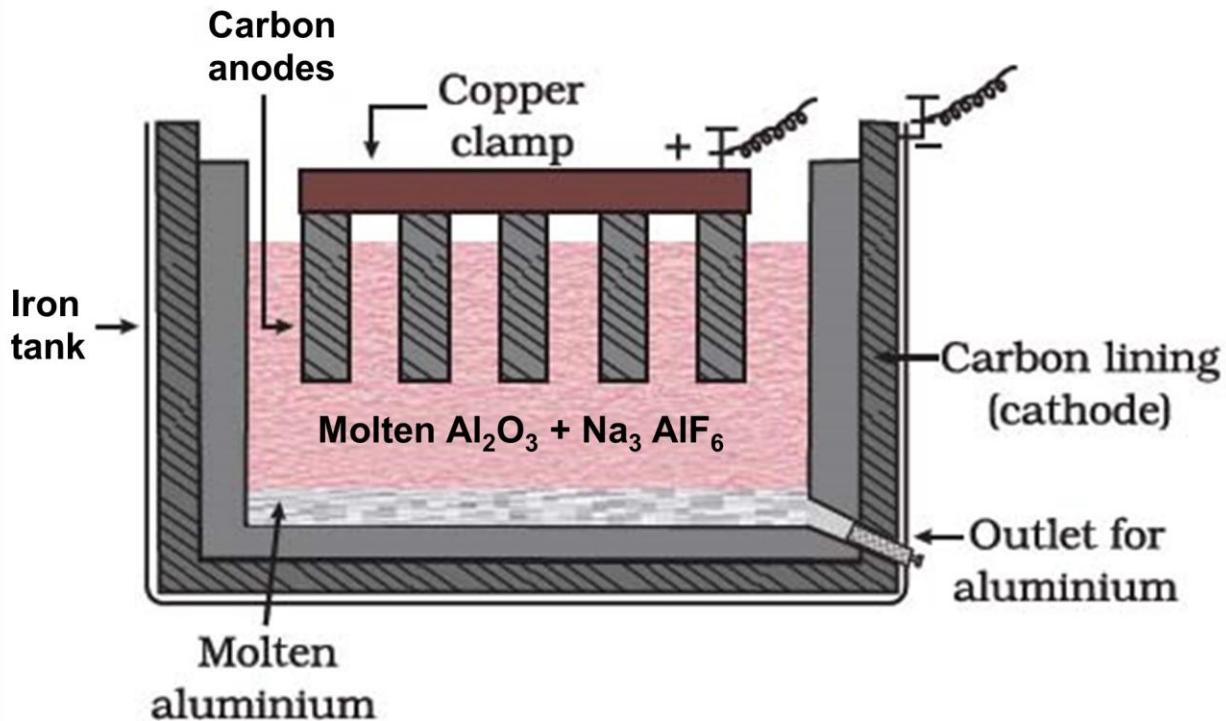
### (ii) Electrolytic reduction of Alumina:

In the metallurgy of aluminium, purified  $\text{Al}_2\text{O}_3$  obtained from bauxite is mixed with  $\text{Na}_3\text{AlF}_6$  or  $\text{CaF}_2$  which lowers the melting point of the mix and makes it conductivity. The fused matrix is electrolysed. Electrolysis is carried out in an iron or steel tank. The tank is lined inside with the graphite that acts as cathode.

Anode consists of a number of carbon or copper rods. Suspended from the top of the electrolytic cell. The anodes are immersed partially into the electrolyte. The electrolyte consists of a fused mixture of alumina, cryolite and fluorspar. The surface of the electrolyte is covers with powdered coke. This prevents the oxidation of the metal formed in electrolysis.

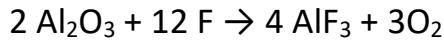
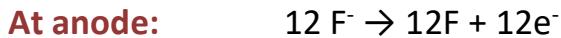
The following reactions takes place in the electrolytic cell.





*Electrolytic cell for the extraction of aluminium*

Aluminium ions move towards the cathode (i.e. carbon lining) and they are discharged. Aluminium metal is formed. Fluoride ions are discharged to give fluorine at the anode.

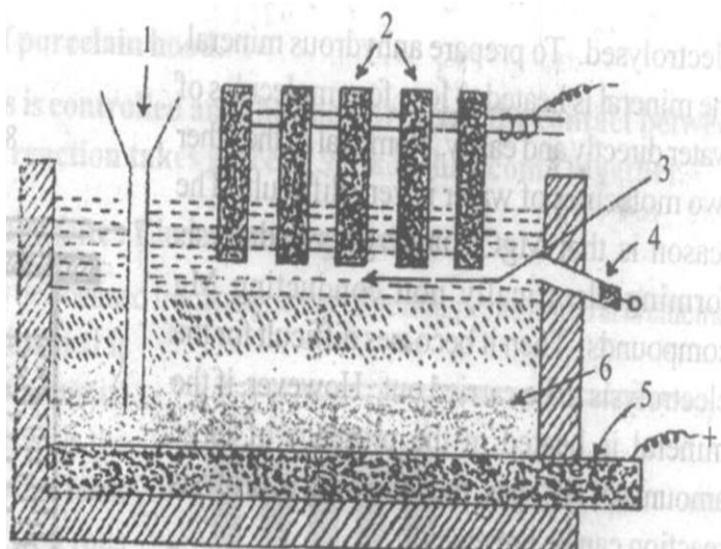


Aluminium produced at the cathode, sinks to the bottom to the bottom of the cell. It is removed from time to time through tapping hole. Fluorine formed at the anode reacts with alumina. Alumina is added at intervals. In this process, 99% pure aluminium is obtained.

### (iii) Refining of Aluminium:

Aluminium obtained by the above process contains impurities like Si, Cu, etc. it is further purified by Hooke's electrolytic method.

The electrolytic cell used for refining of aluminium consists of an iron tank lined inside with carbon. It contains three layers of fused masses. These layers differ in their specific gravities. The upper layer is of pure aluminium. A number of graphite rods acts as cathode. They are suspended from the top into the upper layer. The middle layer consists of a fused mixture of fluorides of sodium, barium and aluminium. This layer acts us an electrolyte. The bottom layer contains impure aluminium. The carbon lining of the tank acts as anode. To increase the density of impure Al layer copper and silicon are added.



1. Impure Al
2. Carbon cathodes
3. Pure Al
4. Opening to remove metal
5. Carbon lining
6. Impure Al

On passing current Aluminium ions from the middle layer, are discharged at the cathode layer (upper layer). Pure Al is deposited in the upper layer. At the same time an equivalent amount of aluminium passes into the middle layer from the bottom layer. 99.89% Al is the result of this process.

### **Assignment Questions:**

1. Describe a method for the refining of impure Al.
2. What is Baeyer's Process? Describe it.

### **Example set:**

1. Bauxite is a mineral of \_\_\_\_\_

- a. Ba
- b. B
- c. Br
- d. Al

**Solution:** d)

2. Formula of cryolite is \_\_\_\_\_
- a.  $\text{Al}_2\text{O}_3$
  - b.  $\text{Na}_3\text{AlF}_6$
  - c.  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
  - d.  $\text{KAlSi}_3\text{O}_8$

**Solution:** b)

3. Purification of aluminium by electrolytic refining is known as \_\_\_\_\_
- a. Hall's process
  - b. Baeyer's process
  - c. Hall – Heroult process
  - d. Hoope's process

**Solution:** d)

4. Epson salt is \_\_\_\_\_
- a.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
  - b.  $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$
  - c.  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$
  - d.  $\text{MgSO}_4 \cdot 10\text{H}_2\text{O}$

**Solution:** a)

5. Carnalite is a mineral of \_\_\_\_\_
- a. Be
  - b. Mg
  - c. Ca
  - d. Sr

**Solution:** b)

6. Write any three minerals of Al?

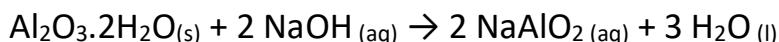
**Solution:**

Bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ); Corundum ( $\text{Al}_2\text{O}_3$ ); Cryolite ( $\text{Na}_3\text{AlF}_6$ )

7. What happens when hydrated aluminium oxide is heated with conc. NaOH solution?

**Solution:**

Alumina reacts with NaOH and forms sodium meta aluminate



**Problem set:**

1. In the electrolysis of alumina, cryolite is added to \_\_\_\_\_
  - a. Decrease the melting point of alumina
  - b. Increase the electrical conductivity
  - c. Both a and b
  - d. Remove impurities from alumina

**Solution:** c)

2. Red Bauxite contains \_\_\_\_\_ as major impurity which can be purified \_\_\_\_\_ process.
  - a. Iron oxide, Baeyer's or Hall's
  - b. Iron oxide, serpek's
  - c. Sand, Serpek's
  - d. Sand, Hall's

**Solution:** a)

3. Method used to remove silica impurities from the Bauxite.
  - a. Hall's method
  - b. Baeyer's method

- c. Serpek's method
- d. Hoope's method

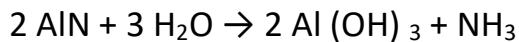
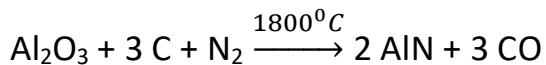
**Solution:** c)

4. How is bauxite purified by Serpek's process?

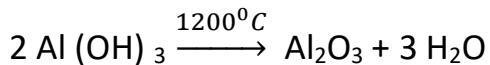
**Solution:**

**By Serpek's process:**

In this process, most of the silica of the bauxite is volatilized. Powdered bauxite and coke are mixed and present in heated in a nitrogen atmosphere at  $1800^{\circ}\text{C}$  to get dehydrated aluminum hydroxide.



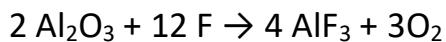
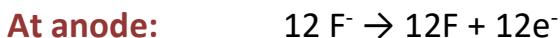
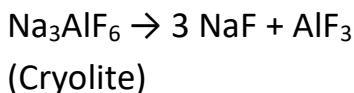
The Aluminium hydroxide thus obtained is heated to  $1050^{\circ}\text{C}$  (calcined) the Aluminium hydroxide decomposes to Alumina, giving of water vapour in this process.



5. Write the equations for the chemical reactions that take place in the electrolysis of fused alumina?

**Solution:**

The following reactions take place in the electrolytic cell.

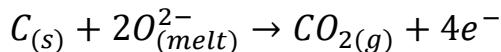
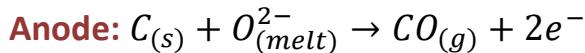
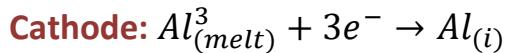


### **Exercise questions:**

1. What is the role of cryolite in the metallurgy of aluminium?
2. What is the role of graphite rod in the electrometallurgy of aluminium?
3. Outline the principles of refining of metals by the Electrolytic refining methods:
4. Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese etc. Explain why?

### **Solutions to exercise questions:**

1. Cryolite ( $\text{Na}_3\text{AlF}_6$ ) has two roles in the metallurgy of aluminium: They are
  - a. To decrease the melting point of the mixture from 2323 K to 1140 K.
  - b. To increase the electrical conductivity of  $\text{Al}_2\text{O}_3$ .
2. In the electrometallurgy of aluminium, a fused mixture of purified alumina ( $\text{Al}_2\text{O}_3$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ) and fluorspar ( $\text{CaF}_2$ ) is electrolysed. In this electrolysis, graphite is used as the anode and graphite-lined iron is used as the cathode. During the electrolysis, Al is deposited at the cathode, while CO and  $\text{CO}_2$  are liberated at the anode, according to the following equations.



If a metal is used instead of graphite as the anode, then  $\text{O}_2$  will be liberated. This will not only oxidise the metal of the electrode, but also convert some of the Al liberated at the cathode back into  $\text{Al}_2\text{O}_3$ . Hence, graphite is used for preventing the formation of  $\text{O}_2$  at the anode. Moreover, graphite is better and is cheaper than other metals.

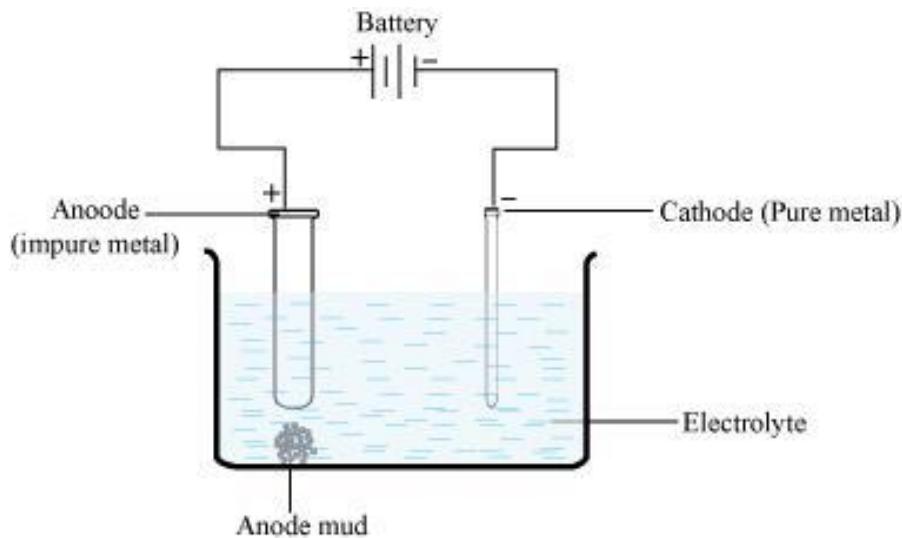
### **3. Electrolytic refining:**

Electrolytic refining is the process of refining impure metals by using electrolysis principle. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the metal to be refined,

is taken as the electrolyte. When an electric current is passed, metal ions from the electrolyte are deposited at the cathode as pure metal. The impure metal from the anode dissolves into the electrolyte in the form of ions. The impurities present in the impure metal gets collected below the anode. This is known as anode mud.

**Anode:**  $M \rightarrow M^{n+} + ne^-$  (Anode material dissolves)

**Cathode:**  $M^{n+} + ne^- \rightarrow M$  (Metal deposited)



4. Aluminium has great affinity for oxygen. It acts as a reducing agent when the metal having highest melting point is to be extracted from its oxide.

**Ex:**  $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$

## Module – 12.1

### Surface Chemistry

Surface chemistry is the study of the processes that occur at the interface of two bulk phases. The bulk phases can be of the type solid – gas, solid – liquid, liquid – gas and liquid – liquid. There is no interface between gases because of their complete miscibility. The bulk phase can be solutions or pure compounds.

**Sorption**, which includes both absorption and adsorption, is a process in which a substance moves from one phase to be accumulated in another phase. Dyes get adsorbed as well as absorbed in the cotton fibers, i.e., sorption

#### Absorption and Adsorption:

In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.

**Example:** sponge in H<sub>2</sub>O, chalk in ink etc

In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.

**Example:** Inert gases on charcoal

Water vapor is absorbed by calcium chloride while it is adsorbed by silica gel. In the same manner, ammonia is absorbed by water and is adsorbed by charcoal.

#### Adsorption:

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface, is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore (charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc.) act as good adsorbents.

### Examples of adsorption:

- a. If a gas like  $O_2$ ,  $H_2$ ,  $CO$ ,  $Cl_2$ ,  $NH_3$  or  $SO_2$  is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
- b. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate is colourless. The molecules of the dye, accumulate said to be on the surface of charcoal, i.e., are adsorbed.
- c. Aqueous solution of raw sugar (Molasses), when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- d. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption. I.e. it is the reverse process of adsorption.

**Types of adsorption:** Adsorption can be classified into two categories as described below,

#### 1. Depending upon the concentration:

In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.

**a. Positive adsorption:** If the concentration of an adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption.

**Example:**  $H_2$  on activated carbon,  $CH_4$  on activated carbon, When a concentrated solution of  $KCl$  is shaken with animal charcoal, it shows positive adsorption.

b. **Negative adsorption:** If the concentration of the adsorbate is less on the surface than its concentration in the bulk then it is called negative adsorption.

**Example:** When a dilute solution of KCl is shaken with animal charcoal, it shows negative adsorption.

## 2. Depending upon the nature of force existing between adsorbate molecule and adsorbent:

a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.

b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

### Comparison between physisorption and chemisorptions:

Physisorption (van der Waals adsorption)	Chemisorption (Langmuir adsorption)
Low heat of adsorption usually in range of 20 – 40 kJ/mol	High heat of adsorption in the range of 50 – 400 kJ/mol
Forces of attraction are van der Waals forces.	Forces of attraction are chemical bond forces.
It is readily reversible	It is irreversible
It usually takes place at low temperatures and decreases with increasing temperature.	It takes place at high temperature.
It is related to the case of liquefaction of the gas.	It is not related.
It forms multimolecular layers on the adsorbent surface.	It forms monomolecular layer on the adsorbent surface.
It does not require an activation energy.	It requires high activation energy.
In case of gaseous adsorbates	In case of gaseous adsorbates

decrease of pressure on the surface causes desorption.

decrease of pressure on the surface does not cause desorption.

### Assignment questions:

1. What is adsorption?

#### Solution:

**Adsorption:** In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.

**Example:** Inert gases on charcoal.

2. What is physisorption?

#### Solution:

**Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.

3. Write any two characteristics of chemisorption?

#### Solution:

- a) High heat of adsorption in the range of 50 – 400 kJ/mol
- b) Forces of attraction are chemical bond forces.
- c) It is irreversible
- d) It takes place at high temperature.

4. Write a note on the types of adsorption

**Solution:**

**Types of adsorption:** Adsorption can be classified into two categories as described below,

**1. Depending upon the concentration:**

In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.

a. **Positive adsorption:** If the concentration of an adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption.

**Example:** H<sub>2</sub> on activated carbon, CH<sub>4</sub> on activated carbon, When a concentrated solution of KCl is shaken with animal charcoal, it shows positive adsorption.

b. **Negative adsorption:** If the concentration of the adsorbate is less on the surface than its concentration in the bulk then it is called negative adsorption.

**Example:** When a dilute solution of KCl is shaken with animal charcoal, it shows negative adsorption.

**2. Depending upon the nature of force existing between adsorbate molecule and adsorbent:**

a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.

b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

5. How do you differentiate physisorption from chemisorptions?

**Solution:**

<b>Physisorption (van der Waals adsorption)</b>	<b>Chemisorption (Langmuir adsorption)</b>
Low heat of adsorption usually in range of 20 – 40 kJ/mol	High heat of adsorption in the range of 50 – 400 kJ/mol
Forces of attraction are van der Waals forces.	Forces of attraction are chemical bond forces.
It is readily reversible	It is irreversible
It usually takes place at low temperatures and decreases with increasing temperature.	It takes place at high temperature.
It is related to the case of liquefaction of the gas.	It is not related.
It forms multimolecular layers on the adsorbent surface.	It forms monomolecular layer on the adsorbent surface.
It does not require an activation energy.	It requires high activation energy.
In case of gaseous adsorbates decrease of pressure on the surface causes desorption.	In case of gaseous adsorbates decrease of pressure on the surface does not cause desorption.
It is not very specific.	It is highly specific.

**Review questions:**

**Example set:**

1. Chemisorption is
  - a. Multimolecular in nature
  - b. Reversible
  - c. Often specific and directional
  - d. Not very specific

**Solution:** c)

2. The two phenomenon, adsorption and absorption together are known as
  - a. Desorption
  - b. Sorption
  - c. Both a) and b)
  - d. None

**Solution:** b)

3. Physical adsorption
  - a. Is reversible
  - b. decreases with temperature
  - c. is exothermic
  - d. All

**Solution:** d)

4. Which of the following is not correct about adsorption?
  - a. Adsorption is a surface phenomenon
  - b. Adsorption is a bulk phenomenon
  - c. Adsorption is a physical phenomenon
  - d. Adsorption is a chemical phenomenon

**Solution:** b)

5. What is absorption?

**Solution:** In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.

**Example:** sponge in H<sub>2</sub>O, chalk in ink etc

6. What is chemisorption?

**Solution: Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption.

7. Explain types of adsorption based on concentration?

**Solution: Depending upon the nature of force existing between adsorbate molecules and adsorbent:**

- a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
- b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. i.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

**Problem set:**

1. Physical adsorption is characterized as \_\_\_\_ process
  - a. Highly specific
  - b. Reversible
  - c. Irreversible
  - d. Monolayer adsorption

**Solution: b)**

2. Gas masks containing activated charcoal are used to remove poisonous gases from atmosphere. They function on the principle of
  - a. Adsorption
  - b. Absorption
  - c. Sorption
  - d. All

**Solution: a)**

3. Chemical adsorption is \_\_\_\_
  - a. An exothermic process
  - b. An irreversible change
  - c. An unilayer formation
  - d. All

**Solution:** d)

4. Adsorption of H<sub>2</sub> or O<sub>2</sub> on activated charcoal is
  - a. A physical adsorption
  - b. A chemical adsorption
  - c. Both physical and chemical adsorptions
  - d. Neither physical nor chemical adsorption

**Solution:** a)

5. Distinguish between adsorption and absorption. Give examples.

**Solution: Absorption and Adsorption:**

In the process of absorption molecules of one phase interpenetrate uniformly among those of another phase to form a solution with the second phase.

**Example:** sponge in H<sub>2</sub>O, chalk in ink etc

In adsorption, molecules of one phase are present in higher concentration at the surface of the second phase.

**Example:** Inert gases on charcoal.

6. Distinguish between physical adsorption and chemical adsorption

**Solution:**

- a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are van der Waals forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or van der Waals adsorption. It can be easily reversed by heating or decreasing the pressure.
- b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are of a chemical nature. I.e. are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

### **Exercise questions:**

1. What is the process involved in the Dewar method of separation of inert gases?
2. Why does physisorption decrease with the increase of temperature?
3. Why is adsorption always exothermic?

### **Solutions to exercise questions:**

1. Van der Waals adsorption
2. Physisorption is exothermic in nature. Therefore, in accordance with Le-Chateliere's principle, it decreases with an increase in temperature. This means that physisorption occurs more readily at a lower temperature.
3. Adsorption is always exothermic. This statement can be explained in two ways.
  - a. Adsorption leads to a decrease in the residual forces on the surface of the adsorbent. This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is an exothermic change.
  - b. When a gas is adsorbed on a solid surface, its movement is restricted leading to a decrease in the entropy of the gas i.e.,  $\Delta S$  is negative. Now for a process to be spontaneous,  $\Delta G$  should be negative.  $\Delta H$  of adsorption is always negative.

Therefore,  $\Delta G = \Delta H - T\Delta S$ ;

Since  $\Delta S$  is negative,  $\Delta H$  is negative to make  $\Delta G$  negative  $\Delta H > T\Delta S$ . Hence, adsorption is always exothermic.

## Module – 12.2

### Factors affecting adsorption

Adsorption of gases on solids depends on the following factors:

- Nature of the gas (adsorbate)
- Nature of the solid (adsorbent)
- Surface area of the solid
- Pressure of the gas
- Temperature

#### a. Nature of the adsorbate:

Since physical adsorption is non – specific, every gas (i.e. adsorbate) gets adsorbed on the surface of any solid. How much of the gas will get adsorbed depends on the nature of the gas. Under any given condition of temperature and pressure, the easily liquefiable gases such as NH<sub>3</sub>, HCl and SO<sub>2</sub> are adsorbed more than the gases like H<sub>2</sub>, N<sub>2</sub> and CO. The ease with which a gas can be liquefied is determined by its critical temperature, T<sub>c</sub>. T<sub>c</sub> is the temperature above which a gas cannot be liquefied, and however high the applied pressure may be. This implies that gases with high critical temperature values can be easily liquefied as compared to gases with low critical temperature values. The table given below illustrates the correlation between the extent of adsorption of gases on charcoal with their ease of liquefaction.

#### Volume of gases at N.T.P adsorbed by 1g charcoal at 288 K

Gas	H <sub>2</sub>	N <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	HCl	NH <sub>3</sub>	SO <sub>2</sub>
Volume adsorbed (cc)	4.7	8.0	9.3	16.2	48	72	181	380

Ease of Liquefaction → increases

Since chemisorption is specific in nature, a gas is chemisorbed only when it forms chemical bonds with the adsorbent. A gas which is physisorbed at a certain temperature can be chemisorbed when the temperature is increased dramatically. For e.g., at 83 K nitrogen (N<sub>2</sub>) is physisorbed on iron surface as N<sub>2</sub> molecules. At room temperature there is no physisorption of N<sub>2</sub> on iron surface. However, at 773K nitrogen is chemisorbed on iron surface as nitrogen atoms.

### **b. Nature of the adsorbent:**

The nature of the adsorbent has profound effect on the process of adsorption. Solids with porous structure are potentially good adsorbents. Among them, activated carbon is the most common adsorbent for gases which are easily liquefied. Activated carbon is used in gas masks to adsorb poisonous gases such as methane ( $\text{CH}_4$ ).

Activated carbon is prepared from a variety of raw materials including wood, lignite, coal, bone, nut shells and petroleum residues. The new material is activated in an atmosphere of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$  water vapor air or other selected gases at a temperature between 573 K and 1273 K. This is often followed by quenching in air or water. Adsorption on activated carbon is associated with the presence of small and uniform pores. The surface area of activated carbon is approximately  $1000 \text{ m}^2/\text{g}$ .

Apart from activated carbon, silica gel, aluminium oxide and clay are used as adsorbents. It is common knowledge that small satchets containing silica gel are used in electronic equipments such as camera to keep the lenses dry. As mentioned earlier, silica gel is used to adsorb water vapor, which is always present in the humid weather conditions.

### **c. Surface area of the solid adsorbent:**

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. **larger the surface area of the adsorbent, greater is the extent of adsorption.**

Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

### **d. Pressure of the gas - Adsorption Isotherms:**

The extent of adsorption of a gas on a solid generally increases with pressure. The extent of adsorption is given by  $x/m$ , (the ratio of the mass (x) of the adsorbate and the mass (m) of the adsorbent) when a dynamic equilibrium has been attained. The plot of extent of adsorption versus pressure of the gas, at a given temperature, is called the adsorption isotherm. Adsorption isotherms of different shapes have been observed in various experiments. Adsorption isotherms are

usually described by different empirical equations. Here, the two most common adsorption isotherms namely, Freundlich isotherm and Langmuir isotherm will be discussed.

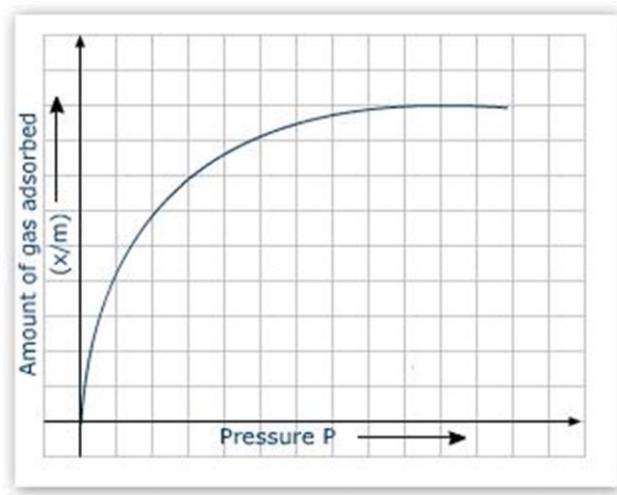
### Freundlich Adsorption Isotherm:

This type of isotherm is described by the empirical equation

$$\frac{x}{m} = KP^{\frac{1}{n}} \quad (\text{where } n > 1) \quad \dots \dots (1)$$

Where K and n are the parameters which depend on the nature of the gas, and P is the pressure.

At equilibrium pressure,  $P_s$ ,  $x/m$  reaches its maximum value, that is, no further adsorption takes place even if the pressure is increased. A saturation state has been attained. The adsorption isotherm which conforms to Freundlich equation is shown.



**Freundlich adsorption isotherm**

Since n is greater than one, qualitatively, it can be said that the extent of adsorption  $x/m$  does not increase rapidly with increase in pressure as shown in the above figure. Freundlich equation can be transformed into a linear form by taking the logarithms on both sides of the equation 1.

$$\log \left( \frac{x}{m} \right) = \log K + \frac{1}{n} \log P \quad \dots \dots (2)$$

Hence, if the plot of  $\log(x/m)$  versus  $\log P$  yields a straight line, it implies that the adsorption process conforms to Freundlich isotherm. From the intercept, the parameter K is obtained, while the slope is equal to  $(1/n)$ .

### Langmuir Isotherm:

Langmuir adsorption isotherm is based on the following assumptions.

- a. Adsorption proceeds to form only monolayers on the surface of the adsorbent.
- b. All the sites available on the adsorbent surface are equivalent and the surface is perfectly uniform, that is flat.
- c. The ability of a gas molecule to get adsorbed at a particular site is independent of the occupation of neighboring sites. This implies that there is no interaction between adjacent adsorbed molecules.
- d. A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules.

Initially, since the surface is completely free of any gas molecules, every molecule of the gas that strikes the surface of solid may get adsorbed. After some time, only those gas molecules may get adsorbed which strike the part of the surface that is not already covered. This means, that initially the rate of adsorption is high and then decreases as less surface is available for adsorption. The adsorbed gas molecules escape from the surface of the adsorbent.

A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules. It implies that the adsorbed molecules also undergo desorption, probably due to thermal agitation. When the rate of adsorption equals the rate of desorption, dynamic equilibrium is established.

If  $q$  is the fraction of the total available surface covered with gas molecules, at any instant, then  $(1-q)$  is the fraction of the surface of the solid which is vacant. From kinetic theory of gases, it is known that the rate at which gas molecules collide per unit area of a surface is directly proportional to the pressure of the gas. The rate of adsorption depends on both the pressure of the gas and fraction of surface available for adsorption. Hence,

$$\text{Rate of adsorption} = K_a (1 - \theta) P \dots (3)$$

The rate of desorption is directly proportional to the fraction of the surface covered with gas molecules.

i.e. Rate of desorption =  $K_d (\theta)$  ....(4)

At equilibrium, the rate of adsorption is equal to the rate of desorption i.e.,

$$K_a (1 - \theta) P = K_d (\theta)$$

$$\frac{(1 - \theta)}{\theta} = \frac{K_d}{K_a P}$$

$$\text{Or } \left(\frac{1}{\theta} - 1\right) = \frac{K_d}{K_a P}, \text{ Then}$$

$$\text{or, } \theta = \frac{K_a P}{K_d + K_a P}$$

$$\text{or, } \theta = \frac{KP}{1+KP} \quad \dots \dots (5)$$

$$\text{Where } K = \frac{K_a}{K_d} = \text{constant}$$

Now, the extent of adsorption ( $x/m$ ) is proportional to the fraction of surface covered. Therefore,

$$\frac{x}{m} = k\theta = \frac{kKP}{1+KP} \quad \dots \dots (6) \text{ where 'k' is a constant of proportionality.}$$

$$\text{or, } \frac{x}{m} = \frac{\alpha P}{1+KP} \quad \dots \dots (7) \quad (\text{where } \alpha = kK)$$

This is the equation which describes the Langmuir adsorption isotherm. Here 'α' and K are the Langmuir parameters and are characteristic of a particular system at a particular temperature.

Freundlich and Langmuir adsorption isotherms are also applicable to adsorption processes in solutions. In place of equilibrium pressures, equilibrium concentrations of the adsorbates are used and the isotherms are expressed in the forms,

$$\frac{x}{m} = Kc^{\frac{1}{n}} \quad (n > 1) \text{ (Freundlich isotherm)}$$

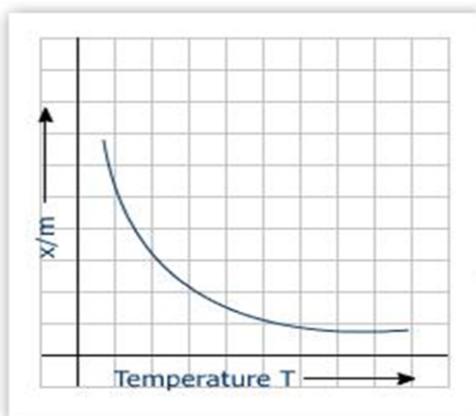
$$\frac{x}{m} = \frac{ac}{1+Kc} \quad (\text{Langmuir isotherm})$$

Where 'c' is the concentration of the solute in solution.

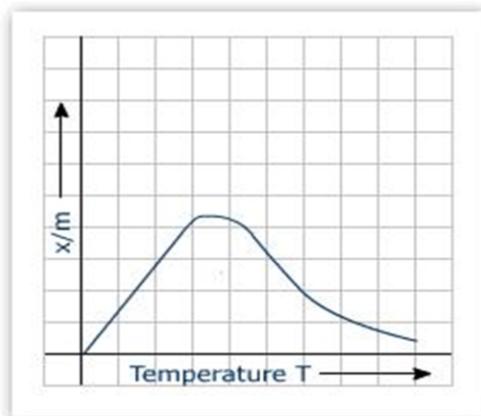
### Effect of temperatures on adsorption:

Generally physisorption takes place at low temperatures while chemisorptions takes place at high temperatures. At 463 K, N<sub>2</sub> gas undergoes physisorption on iron metal. But at 723 K iron nitride compound is formed due to chemisorption. So, as the temperature rises, physisorption may change in to chemisorptions or desorption may also take place (as in the case of inert gases on activated charcoal).

The amount of gas adsorbed by unit mass of adsorbent (i.e.,  $\frac{x}{m}$ ) changes with temperature. The process of adsorption is exothermic in nature. Hence according to Le Chatelier principle, the extent of adsorption decreases with a rise in temperature. This is very true in the case of physical adsorption. But in case of chemical adsorption the effect of temperature is complex. The amount of ( $\frac{x}{m}$  value) increases first with increase in temperature, reaches a maximum and then decreases on further rising the temperature. The change in the amount of adsorption ( $\frac{x}{m}$ ) with temperature for physical and for chemical adsorptions are shown in the figures given below. These graphs that show the variation of  $\frac{x}{m}$  with temperature are known as "adsorption isobars". (graphs drawn at constant pressure).



**a. Physical adsorption**



**b. Chemisorption**

**Variation of  $\frac{x}{m}$  with temperature (absorption isobars)**

The adsorption isobars are used to distinguish physical adsorption from chemical adsorption. As can be seen from the above graphs, their shapes are different and hence physisorption and chemisorptions processes can be distinguished.

#### **Application of adsorption:**

The phenomenon of adsorption finds a number of applications. Important applications are given as follows.

##### **1. Production of high vacuum**

##### **2. In Gas masks :**

This apparatus is used to adsorb poisonous gases (e.g.  $\text{Cl}_2$ , CO oxide of sulphur etc.) and thus purify the air for breathing.

##### **3. For desiccation or dehumidification:**

These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

##### **4. Removal of colouring matter from solution :**

- Animal charcoal removes colours of solutions by adsorbing coloured impurities.
- Animal charcoal is used as decolouriser in the manufacture of cane sugar.

## **5. Heterogeneous catalysis :**

Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst. For example,

- a. Finely powdered nickel is used for the hydrogenation of oils.
- b. Finely divided vanadium pentoxide ( $V_2O_5$ ) is used in the contact process for the manufacture of sulphuric acid.

## **6. Separation of inert gases :**

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

## **7. Softening of hard water:**

- a. The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate)
- b.  $Ca^{++}$ ,  $Mg^{++}$  ions which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.



- c. The exhausted zeolite is regenerated with 10% of sodium chloride solution.



## **8. De – Ionisation of water:**

- a. Water can be de-ionised by removing all dissolved salts with the help of cation and anion-exchanger resins.
- b. Cation-exchanger is an organic synthetic resin such as polystyrene-containing a macroanion ( $R-SO_3^-$  etc) which has adsorbed  $H^+$  ions.
- c. A resin containing a basic group ( $R_3Na^+$  etc.) Which has adsorbed  $OH^-$  ions acts as anion exchanger.

## **9. In curing diseases :**

A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.

### **10.Cleaning agents:**

Soap and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

### **11.Froth floatation process:**

A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method.

### **12.In adsorption indicators:**

Surface of certain precipitates such as silver halide, have the property of adsorbing some dyes like eosin, fluorescein etc. the colour is used to detect the end point in the volumetric analysis.

### **13.In dyeing:**

Many dyes get adsorbed on the cloth either directly or by the use of mordants.

### **Assignment questions:**

1. Give the mathematical equation relating the pressure (P) and the extent of adsorption ( $x/m$ ) of gas on a metal surface
2. Give an account of adsorption of gases by metals with examples
3. Discuss the factors that effect adsorption of gases on metals

### **Review questions:**

#### **Example set:**

1. The extent of adsorption of a gas on a solid depends on
  - a. Nature of gas
  - b. Pressure of gas
  - c. Temperature of the system
  - d. All

#### **Solution: d)**

2. For adsorption of gas on solid surface, the plots of  $\log x/m$  vs  $\log P$  is linear with a slope equal to
  - a. K

- b.  $\log K$
- c.  $\ln K$
- d.  $1/n$  ( $n$  being integer greater than unity)

**Solution:** d)

3. Which of the following gases is adsorbed strongly by charcoal
  - a.  $H_2$
  - b.  $N_2$
  - c.  $O_2$
  - d.  $NH_3$

**Solution:** d)

4. Freundlich adsorption isotherm gives a straight line on plotting
  - a.  $\frac{x}{m}$  vs  $P$
  - b.  $\log \frac{x}{m}$  vs  $P$
  - c.  $\log \frac{x}{m}$  vs  $\log P$
  - d.  $\frac{x}{m}$  vs  $\frac{1}{P}$

**Solution:** c)

5. Give an account of Langmuir adsorption isotherm; Freundlich isotherm

**Solution:**

**Langmuir adsorption isotherm :**The extent of adsorption ( $x/m$ ) is proportional to the fraction of surface covered. Therefore,

$$\frac{x}{m} = K\theta = \frac{kKP}{1+KP} \quad \dots \dots (6) \text{ where 'K' is a constant of prop}$$

$$\text{or, } \frac{x}{m} = \frac{\alpha P}{1+KP} \quad \dots \dots (7) \quad (\alpha = kK)$$

This is the equation which describes the Langmuir adsorption isotherm. Here ' $\alpha$ ' and  $K$  are the Langmuir parameters and are characteristic of a particular system at a particular temperature.

### **Freundlich Adsorption Isotherm:**

This type of isotherm is described by the empirical equation

$$\frac{x}{m} = KP^n \quad (\text{where } n > 1) \quad \dots \dots (1)$$

Where K and n are the parameters which depend on the nature of the gas, and P is the pressure.

6. Give the effect of temperature adsorption of gases by metals

**Solution:** The amount of gas adsorbed by unit mass of adsorbent (i.e.,  $\frac{x}{m}$ ) changes with temperature. The process of adsorption is exothermic in nature. Hence according to Le Chatelier principle, the extent of adsorption decreases with a rise in temperature. These graphs that show the variation of  $\frac{x}{m}$  with temperature are known as "adsorption isobars".

### **Problem set:**

1. Which is correct in case of van der Waals adsorption
  - a. High temperature, low pressure
  - b. Low temperature, high pressure
  - c. Low temperature, low pressure
  - d. High temperature, high pressure

**Solution:** b)

2. Which can adsorb larger volume of hydrogen gas
  - a. A palladium block
  - b. Finely divided palladium
  - c. Broken pieces of palladium
  - d. All equally adsorb

**Solution:** b)

3. The gases which liquefy more easily are adsorbed more readily than the permanent gases because the easily liquefiable gases have greater
  - a. Van der Waals forces
  - b. Molecular forces of attraction
  - c. Cohesive forces

- d. All the above

**Solution:** d)

4. Which equation represents Langmuir adsorption
- $x/m = \alpha$
  - $x/m \propto P$
  - $x/m = 1/P$
  - $x/m > P$

**Solution:** b)

5. Discuss the effect of the nature of the adsorbate on adsorption

**Solution:**

#### Nature of the adsorbate:

Since physical adsorption is non – specific, every gas (i.e. adsorbate) gets adsorbed on the surface of any solid. How much of the gas will get adsorbed depends on the nature of the gas. Under any given condition of temperature and pressure, the easily liquefiable gases such as  $\text{NH}_3$ ,  $\text{HCl}$  and  $\text{SO}_2$  are adsorbed more than the gases like  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{CO}$ . The ease with which a gas can be liquefied is determined by its critical temperature,  $T_c$ .  $T_c$  is the temperature above which a gas cannot be liquefied, and however high the applied pressure may be. This implies that gases with high critical temperature values can be easily liquefied as compared to gases with low critical temperature values. The table given below illustrates the correlation between the extent of adsorption of gases on charcoal with their ease of liquefaction.

#### Volume of gases at N.T.P adsorbed by 1g charcoal at 288 K

Gas	$\text{H}_2$	$\text{N}_2$	CO	$\text{CH}_4$	$\text{CO}_2$	HCl	$\text{NH}_3$	$\text{SO}_2$
Volume adsorbed (cc)	4.7	8.0	9.3	16.2	48	72	181	380

Ease of Liquefaction  increases

Since chemisorption is specific in nature, a gas is chemisorbed only when it forms chemical bonds with the adsorbent. A gas which is physisorbed at a certain temperature can be chemisorbed when the temperature is increased

dramatically. For e.g., at 83 K nitrogen ( $N_2$ ) is physisorbed on iron surface as  $N_2$  molecules. At room temperature there is no physisorption of  $N_2$  on iron surface. However, at 773K nitrogen is chemisorbed on iron surface as nitrogen atoms.

6. Does surface area have an effect on adsorption of a gas? Explain

**Solution: Surface area of the solid adsorbent:**

The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. **larger the surface area of the adsorbent, greater is the extent of adsorption.**

Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

**Exercise questions:**

1. The curve showing variation of  $x/m$  with temperature is inverted "V" shape. What is the type of adsorption?
2. Why are powdered substances more effective adsorbents than their crystalline forms?
3. Give reasons for why a finely divided substance is more effective as an adsorbent.

**Solutions to exercise questions:**

1. Chemisorption
2. Powdered substances are more effective adsorbents than their crystalline forms because when a substance is powdered, its surface area increases and physisorption is directly proportional to the surface area of the adsorbent.
3. Adsorption is a surface phenomenon. Therefore, adsorption is directly proportional to the surface area. A finely divided substance has a large surface area. Both physisorption and chemisorption increase with an increase in the surface area. Hence, a finely divided substance behaves as a good adsorbent.



## Module – 12.3, 12.4 & 12.5

### The Colloidal State

#### Introduction:

**The foundation of colloidal chemistry was laid down by an English scientist, Thomas Graham, in 1861. The credit for the various advances in this field goes to eminent scientists like Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar and others. Thomas Graham classified the soluble substances into two categories depending upon the rate of diffusion through animal and vegetable membranes or parchment paper.**

a. **Crystalloids:** They have higher rate of diffusion and diffused from parchment paper.

**Examples:** All strong acids, bases and salts and organic compounds such as sugar, urea etc.

b. **Colloids (Greek word, kolla, meaning glue-like):** They have slower rate of diffusion and can not diffuse through from parchment paper.

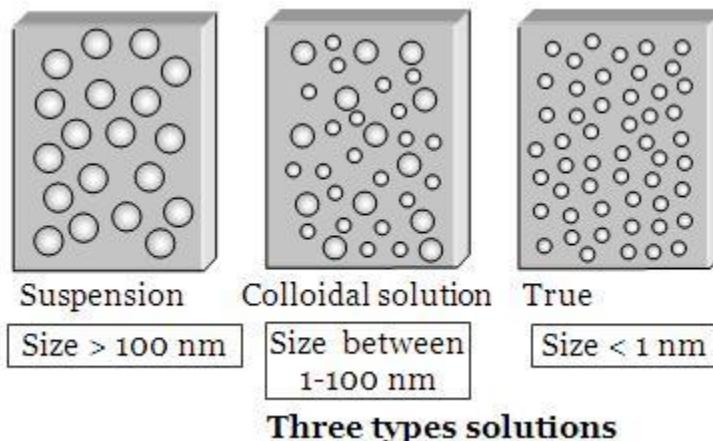
**Examples:** Starch, gelatin, gum, silicic acid and hemoglobin etc.

The above classification was discarded i.e., **the terms colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state. The colloidal state depends on the particle size.** It is regarded as intermediate state between true solution and suspension.

Features of the three types of solutions

Property	Suspension	Colloidal solution	True solution
Nature	Heterogeneous	Heterogeneous	Homogeneous
Particle size	> 100 nm	1 nm – 100 nm	< 1 nm
Separation by			

(i) Ordinary filtration	Possible	Not possible	Not possible
(ii) Ultra- filtration	Possible	Possible	Not possible
Settling of particles	Settle under gravity	Settle only on centrifugation	Do not settle
Appearance	Opaque	Generally transparent	Transparent
Diffusion of particles	Does not diffuse	Diffuses slowly	Diffuses rapidly



### Phases of colloids and their classification:

**Phases of colloids:** We know that a colloidal solution is of heterogeneous nature. It consists of two phases which are as follows

**Internal phase or Dispersed phase (Discontinuous phase):** It is the component present in small proportion and is just like a solute in a solution. For example in the colloidal solution of silver in water (silver acts as a dispersed phase)

**External phase or Dispersion medium (continuous phase):** It is generally component present in excess and is just like a solvent in a solution. For example, in the colloidal solution of silver in water. Water act as a dispersion medium.

**Classification of colloids:** The colloids are classified on the basis of the following criteria

**a. Classification based on the physical state of the dispersed phase and dispersion medium:** Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible.

#### Different types of colloidal systems:

Dispersed phase	Dispersion Medium	Colloidal System	Examples
Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists, fine insecticide sprays
Solid	Gas	Aerosol of solids	Smoke, volcanic dust, haze
Gas	Liquid	Foam or froth	Soap lather. Lemonade froth, foam, whipped cream, soda water
Liquid	Liquid	Emulsions	Milk, emulsified oils, medicines
Solid	Liquid	Sols	Most paints, starch in water, proteins, gold sol, arsenic sulphide sol, ink
Gas	Solid	Solid foam	Pumice stone, styrene rubber, foam rubber
Liquid	Solid	Gels	Cheese, butter, boot polish, jelly, curd
Solid	Solid	Solid sols (coloured glass)	Ruby glass, some gem stones and alloys

**b. Classification based on Nature of interaction between dispersed phase and dispersion medium:** Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as (i) Lyophilic and (ii) Lyophobic sols.

- i. **Lyophilic colloids (water loving):** “The colloidal solutions, in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called **lyophilic colloidis.**”

- ii. **Lyophobic colloids (water heating):** “The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called **lyophobic colloids.**”

#### **Distinction between lyophilic and lyophobic sols:**

Property	Lyophilic sols (suspensoind)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $\text{Al(OH}_3\text{)}$ , $\text{Fe(OH}_3\text{)}$ metal sulphides like $\text{AS}_2\text{S}_3$ etc.

- c. **Classification based on types of particle of dispersed phase:** Depending upon the type of the particles of the dispersed phase, the colloids also can be classified.
- i. **Multimolecular colloids:** When on dissolution, atoms or smaller molecules of substances (having diameter less than 1nm) aggregate together to form

particles of colloidal dimensions, the particles thus formed are called **multimolecular colloids**.

In these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 nm.

For example, sols of gold atoms and sulphur molecules. In these colloids, the particles are held together by **van der Waal's forces**. They have usually **lyophilic character**.

ii. **Macromolecular colloids:** These are the substances having big size molecules (called macromolecules) which on dissolution form particles of the size in the colloidal range. Such substances are called **macromolecular colloids**. These macromolecules forming the dispersed phase are generally **polymers** having very high molecular masses.

Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.

They have usually **lyophobic character**.

iii. **Associated colloids:** These are the substances which on dissolved in a medium behave as normal electrolytes at low concentration but behave, as colloidal particles at higher concentration due to the formation of aggregated particles. The particles aggregates thus formed are called **micelles**.

Their molecules contain both **lyophilic** and **lyophobic** groups.

### Properties of Colloidal Sols:

#### Heterogeneous nature:

Colloidal sols are biphasic in nature. It consists of the dispersed phase and the dispersion medium. In the colloidal solution, each particle is contained within its own surface boundary and therefore has a separate existence from the dispersion medium.

### **Colligative properties:**

Colloidal particles have high average molecular masses. Therefore the mole fraction of the dispersed phase is very low. Hence, in colloidal solutions the relative lowering of vapor pressure, elevation in boiling point, depression in freezing point and osmotic pressure is very low.

### **Optical properties:**

Although a colloidal solution appears to be homogenous because the dispersed particles are too small to be seen, it can be distinguished from a true solution by its ability to scatter light.

The scattering of light by colloidal sized particles is called the Tyndall effect. This effect was first observed by Tyndall in 1869. A strong beam of light was passed through a colloidal sol placed in a dark place. The path of the beam got illuminated. The illuminated path of the beam is called Tyndall cone.



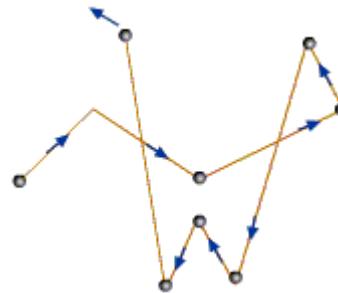
### **Demonstration of Tyndall effect**

### **Mechanical Properties:**

#### **Brownian movement:**

Brownian movement was first discovered by Robert Brown, a botanist, in 1827. He observed that pollen grains in water do not remain at rest but move about continuously and randomly. This random continuous movement (Brownian motion) was observed in colloidal sol when the sol was viewed under a ultra

microscope. Brownian motion in colloidal sols arises due to the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impact of the molecules of dispersion medium on the colloidal particles are unequal. This leads to the zig-zag (random) motion of the colloidal particles.



### Zig-zag or Brownian motion

This random movement decreases as the size of the particles increases because the effect of the impacts average out. When the size of the dispersed particles increases beyond the colloidal range, Brownian motion stops, i.e., no Brownian movement is observed.

The significance of Brownian movement is that

- It provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
- It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.

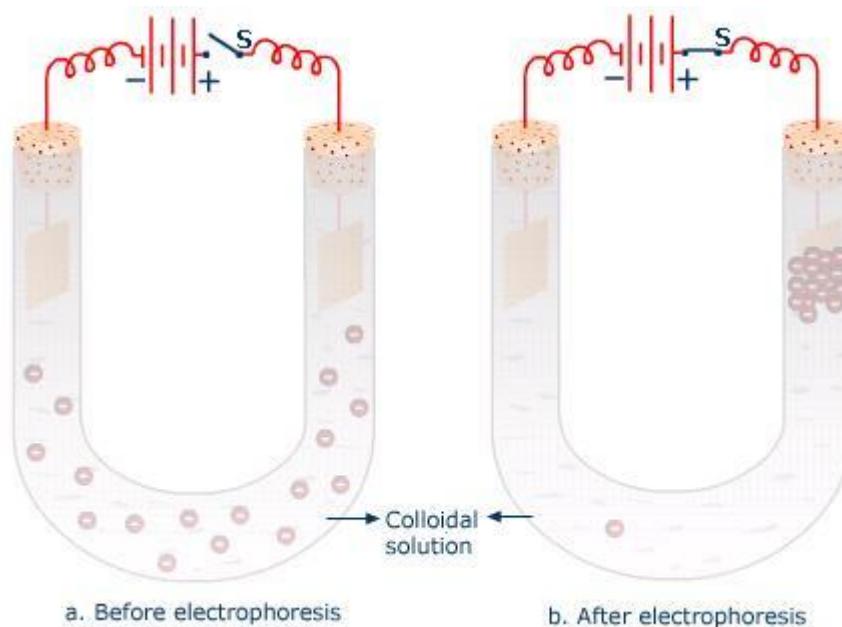
### Electrical Properties:

#### Electrophoresis:

The colloidal particles are electrically charged and they carry a charge, that is, either the colloids are negatively charged or positively charged. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Since the colloids carry charge, they repel each other and do not combine to form bigger aggregates. This is the reason why a sol is stable. The existence of charge on the colloidal particles is inferred from the observation that the colloidal

particles move either towards the cathode or anode when the colloidal sol is placed in an electric field. This phenomenon of colloidal charged particles moving towards the oppositely charged electrodes in the presence of an electric field is called electrophoresis.

Electrophoresis is carried out by placing the colloidal solution in a U tube which is fitted with platinum electrodes.



### Apparatus for electrophoresis

When electric current is passed, the charged colloidal particles move towards the oppositely charged electrode. A colloidal sol of  $\text{SS}_2\text{S}_3$ , which is negatively charged will move towards the anode when placed in an electric field.

### Emulsion:

**"The colloidal systems in which one liquid are dispersed in another liquid is called emulsions the two liquids otherwise being mutually immiscible."**

or

**"Emulsion are the colloidal solutions in which both the dispersed phase and the dispersion medium are liquids."**

A good example of an emulsion is milk in which fat globules are dispersed in water. The size of the emulsified globules is generally of the order of  $10^{-6}$  m. Emulsions resemble lyophobic sols in some properties.

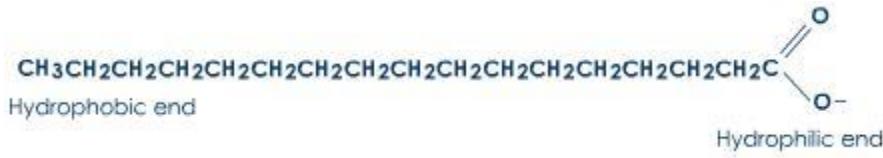
- a. **Types of Emulsion :** Depending upon the nature of the dispersed phase, the emulsions are classified as;
- b. **Oil-in-water emulsions (O/W):** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium (**continuous phase**) is called an oil-in-water emulsion. Ex: Milk
- c. **Water-in-oil emulsion (W/O):** The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsions are also termed **oil emulsions**. Ex: **Butter** and **cold cream**

#### Micelles:

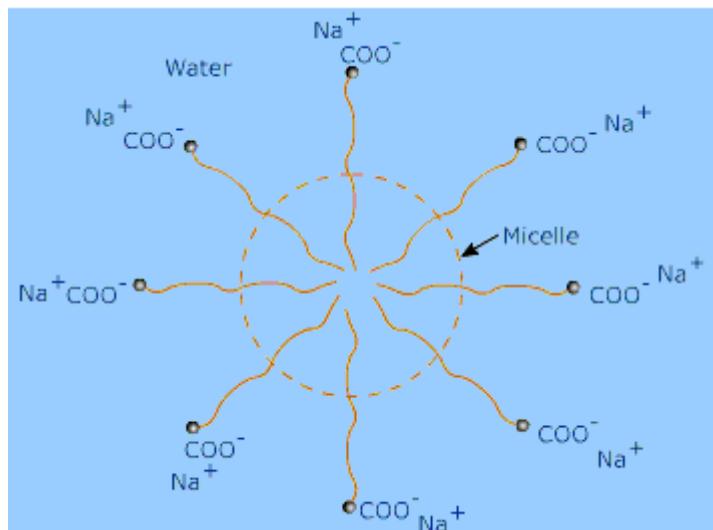
Micelles have both a lyophilic and lyophobic parts. Micelles may consist of more than 100 molecules. Certain substances behave as strong electrolytes at low concentration but at higher concentrations these substances exhibit colloidal characteristics due to the formation of aggregated particles. These aggregated particles are called micelles. **Micelles are called associated colloids.** The formation of micelles takes place only above a particular temperature called **Kraft Temperature (T<sub>k</sub>)** and above a particular concentration called the **Critical micelle concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active molecules such as soaps and synthetic detergents form associated colloids in water. For soaps, the CMC is about  $10^{-4}$  to  $10^{-3}$  mol L<sup>-1</sup>.

#### Mechanism of Micelle Formation:

Micelles are formed by specific molecules which have lyophilic as well as lyophobic ends. Ordinary soap which contains sodium stearate ( $C_{17}H_{35}COONa$ ) forms micelle in water. The stearate ion has a long hydrocarbon end that is hydrophobic (because it is nonpolar) and a polar carboxyl group ( $COO^-$ ) that is hydrophilic.



When the concentration of sodium stearate is below its CMC, then it behaves as a normal electrolyte and ionizes to give  $\text{Na}^+$  and  $\text{C}_{17}\text{H}_{35}\text{COO}^-$  ions. As the concentration exceeds the CMC, the hydrophobic end starts receding away from the solvent and approach each other. However, the polar  $\text{COO}^-$  part interacts with water. This leads to the formation of a cluster having the dimensions of a colloid particles. In each cluster a large number of stearate groups clump together in a spherical manner such that the hydrocarbon parts interact with one another and the  $\text{COO}^-$  groups remains projected in water to the surface.



### Aggregation of $\text{RCOO}^-$ ions to form a micelle

#### Assignment questions:

1. What are “colloids”? Give the difference between “colloidal solution” and “true solution”?
2. In how many ways are colloids classified? Give a brief explanation of each.
3. Explain tyndall effect, Brownian movement

**Example set:**

1. The colloidal system of a solid dispersed in a liquid medium is called
  - a. Aerosol
  - b. Sol
  - c. Gel
  - d. Foam

**Solution:** b)

2. The number of phases that can be present in a simple colloidal solution is
  - a. 2
  - b. 4
  - c. 3
  - d. 1

**Solution:** a)

3. An emulsion is a colloidal solution consisting of
  - a. Solids only
  - b. Liquids only
  - c. A number of components always
  - d. One solid and one liquid only

**Solution:** b)

4. Milk is
  - a. Fat dispersed in water
  - b. Water dispersed in fat
  - c. Water dispersed in oil
  - d. A homogeneous solution only and not a colloid.

**Solution:** a)

5. In Brownian movement or motion the paths of the dispersed phase particles are
  - a. Linear

- b. Zig – Zag
- c. Uncertain
- d. Circular

**Solution:** b)

6. What are lyophilic, lyophobic colloids? Give examples

**Solution:**

**Distinction between lyophilic and lyophobic sols:**

Property	Lyophilic sols (susensoid)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $\text{Al(OH}_3\text{)}$ , $\text{Fe(OH}_3\text{)}$ metal sulphides like $\text{AS}_2\text{S}_3$ etc.

7. How are emulsions classified? Give two examples of each.

### **Solution:**

**Types of Emulsion :** Depending upon the nature of the dispersed phase, the emulsions are classified as;

- a. **Oil-in-water emulsions (O/W):** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium (**continuous phase**) is called an oil-in-water emulsion. Ex: Milk
- b. **Water-in-oil emulsion (W/O):** The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsions are also termed **oil emulsions.** Ex: Butter and cold cream

### **Problem set:**

1. The size of the colloidal particles is in the range of
  - a.  $10^{-7} - 10^{-9}$  pm
  - b.  $10^{-9} - 10^{-11}$  m
  - c.  $10^{-5} - 10^{-7}$  cm
  - d.  $10^{-2} - 10^{-3}$  nm

### **Solution: c)**

2. Which of the following forms a colloidal solution in water
  - a. NaCl
  - b. Gelatin
  - c. Starch
  - d. Both b) and c)

### **Solution: d)**

3. Cloud is \_\_\_\_\_ type of a colloidal.
  - a. Liquid in gas.
  - b. Gas in a liquid.
  - c. Liquid in liquid.
  - d. Liquid in solid.

**Solution:** b)

4. Tyndall effect in colloidal solution is due to
  - a. Absorption of light
  - b. Scattering of light
  - c. Reflection of light
  - d. Presence of electrically charged particles

**Solution:** b)

5. Lyophilic sols are more stable than lyophobic sols because
  - a. The colloidal particles have positive charge
  - b. The colloidal particles have negative charge
  - c. The colloidal particles are solvated
  - d. There are strong electrostatic repulsions

**Solution:** c)

6. What is a micelle? Give one example and the mechanism of its formation.

**Solution:**

**Micelles:**

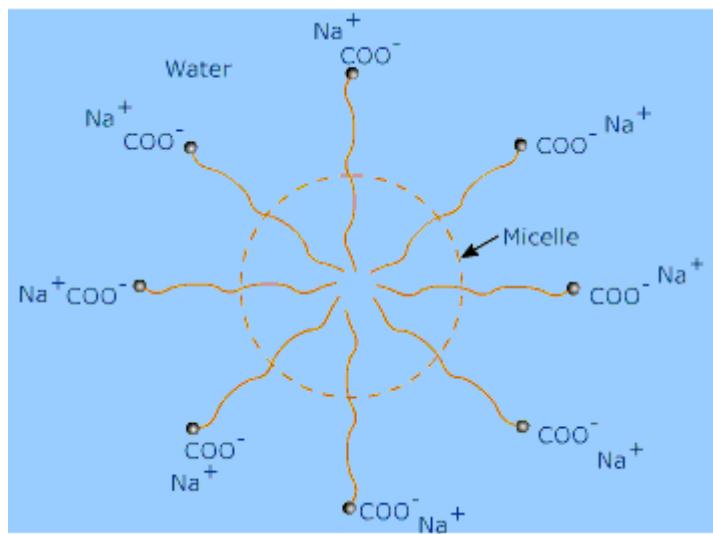
Micelles have both a lyophilic and lyophobic parts. Micelles may consist of more than 100 molecules. Certain substances behave as strong electrolytes at low concentration but at higher concentrations these substances exhibit colloidal characteristics due to the formation of aggregated particles. These aggregated particles are called micelles. **Micelles are called associated colloids.** The formation of micelles takes place only above a particular temperature called **Kraft Temperature ( $T_k$ )** and above a particular concentration called the **Critical micelle concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active molecules such as soaps and synthetic detergents form associated colloids in water. For soaps, the CMC is about  $10^{-4}$  to  $10^{-3}$  mol L<sup>-1</sup>.

**Mechanism of Micelle Formation:**

Micelles are formed by specific molecules which have lyophilic as well as lyophobic ends. Ordinary soap which contains sodium stearate ( $C_{17}H_{35}COONa$ ) forms micelle in water. The stearate ion has a long hydrocarbon end that is hydrophobic (because it is nonpolar) and a polar carboxyl group ( $COO^-$ ) that is hydrophilic.



When the concentration of sodium stearate is below its CMC, then it behaves as a normal electrolyte and ionizes to give  $Na^+$  and  $C_{17}H_{35}COO^-$  ions. As the concentration exceeds the CMC, the hydrophobic end starts receding away from the solvent and approach each other. However, the polar  $COO^-$  part interacts with water. This leads to the formation of a cluster having the dimensions of a colloid particles. In each cluster a large number of stearate groups clump together in a spherical manner such that the hydrocarbon parts interact with one another and the  $COO^-$  groups remains projected in water to the surface.



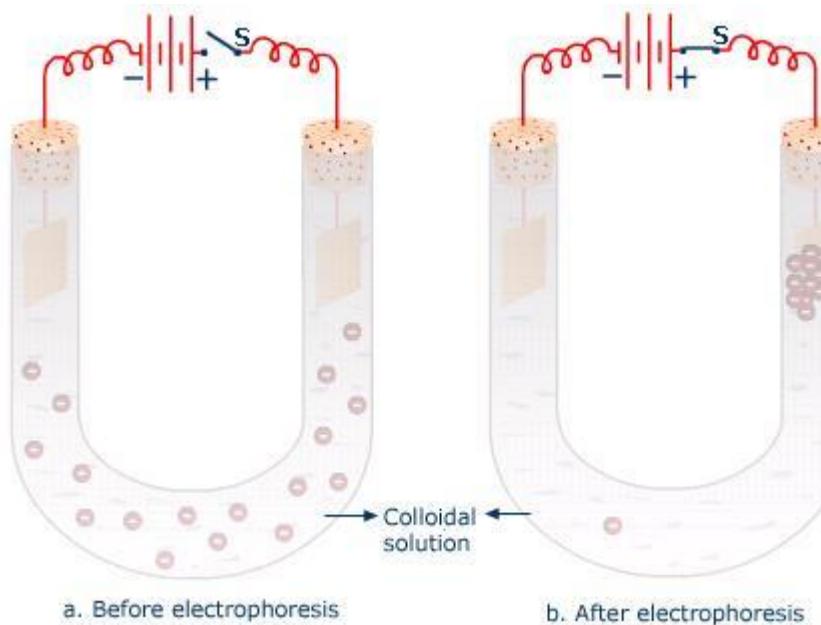
### Aggregation of $RCOO^-$ ions to form a micelle

7. Explain electrophoresis

### Solution: Electrophoresis:

The colloidal particles are electrically charged and they carry a charge, that is, either the colloids are negatively charged or positively charged. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Since the colloids carry charge, they repel each other and do not combine to form bigger aggregates. This is the reason why a sol is stable. The existence of charge on the colloidal particles is inferred from the observation that the colloidal particles move either towards the cathode or anode when the colloidal sol is placed in an electric field. This phenomenon of colloidal charged particles moving towards the oppositely charged electrodes in the presence of an electric field is called electrophoresis.

Electrophoresis is carried out by placing the colloidal solution in a U tube which is fitted with platinum electrodes.



### Apparatus for electrophoresis

When electric current is passed, the charged colloidal particles move towards the oppositely charged electrode. A colloidal sol of  $\text{AS}_2\text{S}_3$ , which is negatively charged will move towards the anode when placed in an electric field.

### Exercise questions:

1. Comment on the statement that “colloid is not a substance but a state of substance”. Justify your comment.
2. Action of soap is due to emulsification and micelle formation. Comment.
3. Why hydrophobic sols are easily coagulated?
4. Explain what is observed in the following processes
  - a. When a beam of light is passed through a colloidal sol.
  - b. An electrolyte, NaCl is added to hydrated ferric oxide sol.
  - c. Electric current is passed through a colloidal sol? specify

### Solutions to exercise questions:

1. Common salt (a typical crystalloid in an aqueous medium) behaves as a colloid in a benzene medium. Hence, we can say that a colloidal substance does not represent a separate class of substances. When the size of the solute particle lies between 1 nm and 1000 nm, it behaves as a colloid.

Hence, we can say that colloid is not a substance but a state of the substance which is dependent on the size of the particle. A colloidal state is intermediate between a true solution and a suspension.

2. The cleansing action of soap is due to emulsification and micelle formation. Soaps are basically sodium and potassium salts of long chain fatty acids, R-COO<sup>-</sup>Na<sup>+</sup>. The end of the molecule to which the sodium is attached is polar in nature, while the alkyl-end is non-polar. Thus, a soap molecule contains a hydrophilic (polar) and a hydrophobic (non – polar) part.

When soap is added to water containing dirt, the soap molecules surround the dirt particles in such a manner that their hydrophobic parts get attached to the dirt molecule and the hydrophilic parts point away from the dirt molecule. This is known as micelle formation. Thus, we can say that the polar group dissolves in water while the non-polar group dissolves in the dirt particle. Now, as these micelles are negatively charged, they do not coalesce and a stable emulsion is formed.

3. The stability of hydrophilic sols depends on two things. The presence of a charge and the salvation of colloidal particles. On the other hand, the stability of hydrophobic sols is only because of the presence of a charge. Therefore, the

latter are much less stable than the former. If the charge of hydrophobic sols is removed (by addition of electrolytes), then the particles present in them come closer and form aggregates, leading to precipitation

4. a. When a beam of light is passed through a colloidal solution, then scattering of light is observed. This is known as the Tyndall effect. This scattering of light illuminates the path of the beam in the colloidal solution.
- b. When NaCl is added to ferric oxide sol, it dissociates to give  $\text{Na}^+$  and  $\text{Cl}^-$  ions. Particles of ferric oxide sol are positively charged. Thus, they get coagulated in the presence of negatively charged  $\text{Cl}^-$  ions.
- c. The colloidal particles are charged and carry either a positive or negative charge. The dispersion medium carries an equal and opposite charge. This makes the whole system neutral. Under the influence of an electric current, the colloidal particles move towards the oppositely charged electrode. When they come in contact with the electrode, they lose their charge and coagulate.

## Module - 23.1

### d - block Elements

#### Introduction:

The elements that lie in between s-block and P-block are the d-block elements. These elements are called transition elements as they show transitional properties between s and p-block elements. These elements contain partially filled d-orbitals and hence they are called as d-block elements. The general electronic configuration of d-block elements is  $(n-1) d^{1-10} ns^{1-2}$ . The d-block comprises of 3d, 4d, 5d and 6d series of elements.

#### First transition series

This is also called as 3d series which corresponds the filling of 3d orbital. It starts from scandium whose atomic number is 21 and includes 10 elements till zinc whose atomic number is 30.

#### Second transition series

This is also called as 4d series which corresponds the filling of 4d orbital. It starts from yttrium whose atomic number is 39 and includes 10 elements till cadmium whose atomic number is 48.

#### Third transition series

This is also called as 5d series which corresponds the filling of 5d orbital. The first element of this series is lanthanum whose atomic number is 57 and includes 9 elements from hafnium whose atomic number is 72 to mercury whose atomic number is 80.

#### Fourth transition series

This is also called as 6d series which corresponds the filling of 6d orbitals.

## **General trends in properties of first row of transition metals:**

### **Electronic configuration of the elements of first transition series:**

<b>Element</b>	<b>Atomic number</b>	<b>Electronic configuration:</b>
Scandium	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Titanium	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
Manganese	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Zinc	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Chromium and copper exhibit anomalous electronic configurations due to the following reasons.

Electronic configuration of chromium ( $Z = 24$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Electronic configuration of copper ( $Z = 29$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

In case of half filled sub shells there is a maximum number of unpaired electrons in different orbitals. In such cases, the inter electronic repulsions are minimum and there is a maximum possibility of exchange or delocalization of electrons, which further decreases the energy and increases the stability.

#### **Metallic character:**

Most of the transition elements of the first row form metallic bonds due to the presence of incomplete outermost energy level. So, all the transition elements exhibit metallic characters. The strength of the metallic bond depends upon the number of unpaired d-electrons. As the number increases the strength also increases. Due to the absence of unpaired electrons 'Zn' is not a hard metal.

#### **Ionization energy:**

The ionization energies of first row elements gradually increases with increase in atomic number. The ionization energy of Zn is very high than all the other metals which is due to its fully filled d-orbital. The third ionization energy of Mn is very high than the others.

#### **Ionic radii:**

In the first row transition elements the ionic radii decrease with increase in atomic number. The value of ionic radii also depends on the oxidation state of metals. As the oxidation state increases the ionic radius decreases and as the oxidation state decreases the ionic radius increases.

#### **Oxidation states:**

d – block elements shows more than one oxidation states due to availability both ns and  $(n - 1)d$  electrons in the compound formation. The lowest oxidation state is exhibited by using the s – electrons in the outermost orbit

and the maximum oxidation state is given by the sum of the outer s – electrons and unpaired d – electrons.

The maximum oxidation state in first series is +7 exhibited by manganese. In second and third transition series, the maximum oxidation state is +8 in Ruthenium and osmium shown in their oxides.

In a given series of d – block elements the oxidation state increases upto nearly middle element and then decreases. The most stable oxidation state in all the elements of 3d – series is +2.

#### Variable oxidation states of 3d series

I series 3d	Sc $4s^23d^1$	Ti $4s^23d^2$	V $4s^23d^3$	Cr $4s^13d^5$	Mn $4s^23d^5$	Fe $4s^23d^6$	Co $4s^23d^7$	Ni $4s^23d^8$	Cu $4s^13d^{10}$	Zn $4s^23d^{10}$
	II	II	II	II	II	II	II	II	I	II
	III	III	III	III		III	III	III	II	II
		IV			IV					
				VI	VI					
					VII					

#### Colour:

Transition metal ions are generally coloured due to the presence of unpaired d – electrons. Which absorb light from the visible region and thus move to higher energy level. Therefore, one of the colours of the visible spectrum is absorbed and the transition metal ion gets the complementary colour. The transition metal ion with completely filled d – orbitals are colourless. For example  $Zn^{+2}$ ,  $Cd^{+2}$  and  $Hg^{+2}$  are colourless. The colour of transition metal ions is due to excitation of d – orbitals of lower energy to the d – orbitals of higher energy. Since they are completely filled d – orbitals in  $Zn^{+2}$  ( $3d^{10}$ ),  $Cd^{+2}$  ( $4d^{10}$ ) and  $Hg^{+2}$  ( $5d^{10}$ )

ions, these are colourless. The energy required to excite a d – electron of transition metal ion is small. Hydrated copper (+2) ion i.e.  $\text{Cu}(\text{H}_2\text{O})_6^{+2}$  absorbs red colour from the visible light appears blue, the complementary colour of red. Thus  $\text{Cu}(\text{H}_2\text{O})_6^{+2}$  appear blue.

**Example:**

<b>Ion</b>	<b>Colour</b>
$\text{Cu}^{+2}$	Blue
$\text{Fe}^{+2}$	Pale green
$\text{Fe}^{+3}$	Yellow
$\text{Cr}^{+3}$	Green
$\text{Mn}^{+2}$	Pink
$\text{Zn}^{+2}$	Colourless

**$\text{Cu}^{+2}$  ions are coloured and are paramagnetic:**

Electronic configuration of  $\text{Cu}^{+2}$  ion =  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

$\text{Cu}^{+2}$  ion contains one unpaired d – electron. So it is coloured and paramagnetic.

**Magnetic properties:**

Those substances which are weakly attracted by the magnetic field are called paramagnetic substances. This magnetic character arises due to the presence of unpaired electrons. Most of the transition elements and their ions contain unpaired d – electrons. So they are paramagnetic substances.

**Example:**

$\text{Ti}^{+3}$ ,  $\text{Cu}^{+2}$ ,  $\text{Sc}^{+2}$       they have unpaired electrons

Those substances which are repelled by the magnetic field are called diamagnetic substances. This magnetic character arises due to the presence

of paired electrons. Transition metal ions which contain paired electrons show diamagnetic substances.

**Example:**

$Ti^{+4}$ ,  $Cu^+$ ,  $Zn^{+2}$  have all the electrons completely paired.

Those substances which are strongly attracted by the magnetic field are ferromagnetic substances. These also contain unpaired electrons. Iron, cobalt and nickel are ferromagnetic substances.

**Catalytic property:**

Many d – block elements and their compounds act as catalysts in chemical reactions. This property may be either due to their variable valency which enables them to form unstable intermediate compounds or due to providing suitable reaction surfaces.

Some catalysts used in the industries.

Process	Catalyst
Hydrogenation of oils	Ni
Synthesis of ammonia by Haber's process	Fe
Synthesis of nitric acid by Ostwald's process	Pt
Synthesis of sulphuric acid by contact process	$V_2O_5$

**Complex formation:**

d – block metal ions having a great tendency to form complexes due to their small sizes, high charges and due to the presence of vacant d – orbitals.

The bonds involved in the formation of complexes are co – ordinate bonds. So complexes are called co – ordinate compounds. In complexes the groups which donate the electron pairs are called ligands and the metal ions which accept the electron pairs are called central metal ions. The central metal ions and the ligands are represented by a square bracket and other ions are

represented outside the bracket. The square bracket part is a complex ion and it involves as a single unit in chemical reactions.

**Example:**

1.  $K_3[Fe(CN)_6]$  potassium ferricyanide.
2.  $[Cr(NH_3)_6]Cl_3$  hexamminechromium (III) chloride.

In a series the stability of complexes increases with an increase in the atomic number of the elements and in a particular oxidation state with decrease in the size of its atoms. When the d – block metal atom exhibits more than one oxidation state, the highest valent ion forms more stable complex.

**Redox potential of d – block elements:**

Standard reduction potentials of 3d series obtained by the reduction of  $M^{+2}$  ions to M are given below.



Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Reduction potential (Volts)	- 2.1	- 1.6	- 1.2	- 0.91	- 1.18	- 0.44	- 0.28	- 0.25	+ 0.34	+ 0.76

When we observe the values in the table, except copper the remaining elements have higher negative values than standard hydrogen potential (zero). Hence these elements are easily oxidized to give ions.



**Review questions:**

**Example set:**

1. Transition elements are \_\_\_\_\_ block elements.
  - a. s
  - b. p

- c. d
- d. f

**Solution:** c)

2. The first transition element in the 3d series is:

- a. scandium
- b. chromium
- c. nickel
- d. copper

**Solution:** a)

3. The property, which is not characteristic of transition metals, is:

- a. Variable oxidation states
- b. Tendency to form complexes
- c. Formation of colored compounds
- d. Electro negative behaviour

**Solution:** d)

4. Which of the following elements exhibits largest number of oxidation states?

- a. Zn
- b. V
- c. Mn
- d. Ni

**Solution:** c)

5. Transition metals show paramagnetism due to

- a. characteristic configuration
- b. high lattice energy
- c. variable oxidation states
- d. unpaired electrons

**Solution:** d)

6. How do the following properties vary in the first transition series?

- a. Atomic size
- b. Stability of various oxidation states
- c. Ionization energy

**Solution:**

7. What are d – block elements?

**Solution:**

The elements in which differentiating electron is accommodated in the d – subshell are called d – block elements.

8. Name three characteristic properties of d – block elements.

**Solution:**

- a. Formation of coloured compounds
- b. Formation of complex compounds
- c. Paramagnetic in nature

9. Name two elements of 3d – series which show anomalous electronic configuration.

**Solution:**

Chromium, copper

**Problem set:**

1. The general electronic configuration of transition elements is

- a.  $(n - 1) d^{1-5}$
- b.  $(n - 1) d^{1-10} ns^1$
- c.  $(n - 1) d^{1-10} ns^{1 \text{ or } 2}$
- d. None

**Solution:** c)

2. Chromium has the electronic configuration

- a.  $3s^2 3p^6 3d^4 4s^2$

- b.  $3s^2 3p^6 3d^5 4s^1$
- c.  $3s^2 3p^6 3d^6$
- d. None of these

**Solution:** b)

- 3. Which of the following has the maximum number of unpaired d – electrons?
  - a. Zn
  - b.  $Fe^{2+}$
  - c.  $Ni^{3+}$
  - d.  $Cu^+$

**Solution:** b)

- 4. Why  $CuSO_4$  is blue while  $ZnSO_4$  is white?

**Solution:**

$Cu^{2+}$  in  $CuSO_4$  has  $[Ar] 3d^9 4s^0$  configuration. It can undergo d – d transition. It absorbs red light of the visible region and hence  $CuSO_4$  appears blue. Blue is complimentary colour of red. In  $ZnSO_4$ ,  $Zn^{2+}$  has  $3d^{10} 4s^0$  configuration. It cannot undergo d – d transition, hence, they are soft in nature.

- 5. Transition elements form alloys easily. What is the reason?

**Solution:**

Nearly same atomic radii.

- 6. Which ions of first transition series show highest paramagnetism?

**Solution:**

$Fe^{3+}$  and  $Mn^{2+}$ .

### Exercise questions:

- 1. What is the magnetic moment of  $K_3[FeF_6]$ ?
  - a. 5.91 B.M
  - b. 4.89 B.M

- c. 3.87 B.M  
d. 6.92 B.M
2. Why  $\text{Fe}^{+3}$  compounds are more stable?
  3. Why transition metals and their compounds act as catalysts.
  4. Why  $\text{Hg}^{2+}$  and  $\text{Hg}_2^{2+}$  salts are colourless.
  5.  $\text{Cu}^{2+}$  are paramagnetic while  $\text{Cu}^+$  salts are diamagnetic in nature.
  6. Predict the spin only magnetic moment for
    - a.  $\text{Fe}^{2+}$
    - b.  $\text{Mn}^{2+}$
    - c.  $\text{Cr}^{6+}$
    - d.  $\text{Cu}^+$

### Solutions:

1. a)
2.  $3d^5$  configuration, i.e., all the five orbitals are singly occupied.
3. Because of the availability of d – orbitals they can easily form intermediate products which are activated. The sizes of transition metal atoms and ions are also favourable for transitory complex formation with the reactants.
4.  $\text{Hg}^{2+}$  and  $\text{Hg}_2^{2+}$  salts have  $5d^{10}$  configuration, i.e. there is no d – d transition, hence colourless.
5.  $\text{Cu}^{+2}$  configuration is  $3d^9$  (one orbital is singly occupied) – paramagnetic;  $\text{Cu}^+$  configuration is  $3d^{10}$  (all orbitals are doubly occupied) – diamagnetic.
- 6.

<b>Ion</b>	<b>Electronic configuration</b>	<b>No. of unpaired electrons</b>	<b>Magnetic moment</b>
a. $\text{Fe}^{2+}$	$[\text{Ar}]3\text{d}^6 4\text{s}^0$	4	4.90 BM
b. $\text{Mn}^{2+}$	$[\text{Ar}]3\text{d}^5 4\text{s}^0$	5	5.96 BM
c. $\text{Cr}^{6+}$	$[\text{Ar}]3\text{d}^0 4\text{s}^0$	0	0 BM
d. $\text{Cu}^+$	$[\text{Ar}]3\text{d}^{10} 4\text{s}^0$	0	0 BM

# Co-ordination Compounds

## Module 24.1: Introduction, ligands, co-ordination number, IUPAC nomenclature

### Double salts or lattice compounds:

The addition compounds which are stable in solid state only but are broken down into individual constituents when dissolved in water are called double salts or lattice compounds. Their solutions have the same properties as the mixture of individual components. For example, when Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is dissolved in water, it exhibits the properties of  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , i.e., they produce  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  ions in the solution. Thus, each ion has its identity in the double salt.



**Carnallite:**  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ;

**Potash alum:**  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  etc. are the examples of double salts.

### Co-ordination or complex compounds:

The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called **co-ordination compounds or complex compounds**. The properties of their solutions are different from those of their constituents. When crystals of  $\text{CuSO}_4 \cdot 4\text{NH}_3$  are dissolved in water there is hardly any evidence for the presence of  $\text{Cu}^{2+}$  ions or ammonia molecules. A new ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of  $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$  does not give tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but gives the test for a new ion  $[\text{Fe}(\text{CN})_6]^{4-}$ . The ions  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are called **complex ions**.



Thus, a co-ordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple, stable, molecular compounds and retains its identity in the solid as well as in dissolved state.

### Definition of the terms used in coordinate compounds:

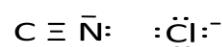
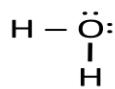
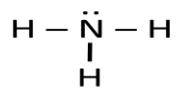
#### 1. Central ion or centre of coordination:

The cation to which one or more neutral molecules or anions are attached is called the central metal ion of coordination. Since, the central ion acts as an acceptor and thus, has to accommodate electron pairs donated by the donor atom of ligand, it must have empty orbitals. This explains why the transition metals, having empty d – orbitals form coordination compounds very readily.

Thus, in the complexes  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  ions respectively are the central metal ions.

#### 2. Ligands:

The neutral molecules; anions or cations which are directly linked with central metal atom or ion in a complex ion are called ligands. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkages. Free ligands have at least one electron pair that is not engaged in bonding. Some examples are:



The ligands act as a donor as it donates one or more electron pairs to the central metal atom or ion which acts as an acceptor. The ligands are thus Lewis bases and central metal ions are Lewis acids and their union involves following two things.

- a. Ligands should have lone pairs of electrons which can be donated to the central metal ion or atom.
- b. The central atom or ion should have vacant orbital's of nearly equivalent energy to accommodate the electrons donated by ligands. This condition is easily fulfilled by atoms or ions of transition metals.

### **Types of ligands:**

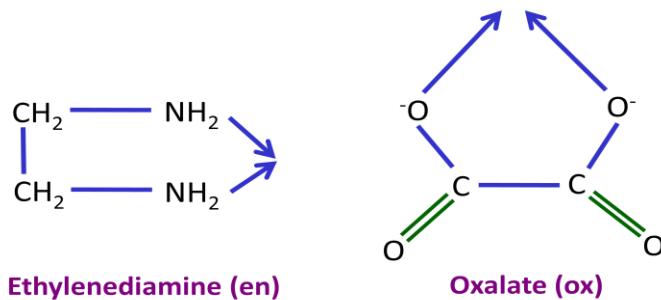
Ligands can be of following types depending on the number of donor atoms present in them.

#### **i. Mono or unidentate ligands:**

They have one donor atom, *i.e.*, they supply only one electron pair to central metal atom or ion.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ ,  $\text{CO}$  etc. are examples of monodentate ligands.

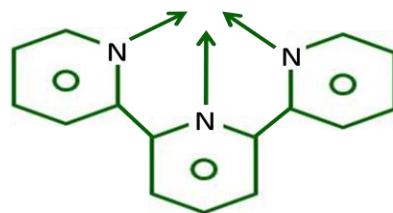
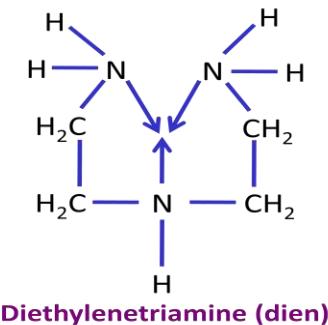
#### **ii. Bidentate ligands:**

Ligands, which have two donor atoms and have the ability to link with the central metal ion at two positions, are called bidentate ligands. Some examples are:



#### **iii. Tridentate ligands:**

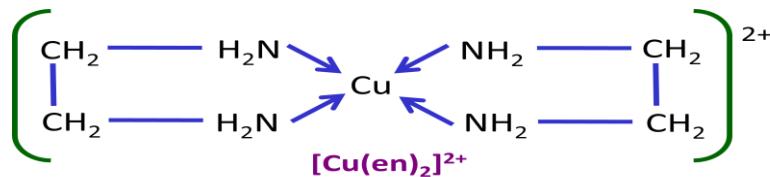
The ligands having three donor atoms are called tridentate ligands. Examples are:



Similarly polydentate ligands are ligands having more than two donor atoms.

#### iv. Chelating ligands:

A bidentate or a polydentate ligand is known as a chelating ligand if, on coordination, it results in the formation of a closed or cyclic ring structure. The complexes, thus formed are called chelates. The word chelate has been derived from the *Greek word chelate meaning claw*. The complex formed by  $\text{Cu}^{2+}$  ion with ethylenediamine is an example of a chelate.



The following are the characteristics of chelates:

- Chelating ligands form more stable complexes than monodentate ligands. This is called chelating effect, all types of polydentate ligands can act as chelating ligands.
- The chelates containing 5 or 6 membered rings including metal atom are comparatively more stable. Chelating ligands which do not contain unsaturated groups (double bonds), in general, form five membered stable complexes while chelating ligands having unsaturated groups (double bonds) form six membered stable complexes.
- Ligands with larger groups form more unstable rings than with smaller groups due to steric hindrance.

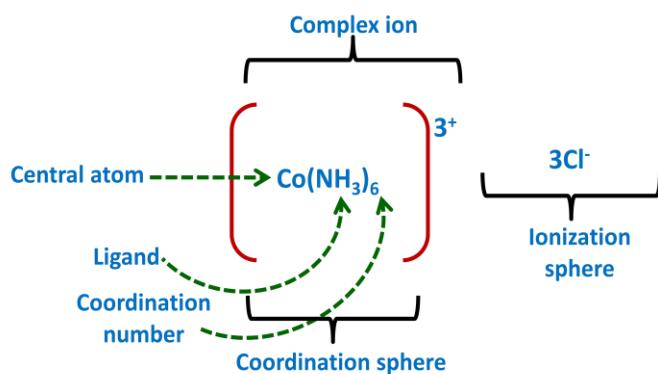
### 3. Co-ordination number:

The total number of ligands attached to the central ion in a complex compound is known as the coordination number of that ion. Thus, the coordination numbers of silver and copper ions in the complexes  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  are 2 and 4 respectively.

### 4. Co-ordination sphere:

The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is written inside square bracket, as for example  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Remember that the central metal atom and the ligands inside the square bracket behave as a single entity.

Thus, the various terms used in a coordination compound can be illustrated as below:



### 5. Oxidation number:

It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example, the oxidation number of Fe, Co and Ni in  $[\text{Fe}(\text{CN}_6)]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $\text{Ni}(\text{CO})_4$  is +2, +3 and 0 respectively.

### Complex ion:

A complex (coordinate) ion is an electrically charged or a neutral species formed by the combination of a central cation with more than one ligand species.

The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it. Charges of some complex compounds are given below:

S.No	Complex compound (ion)	Charge on complex ion
(i)	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	(+2) of Cu + (0) of $\text{NH}_3$ $\therefore$ Net charge = +2
(ii)	$[\text{Fe}(\text{CN})_6]^{4-}$	(+2) of Fe + (-6) of 6 CN $\therefore$ Net charge = -4
(iii)	$(\text{Co}(\text{NH}_3)_5\text{Cl})^{2+}$	(+3) of Co + (0) of $\text{NH}_3$ + (-1) of Cl $\therefore$ Net charge = +2
(iv)	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	(+3) of Co + (0) of $\text{NH}_3$ + (-3) of Cl $\therefore$ Net charge = 0

### Nomenclature of Co-ordination compounds (IUPAC system):

The following rules are adopted for naming all types of coordination compounds:

- If a coordination compound is ionic, the name of cation is given whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.
- Within a complex ion, the ligands are named first followed by the metal ion

#### Naming of the ligands:

- Anionic ligands ending with – ide are named by replacing – ide with suffix – o or replacing – e by – o.

Anion	Symbol	Name as ligand
Chloride	$\text{Cl}^-$	Chlorido
Bromide	$\text{Br}^-$	Bromido
Cyanide	$\text{CN}^-$	Cyano
Oxide	$\text{O}^{2-}$	Oxo
Peroxide	$\text{O}_2^{2-}$	Peroxo
Hydroxide	$\text{OH}^-$	Hydroxo
Sulphide	$\text{S}^{2-}$	Sulphido
Amide	$\text{NH}_2^-$	Amido

Nitride	$\text{N}^{3-}$	Nitrido
Phosphide	$\text{P}^{3-}$	Phosphido

Ligand whose names end in – ite or – ate become – ito or – ato, *i.e.*, by replacing the ending – e with – o.

Anion	symbol	Name of the ligand
Carbonate	$\text{CO}_3^{2-}$	Carbonato
Oxalate	$\text{C}_2\text{O}_4^{2-}$	Oxalato
Sulphate	$\text{SO}_4^{2-}$	Sulphato
Nitrate	$\text{NO}_3^-$	Nitrato
Sulphite	$\text{SO}_3^{2-}$	Sulphito
Acetate	$\text{CH}_3\text{COO}^-$	Acetato
Nitrite	$\left\{ \begin{array}{l} \text{ONO}^- \\ \text{NO}_2^- \end{array} \right.$	(bonded through oxygen) Nitrito – O (bonded through nitrogen) Nitrito – N or Nitro

- b. Neutral ligands are called with the same names as their neutral molecules or with their special names, e.g.,
  - $\text{H}_2\text{O}$  Aquo (Aqua)
  - $\text{NH}_3$  Ammine
  - $\text{CO}$  Carbonyl;
  - $\text{NO}$  Nitrosyl;
  - $\text{CS}$  Thiocarbonyl;
  - $\text{NS}$  Thionitrosyl
- c. Positively charged ligands have suffix – ium.
- $\text{NH}_2 - \text{NH}_3^+$  Hydrazinium;     $\text{NO}_2^+$  Nitronium
- d. If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek prefixes such as di, tri, tetra, penta, hexa etc.
- e. When more than one ligand is present, they are named in alphabetical order without separation by hyphen.
- 3. The oxidation state of the central metal is shown by Roman numerical in bracket immediately following its name.
- 4. Complex positive ions and neutral coordination compounds have no special ending.

5. Complex negative ions always end in the suffix – ate. In most of the cases, the suffix – ate is fixed to names of the metals.

Name of components present in coordination sphere are written continuously without a gap, e.g.,



Some names of the metals in the anionic complexes are given below.

Element	Metal as named in ionic complex
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

6. The name of the neutral coordination compound is given in one word only as the name of  $Ni(CO)_4$  is tetracarbonylnickel (0). The following examples will make the rules more clear.

#### Coordination compounds containing complex cations:



#### Coordination compounds containing complex anions:





### Coordination compounds containing complex cations and anions:



### Non-ionic coordination compounds:



### Writing the formula of a coordination compound from its IUPAC name:

Following rules are followed in writing the formula of a coordination compound:

1. Formula of the cation whether simple or complex is written first followed by that of an anion
2. The coordination sphere is written in square brackets
3. The following sequence of symbols within the coordination sphere is followed:
  - i. Metal atom
  - ii. Anionic ligands
  - iii. Neutral ligands
  - iv. Cationic ligands
  - a. If there are number of ligands of same type (anionic, neutral or cationic), they are listed alphabetically according to first alphabet of their names. For example if  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{Br}^-$  etc., are present, they are written as  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{OH}^-$  and  $\text{SO}_4^{2-}$ .  
When two ligands have same donor atom, the ligands with fewer such atoms is cited first followed by the ligand having more atoms. For example,  $\text{SO}_4^{2-}$ , precedes  $\text{S}_2\text{O}_3^{2-}$ .  
When the numbers of defining atoms are same, subsequent symbol decides the sequence. For example,  $\text{NH}_2^-$  precedes  $\text{NO}_2$  because H comes before O.
4. Polyatomic ligands are enclosed in parentheses but all ligands are formulated without any space in between

5. The number of cations or anions to be written in the formula is calculated on the basis of total negative charge on the anion, as the complex as a whole is electrically neutral.
6. Sometimes abbreviations for certain ligands are used in parentheses instead of their structural formulae. For example,
  - (en) ethylenediamine (ethane – 1, 2 – diamine)
  - (dien) diethylenetriamine
  - (trien) triethylenetetraamine
  - (edta or EDTA) ethane – 1, 2 – diamine tetraacetato
  - (dmg) dimethylglyoximato

Few examples are given here to explain the above rules.

***Example 1:***

Trichlorotriamminecobalt(III)

The metal complex is a neutral substance. The name of the central metal is written first. Its oxidation state, then the ligands and their numbers are written.

Therefore the formula is written as  $[\text{Co}^{\text{III}}(\text{NH}_3)_3(\text{Cl}_3)]$

***Example 2:***

Tetramminecopper(II) hydroxide. The complex is a cationic complex. The formula of the cation is written in the same order as in neutral complex. *i.e.* the central metal, its oxidation state; ligands and their numbers.

Therefore  $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]^{+2}$

The name of the anion only is given and not its number. Therefore hydroxide. The number is inferred from the oxidation state of the complex species.

Therefore complete formula is  $[\text{Cu}(\text{NH}_3)_4](\text{OH})^2$

***Example 3:***

Potassium tetrachloropalatinate(II)

The complex is an anionic complex

The cation is potassium. From the oxidation state of the complex anion, the number of cations is 2.

The anion, obtained by applying the above procedure, is  $[\text{Pt}^{\text{II}}(\text{Cl}_4)]^{-2}$

Therefore complete formula is  $\text{K}_2[\text{PtCl}_4]$

**Assignment Questions:**

1. Mention which of the following substances is a double salt and which is a complex compound?
  - a. Potash alum
  - b. Carnallite
  - c. Mohr's salt
  - d. Potassium ferricyanide
2. Define the terms
  - a. Ligand
  - b. Chelate
3. Give the coordination number of the metal in the following compounds
  - a.  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
  - b.  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$
  - c.  $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - d.  $[\text{Pt}(\text{en})_3]\text{Cl}_4$
4. Write the names of the following complexes
  - a.  $\text{Ag}[\text{NH}_3]_2\text{Cl}$
  - b.  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
  - c.  $\text{K}_4[\text{Fe}(\text{CN})_6]$

**Example Set:**

1. Oxidation state of Fe in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is
  - a. +2
  - b. +3
  - c. -2

d. -3

**Solution:** a)

2. All ligands are
  - a. Lewis acids
  - b. Lewis bases
  - c. Neutral
  - d. Both a) and b)

**Solution:** b)

3. The number of ions formed in aqueous solution by the compound  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  is
  - a. 2
  - b. 3
  - c. 4
  - d. 7

**Solution:** a)

4.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is called
  - a. Hexamminecobalt(III) chloride
  - b. Aminocobalt chloride(III)
  - c. Cobalt chloride hexammine
  - d. Hexammine tricobalt chloride

**Solution:** a)

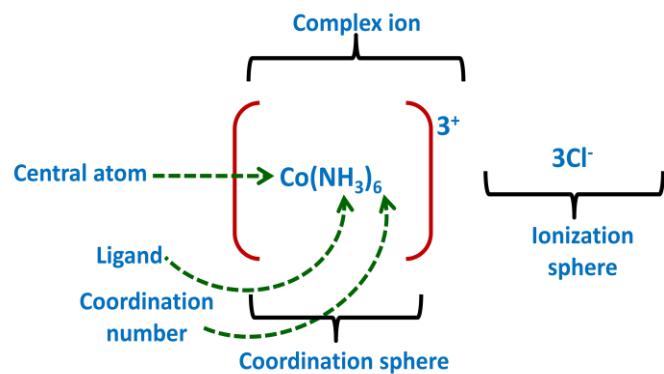
5. Explain the terms co-ordination sphere and oxidation number of a central metal atom.

**Solution:**

**Coordination sphere:** The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is written inside square bracket, as for example  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Remember that the

central metal atom and the ligands inside the square bracket behave as a single entity.

Thus, the various terms used in a coordination compound can be illustrated as below:



### Oxidation number:

It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example, the oxidation number of Fe, Co and Ni in  $[\text{Fe}(\text{CN}_6)]^{4-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $\text{Ni}(\text{CO})_4$  is +2, +3 and zero respectively

Determination of oxidation number and coordination number of a metal atom or ion in a complex is similar to the calculation of oxidation states in the compounds as we know it from earlier studies.

### 6. State the principles involved in the nomenclature of co-ordination compounds

#### Solution:

#### Nomenclature of co-ordination compounds (IUPAC system):

The following rules are adopted these days for naming all types of coordination compounds:

1. If a coordination compound is ionic, the name of cation is given whether or not it is the complex ion followed by the name of the anion just like naming a simple salt. The names of cation and anion are separated by a space.
2. Within a complex ion, the ligands are named first followed by the metal ion

- a. Neutral ligands are called with the same names as their neutral molecules or with their special names, e.g.,  
 $\text{H}_2\text{O}$  Aquo (Aqua)       $\text{NH}_3$  Ammine  
 $\text{CO}$  Carbonyl;                 $\text{NO}$  Nitrosyl;  
 $\text{CS}$  Thiocarbonyl;             $\text{NS}$  Thionitrosyl
  - b. Positively charged ligands have suffix – ium.  
 $\text{NH}_2 - \text{NH}_3^+$  Hydrazinium;     $\text{NO}_2^+$  Nitronium
  - c. If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek prefixes such as di, tri, tetra, penta, hexa etc.
  - d. When more than one ligand is present, they are named in alphabetical order without separation by hyphen.
3. The oxidation state of the central metal is shown by Roman numerical in bracket immediately following its name.
  4. Complex positive ions and neutral coordination compounds have no special ending.
  5. Complex negative ions always end in the suffix – ate. In most of the cases, the suffix – ate is fixed to names of the metals.
7. Write a short note on complex compounds.

**Solution:**

### **Complex compounds:**

The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water they do not break up completely into individual ions, are called coordination compounds or complex compounds. The properties of their solutions are different from those of their constituents. When crystals of  $\text{CuSO}_4 \cdot 4\text{NH}_3$  are dissolved in water there is hardly any evidence for the presence of  $\text{Cu}^{2+}$  ions or ammonia molecules. A new ion,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , is furnished in which ammonia molecules are directly linked with the metal ion. Similarly, the aqueous solution of  $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$  does not give tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions but

gives the test for a new ion,  $\text{Fe}(\text{CN})_6^{4-}$ . The ions  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are called complex ions.



Thus, a coordination or complex compound may be defined as a molecular compound that results from the combination of two or more simple, stable, molecular compounds and retains its identity in the solid as well as in dissolved state.

**Problem Set:**

1. The IUPAC name of  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$  is
  - a. Tetra amino dichloro chromium nitrate
  - b. Tetra amino dichloro chromium (II) nitrate
  - c. Tetra amminedichlorochromium(III) nitrate
  - d. Tetra amino dichloro chromium (II) nitrate

**Solution:** c)

2. EDTA is a \_\_\_ ligand
  - a. Monodentate
  - b. Hexadentate
  - c. Bidentate
  - d. Tridentate

**Solution:** b)

3.  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  is called
  - a. Potassium alumino oxalate
  - b. Potassium alumino (III) oxalate
  - c. Potassium trisoxalatoaluminate(III)
  - d. Potassium trioxalato aluminate (III)

**Solution:** c)

4. The IUPAC name for  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  is
- Hexamminecobalt(III) hexacyano chromate(III)
  - Hexacyano chromium, cobalt hexa ammine (VI)
  - Hexa ammine cobalt (III) hexa cyano chromium (VI)
  - Hexa cyano chromium (III) hexa amine cobalt (III)

**Solution:** a)

5. Distinguish between double salt and complex compound.

**Solution:**

Double salt	Complex compound
<p>1. It is formed by combination of two salts. They lose their identity when dissolved in water  <b>Ex:</b> <math>\text{KCl} + \text{MgCl}_2 + 6\text{H}_2\text{O} \longrightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}</math></p> <p>Carnalite is dissolved in water to give <math>\text{Mg}^{+2}</math>, <math>\text{K}^+</math> and <math>\text{Cl}^-</math> which answer their tests      Other examples are</p> <p>2. Potash alum      3. Cryolite</p>	<p>1. It is formed by combination of two salts which have lost their identity after union  <b>Ex:</b> <math>4\text{KCN} + \text{Fe}(\text{CN})_2 \longrightarrow 4\text{K}[\text{Fe}(\text{CN})_6]</math>  <b>Potassium ferrocyanide</b></p> <p>It is dissolved in water to give <math>\text{K}^+</math> and <math>[\text{Fe}(\text{CN})_6]^{4-}</math> ions. Here <math>\text{Fe}^{+2}</math> and <math>\text{CN}^-</math> ions      Other examples are</p> <p>2. <math>[\text{Co}(\text{NH}_3)_6]\text{Cl}_3</math>      3. <math>[\text{Ni}(\text{CN})_4]^{2-}</math></p>

6. What is the coordination number of the central metal ions in the following complexes
- $[\text{Cu}(\text{NH}_3)_4]^{+2}$
  - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
  - $[\text{Pt}(\text{en})_2]\text{Cl}_2$
  - $[\text{Mo}(\text{CN})_8]^{4-}$
  - $[\text{Fe}(\text{EDTA})]^-$
  - $[\text{Pd}(\text{H}_2\text{O})_2(\text{ONO})_2]\text{I}_2$

**Solution:**

- a.  $\text{NH}_3$  is a monodentate ligand

No. of points of attachment with  $\text{Cu}^{2+} = 4 \times 1 = 4$

C.N of  $\text{Cu}^{2+} = 4$

b.  $\text{C}_2\text{O}_4^{2-}$  is a bidentate ligand

No. of points of attachment  $\text{Fe}^{+3} = 3 \times 2 = 6$

C.N of  $\text{Fe}^{+3} = 6$

c. "en" is a bidentate ligand and  $\text{Cl}^-$  is a monodentate ligand

No. of points of attachment with  $\text{Pt}^{+2} = 2 \times 2 + 2 \times 1 = 6$

C.N of  $\text{Pt}^{+2} = 6$

d.  $\text{CN}^-$  is a monodentate ligand

No. of points of attachment with  $\text{Mo}^{4+} = 8 \times 1 = 8$

C.N of  $\text{Mo}^{4+} = 8$

e. EDTA is a hexadentate ligand

No. of points of attachment with  $\text{Fe}^{+3} = 6 \times 1 = 6$

C.N of  $\text{Fe}^{+3} = 6$

f. No. of points of attachment with  $\text{Pd}^{+4} = 2 \times 1 + 2 \times 1 + 2 \times 1 = 6$

C.N of  $\text{Pd}^{+4} = 6$

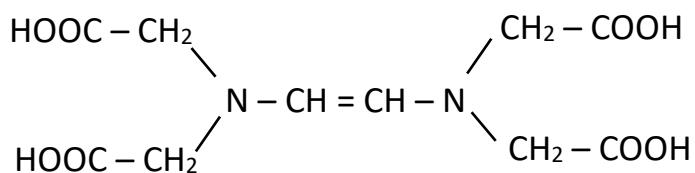
### Exercise Questions:

1. The IUPAC name of  $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$  is

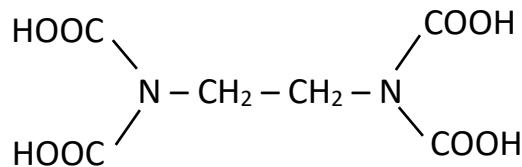
- Tetrachloronickel(II) tetramminenickel (II)
- Tetramminenickel (II) tetrachloronickel (II)
- Tetramminenickel(II) tetrachloronickelate(II)
- Tetrachloronickel (II) tetrachloronickelate (0)

2. The correct structure of ethylenediaminetetraacetic acid (EDTA) is

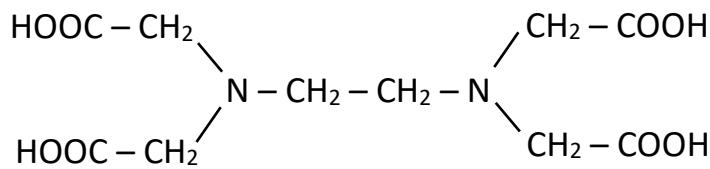
a.



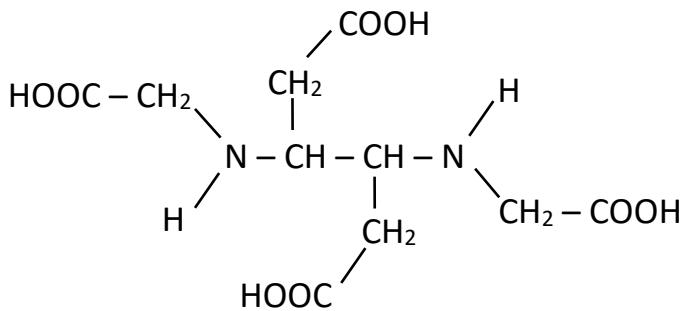
b.



c.



d.



3. What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.
4. Specify the oxidation number of the metals in the following coordination entities.
  - a.  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$
  - b.  $[\text{Co}(\text{Br})_2(\text{en})_2]^{2+}$
  - c.  $[\text{PtCl}_4]^{2-}$
  - d.  $\text{K}_3[\text{Fe}(\text{CN})_6]$
  - e.  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$
5. Write down the IUPAC names of the following compounds.
  - a.  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$
  - b.  $\text{K}_3[\text{Cr}(\text{CN})_6]$

6. Write the formulae of the following complexes

- Pentammine chlorocobalt (III) ion
- Lithium tetrahydrogen aluminate (III)

7.



Identify A and B. Write the IUPAC names of A and B.

8. Write down the IUPAC names of the following compounds:

- $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
- $\text{K}_3[\text{Cr}(\text{CN})_6]$
- $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$

9. Compare qualitatively the first and second ionization potentials of copper and zinc. Explain the observation.

10. Write the IUPAC name of the compound  $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$ . Is this compound coloured?

11. Write the formulae of the following complexes:

- Pentamminechlorocobalt(III) ion
- Lithium tetrahydroaluminate(III) ion

### Solutions to Exercise Questions:

1. c

2. c

3. A ligand may contain one or more unshared pair of electrons which are called the donor sites of ligands. Now, depending on the number of these donor sites, ligands can be classified as follows.

#### a. Unidentate ligands:

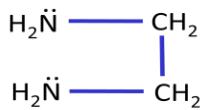
Ligands with only one donor site are called unidentate ligands.

**Example:**  $\text{NH}_3$ ,  $\text{Cl}^-$  etc

#### b. Bidentate ligands:

Ligands that have two donor sites are called bidentate ligands.

**Example:** (a) Ethane – 1, 2 - diamine



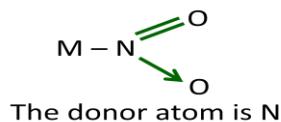
(b) Oxalate ion



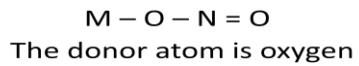
### c. Ambidentate ligands:

Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands.

**Example:** Nitro group



Oxygen group



4.

a. [Co(H<sub>2</sub>O)(CN)(en)]<sup>2+</sup>

Let the oxidation number of Co be x

The charge on the complex is +2

$$[Co(H_2O)(CN)(en)]^{+2}$$

$$[x + 0 + (-1) + 2(0)] = +2$$

$$(x - 1) = +2$$

$$x = +3$$

b. [Pt(Cl)<sub>4</sub>]<sup>2-</sup>

Let the oxidation number of Pt be x

The charge on the complex is -2

$$[Pt(Cl)_4]^{2-}$$

$$[x + 4(-1)] = -2$$

$$(x - 4) = -2$$

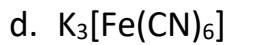
$$x = +2$$

c. [Co(Br)<sub>2</sub>(en)<sub>2</sub>]<sup>2+</sup>

$$[x + 2(-1) + 2(0)] = +1$$

$$(x - 2) = +1$$

$$x = +3$$



i.e.,  $[Fe(CN)_6]^{3-}$

$$[x + 6(-1)] = -3$$

$$(x - 6) = -3$$

$$x = -3 + 6$$

$$x = +3$$



$$[x + 3(0) + 3(-1)] = 0$$

$$(x - 3) = 0$$

$$x = +3$$

5.

a. Pentammine nitrito cobalt (II) chloride

b. Potassium hexacyano chromate (III)

6.

a.  $[Co(NH_3)_5Cl]$

b.  $Li[AlH_4]$

7.



A (blood red)



B (Complex)

IUPAC name of A = pentaquaquothiocyanatoferate (III) ion

B = Hexafluoroferrate (III)

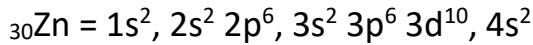
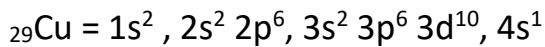
8.

I. Pentamminenitritocobalt (III) chloride

II. Potassium hexacyanochromate (III)

III. Pentamminecarbonatochromium (III) chloride.

9.



On the basis of configuration of Cu and Zn, first ionization potential of Zn is greater than that of copper because in zinc the electron is removed from  $4s^2$  configuration while in copper it is removed from  $4s^1$  configuration. So more amount of energy is required for the removal of electron of  $4s^2$  (completely filled orbital) than that of  $4s^1$  while the second ionization potential of Cu is higher than that of zinc because  $Cu^+$  has  $3d^{10}$  (stable configuration) in comparison to  $Zn^+$  ( $4s^1$  configuration).

10. Pentammine isothiocyanato chromium (III) tetra chlorozincate.

This compound is coloured because  $Cr^{3+}$  has  $3d^3$  configuration (has unpaired electron in d – orbitals) which show colour, through d - d transition.

- 11.

- i. Formula of pentamminechlorocobalt (III) is  $[CoCl(NH_3)_5]^{2+}$ .
- ii. Formula of lithium tetrahydroaluminate (III) is  $LiAlH_4$

# Co-ordination Compounds

## Module 24.2: Theories of Co-ordination compounds

To explain the formation of complex compounds many theories have been suggested. The most successful of the earliest theories is Werner's theory. It is based on certain assumptions which are listed here.

### **Werner's Theory of Co-ordination compounds:**

#### Postulates

1. A complex has always a central metal atom. This may be an ion or a neutral atom.
2. A metal in a complex compounds has two types of valencies, namely primary and secondary valencies.
3. Primary valency (Ionisable valency) corresponds to the oxidation state of metal atom or ion. Secondary valency (Non-ionisable valency) corresponds to the co-ordination number of the central metal.
4. Every metal has a fixed number of secondary valencies or co-ordination number in each of its oxidation states.
5. The co-ordination number of the metal is the number of ligands, which gives the number of coordinate covalent bonds formed with central metal atom or ion, in a complex compound.

In majority of the commonly found complex compounds, the co-ordination number 2 or 4 or 6.

- i) Co(III) and Pt(IV) have 6 co-ordination number

Ex:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  ;  $\text{K}_2[\text{Pt}(\text{Cl})_6]$

- ii) Cu(II), Pt(II), Zn(II) have 4 Co-ordination number

Ex:  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ;  $[\text{Cu}(\text{OH})_4]^{2-}$  ;  $[\text{Pt}(\text{NH}_3)_4]^{+2}$  ;  $[\text{Zn}(\text{CN})_4]^{-2}$  ;  $[\text{ZnCl}_4]^{-2}$

- iii) Ag(I) has 2 Co-ordination number

Ex:  $[\text{Ag}(\text{NH}_3)_2]^+$  ;  $[\text{Ag}(\text{CN})_2]^-$

6. The secondary valencies of the central metal may be satisfied by negative ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CN}^-$  etc..) or by neutral molecules ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$  etc), or by positive ions ( $\text{NH}_2\text{-NH}_3^+$ ,  $\text{NO}^+$  etc)

In some complex compounds both primary and secondary valencies may be satisfied by negative ions.

Ex:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

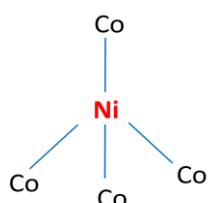
7. The primary valency can be satisfied by negative ions.
8. The ligands are directed in space around the central atom symmetrically in such a way that the complex has a definite structure.

Ex: i) If the complex has 2 ligands, it gives linear structure.

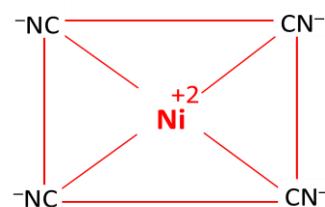


ii) If the complex has 4 ligands, it assumes either a tetrahedral or a square planar structure.

Ex:



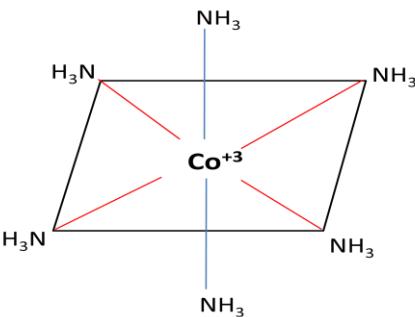
Tetrahedral



Square planar

iii) If the complex has 6 ligands it gives octahedral structure.

Ex:  $[\text{Co}(\text{NH}_3)_6]^{+3}$



Octahedral structure

9. The charge of complex ion is equal to the sum of charges of metal and ligands.

Ex 1 :  $\text{K}_4[\text{Fe}(\text{CN})_6]$

Oxidation state of Fe is +2

Oxidation state of  $\text{CN}^-$  is -1

Charge of complex ion  $[2+6(-1)] = -4$

i.e.,  $[\text{Fe}(\text{CN})_6]^{4-}$

**Ex 2:**  $[\text{Co}(\text{NH}_3)_6]^{+3} [\text{Cl}^-]_3$

Oxidation state of Co is +3

Oxidation state of  $\text{NH}_3$  is 0

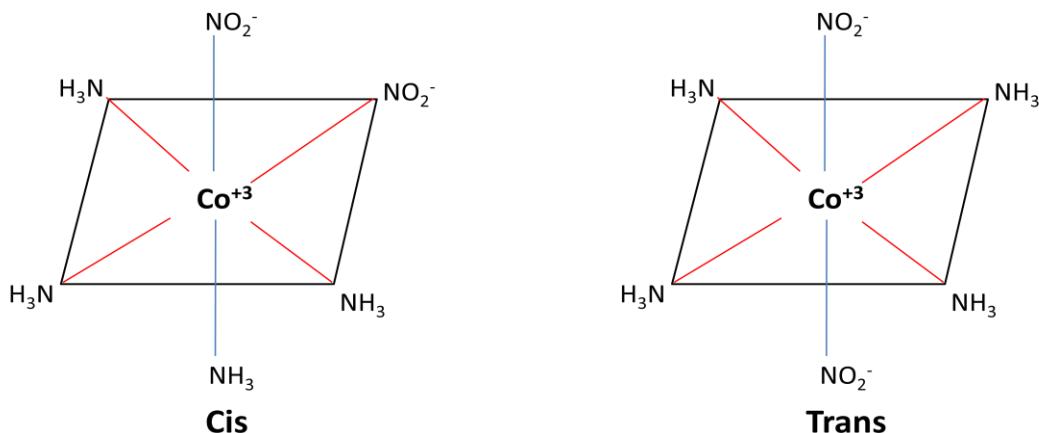
Charge of complex ion  $(+3) + 6(0) = +3$

i.e.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$

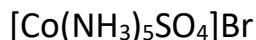
### Advantages of Werner's theory:

- a) Werner's theory can explain the isomerism in complex compounds.

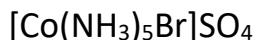
Ex:  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$  give two isomers



- b) We can distinguish the following complex compounds of same molecular formula



(I)



(II)

$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  gives yellow precipitate with  $\text{AgNO}_3$ .

$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  gives white precipitate with  $\text{BaCl}_2$  solution.

### **Defects in Werner's theory:**

Inspite of the capacity to explain the formation of complex compounds, Werner's theory is having many defects. Some of the important drawbacks are enumerated here.

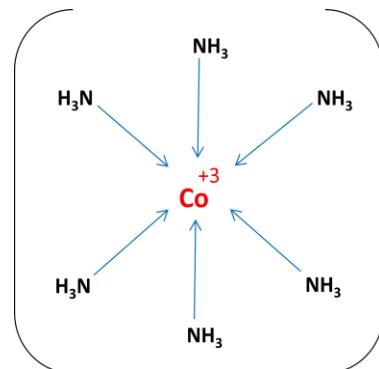
1. Werner's theory does not correlate electronic configuration of the central metal with the formation of the complex compounds. Now it is known that the central metal try to acquire the next inert gas structure through coordinate bond formation. Hence complexes are formed.
2. The postulates of Werner do not offer any explanation to the colour of the complex compounds. It is appropriate at this juncture, to know how the d – d transition takes place and result in the colour to the complex.
3. Werner's theory is incapable of explaining the magnetic behavior. The magnetic property depends on the number of unpaired electrons present in the metal ion. Werner's theory is not related to electronic configuration and so this property could not be explained.

### **Sidgwick Theory of Co-ordination compounds:**

Sidgwick suggested that the bond between the ligands and the metal ion is co-ordinate covalent or semipolar bond. He says that the ligands donate the electron pair to metal ion forming a coordinate covalent bond. Here ligand (L) is donor and metal ion (M) is acceptor.

**It is denoted by “ $L \rightarrow M$ ”**

According to Sidgwick's concept, the structure of the complex ion  $[Co(NH_3)_6]^{3+}$  is represented as



Here, each  $NH_3$  donates a lone pair of electrons to cobalt (III) ion. The donation is represented by an arrow. In the process the central atom acquires the same or

nearest number of electrons as that of its nearest inert gas. This number is known as EAN. The principle is referred commonly as EAN rule.

### **Effective atomic number (EAN):**

“The total number of electrons the central metal ion possesses including those gained from ligands in the bonding, is called Effective Atomic Number (EAN)”

In many complexes it is equal to the atomic number of the nearest inert gas.

EAN value of metal can be calculated as follows using the relation.

$$\text{EAN} = \{(\text{Atomic number of metal}) - (\text{Oxidation state of metal}) + [2 \times \text{number of ligands}]\}$$

Many complexes obey EAN rule

S.No	Complex compound	Central metal	At. no. of the metal	No. of e's lost = Ox. State(x)	No. of e's gained (y)	EAN of the metal = (z-x+y)	At. No. of next inert gas
1.	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	Co	27	3	12	(27-3+12)=36	36(Ar)
2.	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	Fe	26	2	12	(26-2+12)=36	36(Ar)
3.	[Pd(NH <sub>3</sub> ) <sub>6</sub> ]SO <sub>4</sub>	Pd	46	4	12	(46-4+12)=54	54(Xe)
4.	[PtCl <sub>6</sub> ] <sup>-2</sup>	Pt	78	4	12	(78-4+12)=86	86(Rn)

Some complexes do not obey EAN rule



### **Valence Bond Theory:**

This theory was developed by Pauling. This can explain the kind of bonding, shape and magnetic properties of complex compounds. Main points are...

1. The central metal atom or ion makes available the necessary number of vacant orbitals to suit its co-ordination number. These orbitals are hybridized together, depending on the structure and shape hybrid orbitals.
2. The ligands must have at least one lone pair of electrons.
3. The vacant metal orbitals and lone pairs of electrons of the ligand orbitals overlap to form coordinate covalent bonds.

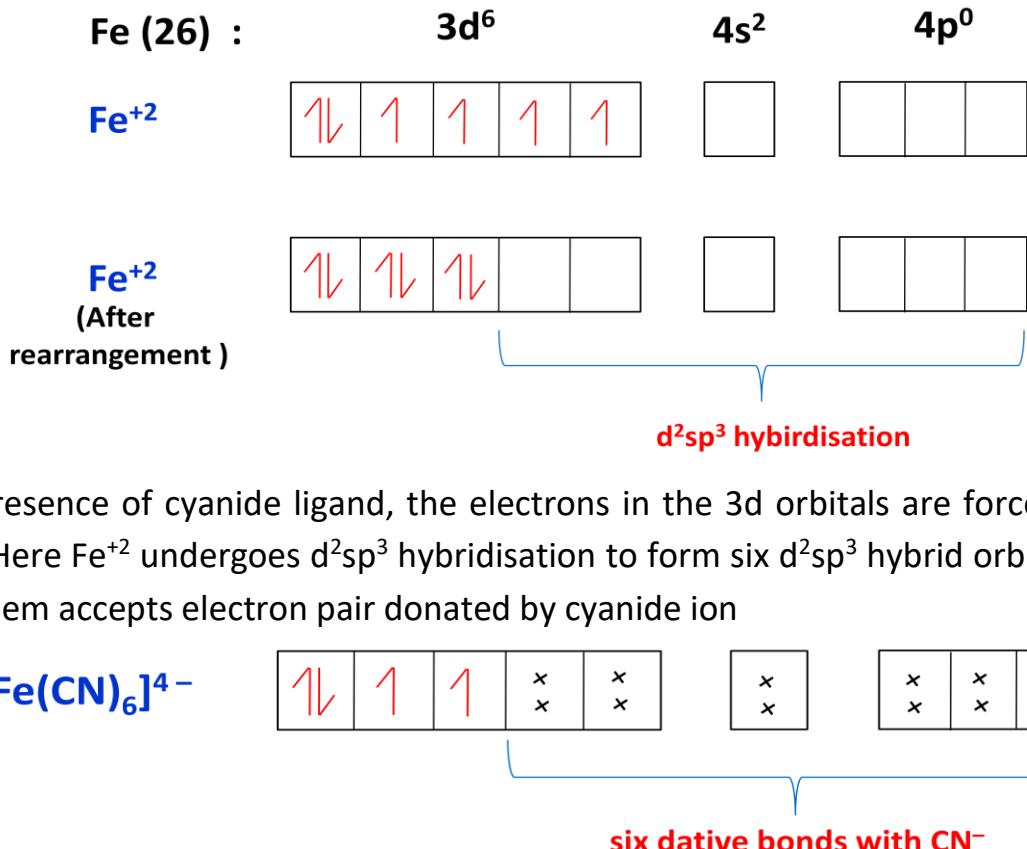
4. The non-bonding metal electrons occupy the inner d-orbital which do not involve in the hybridization.
5. If a complex contains unpaired electrons, it is paramagnetic in nature; if it does not contain unpaired electrons it is diamagnetic in nature.
6. The number of unpaired electrons in complex may indicate the geometry of the complex.
7. From the number of unpaired electrons in the complex the extent of paramagnetism can be calculated.
8. The central metal atom may utilize the d-orbitals of either the penultimate shell or the valence shell resulting in the inner d-orbital complexes or outer d-orbital complexes respectively.
9. Sometimes the electrons undergo rearrangement against the Hund's max multiplicity rule.

## Geometry (shape) and magnetic nature of some complexes (application of Valence bond Theory)

Complex	Configuration	Ox. state	Hybridization	Geometry shape	No. of Unpaired electrons	Magnetic nature
$[\text{NiCl}_4]^{2-}$		+2	$\text{sp}^3$	Tetrahedral	2	Paramagnetic
$[\text{Ni(CN)}_4]^-$		+2	$\text{dsp}^2$	Square planar	0	Diamagnetic
$[\text{Fe(CN)}_6]^{4-}$		+2	$\text{d}^2\text{sp}^3$	Octahedral	0	Diamagnetic
$[\text{Co}(\text{H}_2\text{O})_6]^{+2}$		+2	$\text{sp}^3\text{d}^2$	Octahedral	3	Paramagnetic

### Examples of inner orbital complexes and outer orbital complexes:

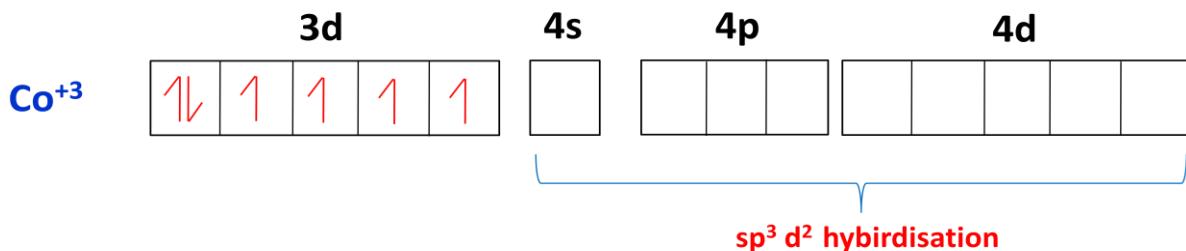
**Ex 1: Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$**  : The electronic configuration of Fe and  $\text{Fe}^{+2}$  ion in Ferrocyanide ion is given below



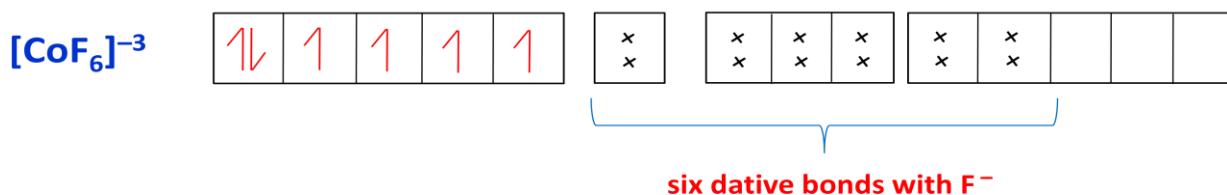
Another inner orbital complex is  $[\text{Co}(\text{NH}_3)_6]^{3+}$

### Outer orbital complex:

**Ex-1: Formation of  $[\text{CoF}_6]^{3-}$** : The electronic configuration of  $\text{Co}^{+3}$  ion is given below (outer orbitals configuration is  $3d^6 4s^0$ )



The fluoride ion is a weak ligand and cannot force the pairing up of electrons.



### Drawbacks of Valence Bond Theory:

1. It is a qualitative approach describing bonding in co-ordination compounds.
2. The theory fails to explain the finer aspects of the magnetic properties of co-ordination compounds.
3. This theory does not provide an answer to the origin of characteristic colours of complex ions.
4. It does not explain why  $[\text{Co}(\text{NH}_3)_6]^{+3}$  is an inner orbital complex and  $[\text{CoF}_6]^{-3}$  is an outer orbital complex.

### Assignment Questions:

- (1) Write the postulates of Werner's theory.
- (2) Explain Werner's theory giving one example.
- (3) Write the postulates of Valence Bond Theory.
- (4) Explain the formation of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{CoF}_6]^{-3}$  on the basis of VBT (Z of Fe = 26; Z of Co = 27).
- (5) Define EAN.

### Example Set:

1. EAN of Fe in  $[\text{Fe}(\text{CN})_6]^{3-}$  is  
a) 36      b) 27      c) 38      d) 35

**Solution:** d

2. The hybridisation undergone by Ni in  $[\text{Ni}(\text{CN})_4]^{2-}$  ion is  
a)  $\text{dsp}^2$       b)  $\text{sp}^2\text{d}^2$       c)  $\text{d}^2\text{sp}$       d)  $\text{sp}^2$

**Solution:** a

3. Which of the following has a central metal atom that has undergone  $\text{d}^2\text{sp}^3$  hybridisation?

- a)  $[\text{Cr}(\text{NH}_3)_6]^{2+}$
- b)  $[\text{Fe}(\text{CN})_6]^{3-}$
- c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- d) all are correct

**Solution:** d

4. According to Werner's Theory the primary valency of the transition metal ion is equal to
- a) Oxidation state
  - b) Co-ordination number
  - c) Number of electrons in the outer most orbit
  - d) Atomic number

**Solution:** a

5. Write the formula to calculate the EAN of a central metal atom / ion.

**Solution:**  $\text{EAN} = \{(\text{Atomic number of metal}) - (\text{Oxidation state of metal}) + [2 \times \text{number of ligands}]\}$

6. What type of hybridisation undergone by Co in the complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ?

**Solution:**  $d^2sp^3$  hybridisation

7. Write a short note on i) Primary valency ii) Secondary valency of a metal in a complex.

**Solution:**

- i) Primary valency (Ionisable valency) corresponds to the oxidation state of metal atom or ion.
- ii) Secondary valency (Non-ionisable valency) corresponds to the Co-ordination number of the central metal.

8. What are the possible shapes of complex ion with Co-ordination number 4 and 6?

**Solution:** Tetrahedral and square planar.

### Problem Set:

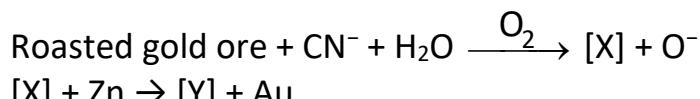
1. According to Werner's Theory the number of secondary valencies of a transition metal ion is equal to the
- a) Oxidation state
  - b) Atomic number
  - c) Co-ordination number
  - d) Unpaired electrons

**Solution:** c

2. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?
- $\text{Cu}(\text{CN})_2$
  - $\text{K}_2[\text{Cu}(\text{CN})_4]$
  - $\text{K}[\text{Cu}(\text{CN})_2]$
  - $\text{K}_3[\text{Cu}(\text{CN})_4]$

**Solution:** d

3. In the process of extraction of gold,



Identify the complexes [X] and [Y]

- $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
- $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
- $\text{X} = [\text{Au}(\text{CN})_2]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$
- $\text{X} = [\text{Au}(\text{CN})_4]^-$ ,  $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$

**Solution:** a

4. The EAN of nickel in  $\text{K}_2[\text{Ni}(\text{CN})_4]$  is

- 35
- 34
- 36
- 38

**Solution:** b

5. Which of the following pairs contain only tetrahedral complexes?

- $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{CuCl}_4]^{2-}$
- $[\text{Ni}(\text{CO})_4]$  and  $[\text{ZnCl}_4]^{2-}$
- $[\text{Ni}(\text{NH}_3)_4]$  and  $[\text{Cu}(\text{NH}_3)_4]^{2-}$
- $[\text{Ni}(\text{NH}_3)_4]$  and  $[\text{Ni}(\text{CO})_4]^{2-}$

**Solution:** b

6. The hybridisation state of the Fe among  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\text{Fe}(\text{CO})_5$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

- $\text{sp}^3\text{d}^2$ ,  $\text{dsp}^3$ ,  $\text{sp}^3\text{d}^2$
- $\text{d}^2\text{sp}^3$ ,  $\text{dsp}^3$ ,  $\text{sp}^3\text{d}^2$
- $\text{d}^2\text{sp}^3$ ,  $\text{sp}^3\text{d}$ ,  $\text{sp}^3\text{d}^2$
- $\text{sp}^3\text{d}^2$ ,  $\text{sp}^3\text{d}$ ,  $\text{d}^2\text{sp}^3$

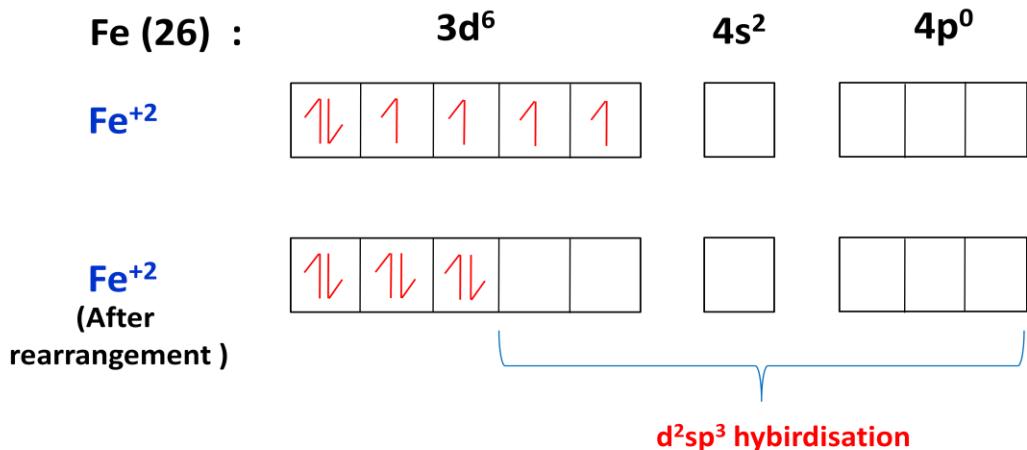
**Solution:** b

7. Explain the terms inner orbital complex and outer orbital complex.

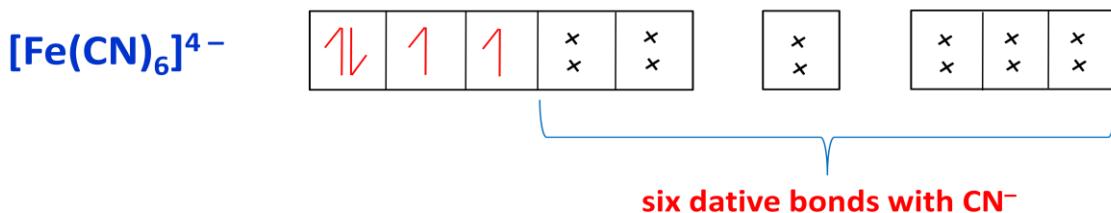
**Solution:**

**Examples of inner orbital complexes and outer orbital complexes:**

**Ex 1: Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$ :** The electronic configuration of Fe and  $\text{Fe}^{+2}$  ion in Ferrocyanide ion is given below



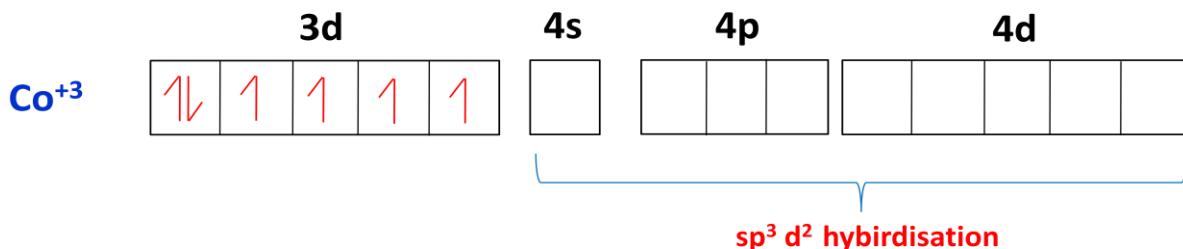
In presence of cyanide ligand, the electrons in the 3d orbitals are forced to pair up. Here  $\text{Fe}^{+2}$  undergoes  $\text{d}^2\text{sp}^3$  hybridisation to form six  $\text{d}^2\text{sp}^3$  hybrid orbitals, each of them accepts electron pair donated by cyanide ion



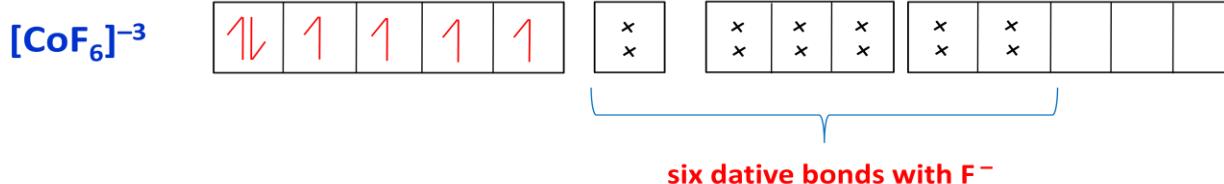
Another inner orbital complex is  $[\text{Co}(\text{NH}_3)_6]^{3+}$

**Outer orbital complex:**

**Ex-1: Formation of  $[\text{CoF}_6]^{3-}$ :** The electronic configuration of  $\text{Co}^{+3}$  ion is given below (outer orbitals configuration is  $3d^6 4s^0$ )



The fluoride ion is a weak ligand and cannot force the pairing up of electrons.



8. Calculate the EAN of the following metals in the following complexes

- a)  $[\text{Co}(\text{NH}_3)_6]^{3+}$     b)  $[\text{Pd}(\text{NH}_3)_6]\text{SO}_4$     c)  $[\text{Fe}(\text{CN})_6]^{4-}$     d)  $[\text{PtCl}_6]^{-2}$

**Solution:**

S.No	Complex compound	Central metal	At. no. of the metal	No. of e's lost = Ox. State(x)	No. of e's gained (y)	EAN of the metal = $(z-x+y)$	At. No. of next inert gas
1.	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Co	27	3	12	$(27-3+12)=36$	36(Ar)
2.	$\text{K}_4[\text{Fe}(\text{CN})_6]$	Fe	26	2	12	$(26-2+12)=36$	36(Ar)
3.	$[\text{Pd}(\text{NH}_3)_6]\text{SO}_4$	Pd	46	4	12	$(46-4+12)=54$	54(Xe)
4.	$[\text{PtCl}_6]^{-2}$	Pt	78	4	12	$(78-4+12)=86$	86(Rn)

9. Discuss the nature of bonding in the following co-ordination entities on the basis of valence bond theory.

- i)  $[\text{Fe}(\text{CN})_6]^{4-}$     ii)  $[\text{FeF}_6]^{3-}$

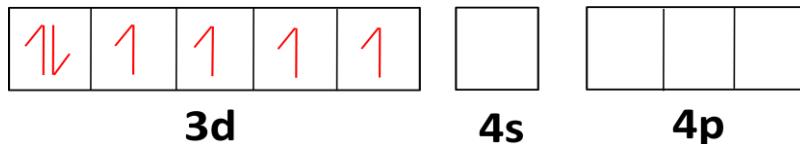
**Solution:**

- i)  $[\text{Fe}(\text{CN})_6]^{4-}$

In the above co-ordination complex, iron exists in the +II oxidation state.

Electronic configuration of  $\text{Fe}^{+2}$  is  $3\text{d}^6 4\text{s}^0$ .

Orbitals of  $\text{Fe}^{+2}$  ion:



As  $\text{CN}^-$  is a strong ligand, it causes pairing of the unpaired 3d electrons.

$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$				
<b>3d</b>		<b>4s</b>		<b>4p</b>		

Since there are six ligands around the central metal ion, the most feasible hybridisation is  $d^2sp^3$ .

$d^2sp^3$  hybridized orbitals of  $Fe^{+2}$  are

<b>3d</b>	<b>4s</b>	<b>4p</b>
$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
$d^2sp^3$		
6 pairs of electrons from 6 $CN^-$ ions		

6 electron pairs form  $CN^-$  ions occupy the six hybrid  $d^2sp^3$  orbitals  
Then,

$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$\times$	$\times$	$\times$	$\times$	$\times$	$\times$
6 pairs of electrons from 6 $CN^-$ ions								

Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons)

ii)  $[FeF_6]^{3-}$

In this complex, the oxidation state of Fe is  $+3$ .

Orbitals of  $Fe^{+3}$  ion are

<b>4s</b>	<b>4p</b>	<b>4d</b>
$1\frac{1}{2}$		

There are 6  $F^-$  ions. Thus, it will undergo  $d^2sp^3$  or  $sp^3d^2$  hybridisation. As  $F^-$  is a weak ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridisation is  $sp^3d^2$ .

3d	4s	4p	4d
1 1 1 1 1			



$sp^3d^2$

3d	4s	4p	4d
1 1 1 1 1	x x	x x x	x x 



$sp^3d^2$

6 electron pairs from  $F^-$  ions

Hence, the geometry of the complex is found to be octahedral.

### Exercise Questions:

1. Amongst  $Ni(CO)_4$ ,  $[Ni(CN)_4]^{2-}$  and  $NiCl_4^{2-}$ 
  - a.  $Ni(CO)_4$  and  $NiCl_4^{2-}$  diamagnetic and  $[Ni(CN)_4]^{2-}$  is paramagnetic.
  - b.  $NiCl_4^{2-}$  and  $[Ni(CN)_4]^{2-}$  are diamagnetic and  $Ni(CO)_4$  is paramagnetic
  - c.  $Ni(CO)_4$  and  $[Ni(CN)_4]^{2-}$  are diamagnetic and  $NiCl_4^{2-}$  is paramagnetic
  - d.  $Ni(CO)_4$  is diamagnetic and  $NiCl_4^{2-}$  and  $[Ni(CN)_4]^{2-}$  are paramagnetic

**Answer:** c

2. Among the following, the compound that is both paramagnetic and colored is
  - a.  $K_2Cr_2O_7$
  - b.  $(NH_4)_2(TiCl_6)$
  - c.  $CoSO_4$
  - d.  $K_3[Cu(CN)_4]$

**Answer:** c

3. The geometry of  $Ni(CO)_4$  and  $[Ni(PPh_3)_2]Cl$  are
  - a. Both square planar

- b. Tetrahedral and square planar, respectively
- c. Both tetrahedral
- d. Square planar and tetrahedral, respectively:

**Answer:** c

4. The complex ion which has no 'd' electrons in the central metal atom is
- a.  $[\text{MnO}_4]^-$
  - b.  $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - c.  $[\text{Fe}(\text{CN})_6]^{3-}$
  - d.  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

**Answer:** a

5. The species having tetrahedral shape is \_\_\_\_
- a.  $[\text{PdCl}_4]^{2-}$
  - b.  $[\text{Ni}(\text{CN})_4]^{2-}$
  - c.  $[\text{Pd}(\text{CN})_4]^{2-}$
  - d.  $[\text{NiCl}_4]^{2-}$

**Answer:** b

6. The spin magnetic moment of cobalt in the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is
- a.  $\sqrt{3}$
  - b.  $\sqrt{8}$
  - c.  $\sqrt{15}$
  - d.  $\sqrt{24}$

**Answer:** c

7. Which kind of isomerism is exhibited by octahedral  $\text{Co}(\text{NH}_3)_4 \text{Br}_2\text{Cl}$
- a. Geometrical and ionization
  - b. Geometrical and optical
  - c. Optical and ionization
  - d. Geometrical only

**Answer:** a

8. Among the following metal carbonyls, the C – O bond order is lowest in
- a.  $[\text{Mn}(\text{CO})_6]^+$
  - b.  $[\text{Fe}(\text{CO})_5]$
  - c.  $[\text{Cr}(\text{CO})_6]$



**Answer:** d

**9.** Among the following the colored compound is

- a.  $\text{CuCl}$
- b.  $\text{K}_3[\text{Cu}(\text{CN})_4]$
- c.  $\text{CuF}_2$
- d.  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$

**Answer:** c

**10.** Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridization of nickel in these complexes, respectively are

- a.  $\text{sp}^3, \text{sp}^3$
- b.  $\text{sp}^3, \text{dsp}^2$
- c.  $\text{dsp}^2, \text{sp}^3$
- d.  $\text{dsp}^2, \text{sp}^2$

**Answer:** b

**11.** The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is

- a. 0
- b. 2.84
- c. 4.90
- d. 5.92

**Answer:** a

**12.** The complex showing a spin – only magnetic moment of 2.82 B.M. is

- a.  $\text{Ni}(\text{CO})_4$
- b.  $[\text{NiCl}_4]^{2-}$
- c.  $\text{Ni}(\text{PPh}_3)_4$
- d.  $[\text{Ni}(\text{CN})_4]^{2-}$

**Answer:** b

**13.**  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?

**Solution:**

Cr is in the +3 oxidation state i.e.  $\text{d}^3$  configuration. Also,  $\text{NH}_3$  is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

3d	4s	4p	4d
1 1 1			

Therefore it undergoes  $d^2sp^3$  hybridisation and the electrons in the 3d orbitals remain unpaired. Hence it is paramagnetic in nature.

In  $[Ni(CN)_4]^{2-}$ , Ni exists in the +2 oxidation state i.e., it has  $d^84s^0$  configuration.

$Ni^{2+}$	3d	4s	4p
	1 1 1 1 1		

$CN^-$  is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then,  $Ni^{2+}$  undergoes  $dsp^2$  hybridisation

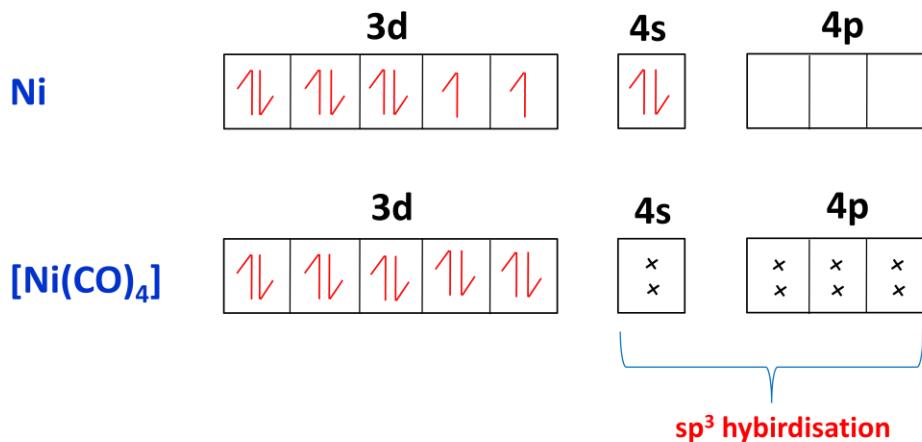
3d	4s	4p
1 1 1 1 1		
 <b><math>dsp^2</math></b>		

As there are no unpaired electrons it is diamagnetic.

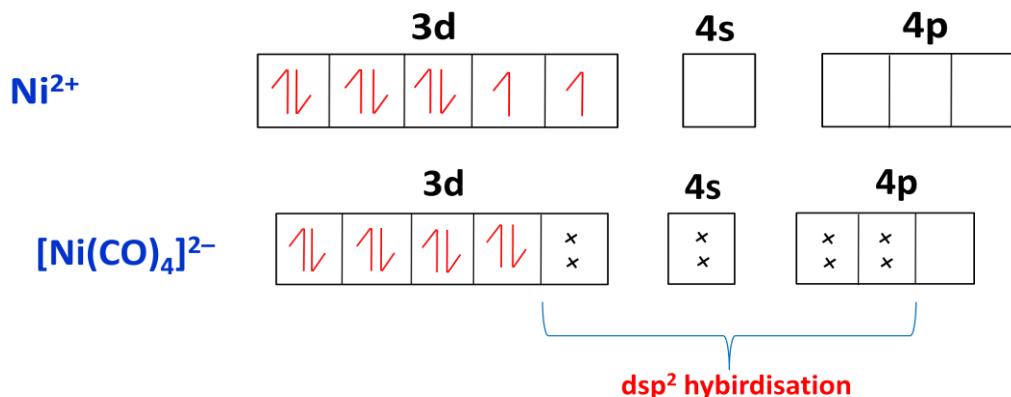
**14.**  $[Ni(CO)_4]$  possesses tetrahedral geometry while  $[Ni(CN)_4]^{2-}$  is a square planar. Explain why?

**Solution:**

In the formation of  $Ni(CO)_4$  nickel is in zero oxidation state. It undergoes  $sp^3$  hybridisation; hence it is tetrahedral in shape.



In the formation of  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{Ni}^{2+}$  ion undergoes  $d\text{s}^2\text{p}^2$  hybridisation, hence it is square planar in shape.



**15.** Explain, why  $\text{NH}_4^+$  ion does not form complexes?

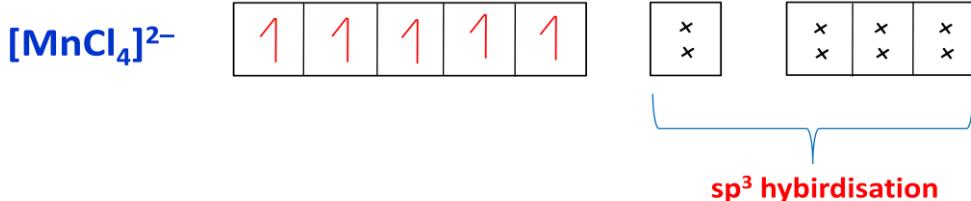
**Solution:**

$\text{NH}_4^+$  Ion does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.

**16.** Calculate the magnetic moment of Mn in  $[\text{MnCl}_4]^{2-}$ .

**Solution:**

In  $[\text{MnCl}_4]^{2-}$  ion,  $\text{Mn}^{2+}$  ion undergoes  $sp^3$  hybridisation. It contains 5d-orbitals singly occupied. Hence, it has high value of magnetic moment.

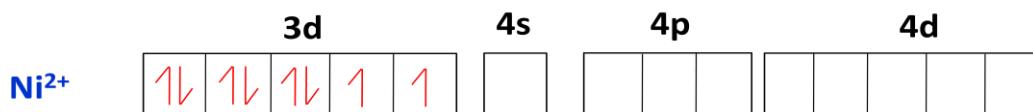


Number of unpaired electrons = 5

$$\begin{aligned}\therefore \mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}\end{aligned}$$

**17.** Explain why octahedral complexes of  $\text{Ni}^{2+}$  must be outer orbital complexes.

**Solution:**



During rearrangement only one 3d-orbital may be made available by pairing the electrons. Thus, inner  $d^2\text{sp}^3$  hybridisation is not possible. So, only  $\text{sp}^3\text{d}^2$  (outer) hybridisation can occur.

**18.** Identify the complexes which are expected to be colored. Explain

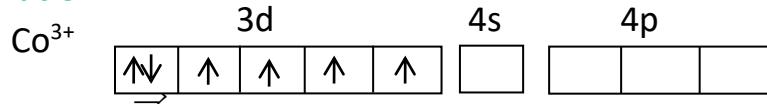
- i.  $[\text{Ti}(\text{NO}_3)_4]$  ii.  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$  iii.  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$  iv.  $\text{K}_3[\text{VF}_6]$

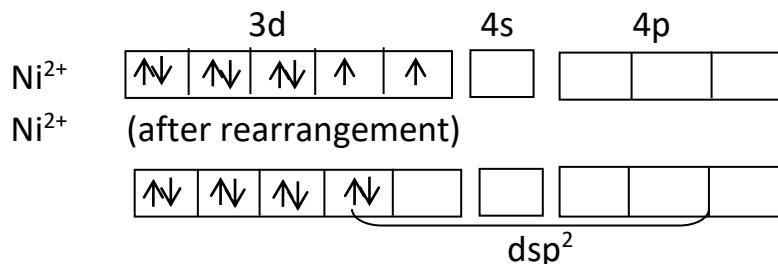
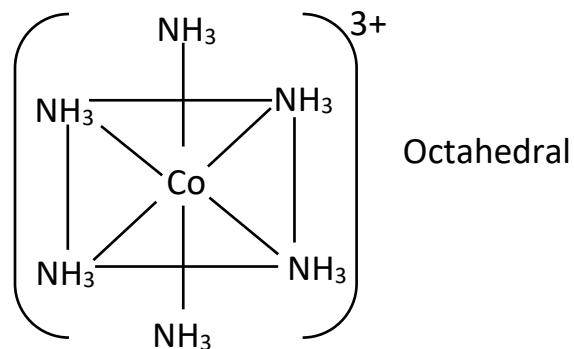
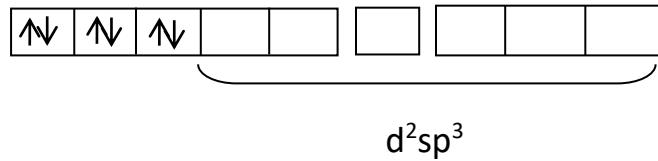
**Solution:**

- i.  $[\text{Ti}(\text{NO}_3)_4]$ ;  ${}_{22}\text{Ti}^{4+}$  :  $[\text{Ar}]3\text{d}^0 4\text{s}^0$
- ii.  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$  ;  ${}_{29}\text{Cu}^+$  :  $[\text{Ar}]3\text{d}^{10} 4\text{s}^0$
- iii.  $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$  ;  ${}_{24}\text{Cr}^{3+}$  :  $[\text{Ar}]3\text{d}^3 4\text{s}^0$
- iv.  $\text{K}_3[\text{VF}_6]$ ;  ${}_{23}\text{V}^{+3}$  :  $[\text{Ar}]3\text{d}^2 4\text{s}^0$

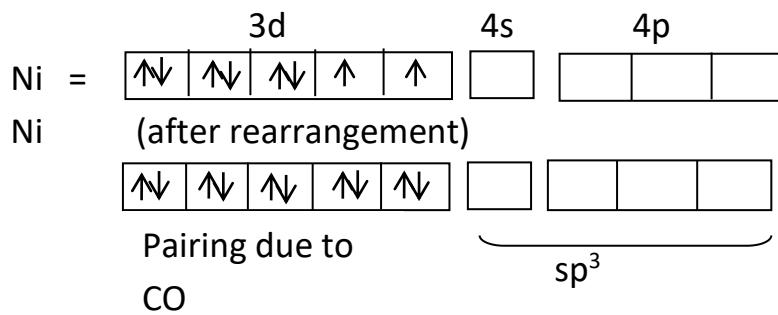
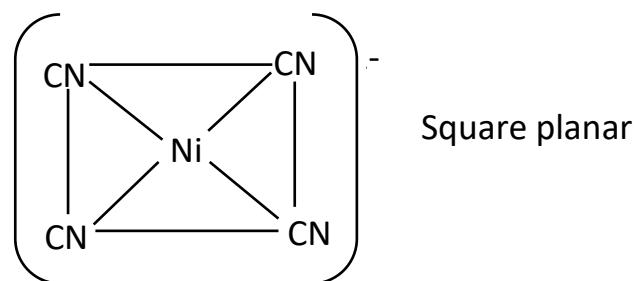
**19.** Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ . Write the hybridization of atomic orbitals of the transition metal in each case.

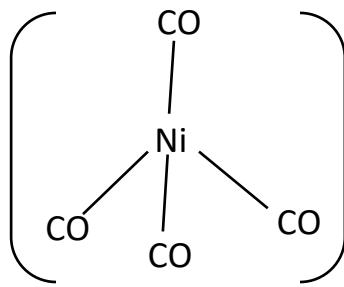
**Solution:**





Pairing due  
to  $\text{CN}^-$





Tetrahedral

- 20.** A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms (A) and (B). The form (A) reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spin only values).

**Solution:**

Compound (A) on treatment with  $\text{AgNO}_3$  gives white precipitate of  $\text{AgCl}$ , which is readily soluble in dil. aq.  $\text{NH}_3$ . Therefore it has at least one  $\text{Cl}^-$  ion in the ionization sphere furthermore chromium has co-ordination number equal to 6. So its formula is  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$ .

Compound (B) on treatment with  $\text{AgNO}_3$  give pale yellow precipitate of  $\text{AgBr}$  soluble in conc.  $\text{NH}_3$ . Therefore it has  $\text{Br}^-$  in the ionization sphere. So its formula is  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$ .

$\text{Cr}^{3+}$  ( $Z = 24$ ) has  $3d^3$  configuration

Hybridization of chromium in both (A) and (B) is  $d^2\text{sp}^3$ .

Spin magnetic moment of (A) or (B),

$$\mu_{\text{spin}} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87 \text{ BM}$$

- 21.** Deduce the structure of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN}_4)]^{2-}$  considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species.

**Solution:**

$\text{Cl}^-$  is a weak ligand which is unable to pair the electrons of  $\text{Ni}^{2+}$ , Hybridisation is  $\text{sp}^3$  and shape will be tetrahedral, with 2 unpaired electrons.

Electronic configuration of  $\text{Ni}^{2+}$  in presence of  $\text{Cl}^-$  ion, a weak ligand.

$$\text{Magnetic moment} = \sqrt{2(2+2)} = 2.82 \text{ BM}$$

On the other hand  $\text{CN}^-$  is a strong ligand which pairs up the electrons of  $\text{Ni}^{2+}$ . Therefore, here hybridization is  $\text{dsp}^2$  and shape will be square planar, with unpaired electrons.  $u = 0$

**22.** Write the IUPAC nomenclature of the given complex along with its hybridization and structure



**Solution:**

The spin magnetic moment,  $\mu$  of the complex in 1.73 BM.

$$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$$

It means that nucleus of the complex; chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

IUPAC name:

Potassium amminetetracyanonitrosochromate(I).

(a) Electronic configuration of  $\text{Cr}^+$ :

3d	4s	4p
↑   ↑   ↑   ↑   ↑		

(b) Electronic configuration of  $\text{Cr}^+$  under the influence of strong field ligand  $\text{CN}^-$

$\text{Cr}^+$	3d	4s	4p
	↑↓   ↑↓		
$d^2\text{sp}^3$			

So, hybridization is  $d^2\text{sp}^3$  and shape is octahedral

# Co-ordination Compounds

## Module 24.3: Isomerism

Two or more molecules having the same molecular formula but different structural or spatial arrangement are called **isomers**.

They are of two types.

- Structural isomerism
- Stereo isomerism

### Stereo isomerism in complex compounds:

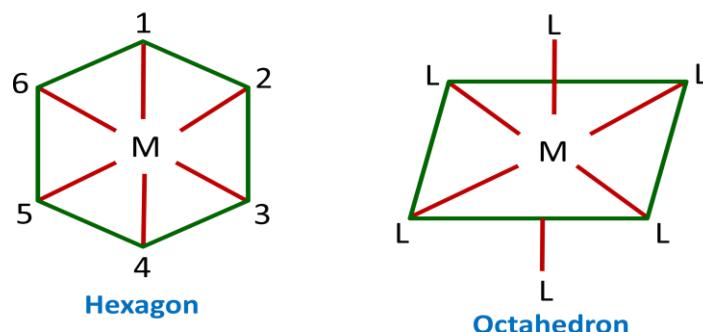
Two or more complexes having same molecular composition but different arrangement of atoms (or) groups in space is called as stereoisomerism.

It is of two types.

- Geometrical isomerism
- Optical isomerism

### Geometrical isomerism in co-ordination number 6 compounds:

The arrangement of six ligands in a complex around the central metal ion is possible in two different ways. Those are regular hexagon and regular octahedron.



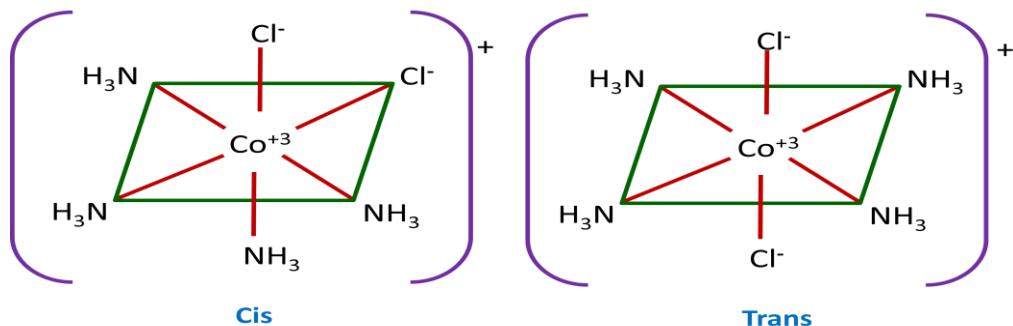
If the complex  $\text{Ma}_4\text{b}_2$  (where M = central metal atom; a,b = ligands) has hexagonal structure it can give three isomers corresponding to (1, 2), (1, 3) and (1, 4) positions of a and b, while octahedral arrangement can give only two isomers. X – ray analysis confirmed that co-ordination number 6 complexes exhibit octahedral arrangement by giving two isomers of  $\text{Ma}_4\text{b}_2$  type. Hence co-ordination number 6 complexes have octahedral structure.

1. No isomerism is possible in  $[\text{Ma}_6]$  or  $\text{Ma}_5\text{b}$  of complexes

**Example:**  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ;  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

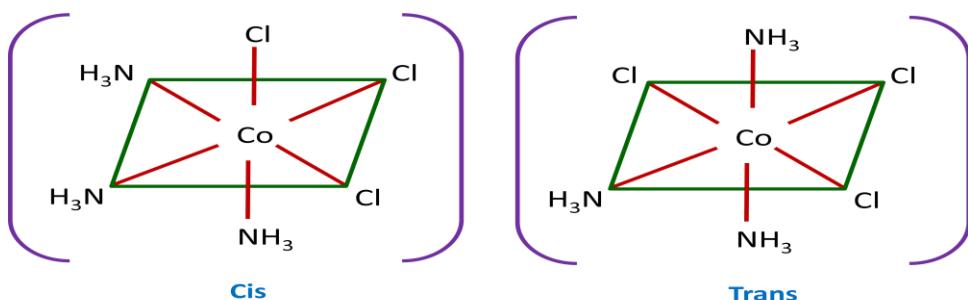
2.  $[\text{Ma}_4\text{b}_2]$  and  $[\text{Ma}_4\text{bc}]$  type of complexes can give two isomers. Those are cis and trans – isomers.

**Example:**  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  gives cis and trans isomers.



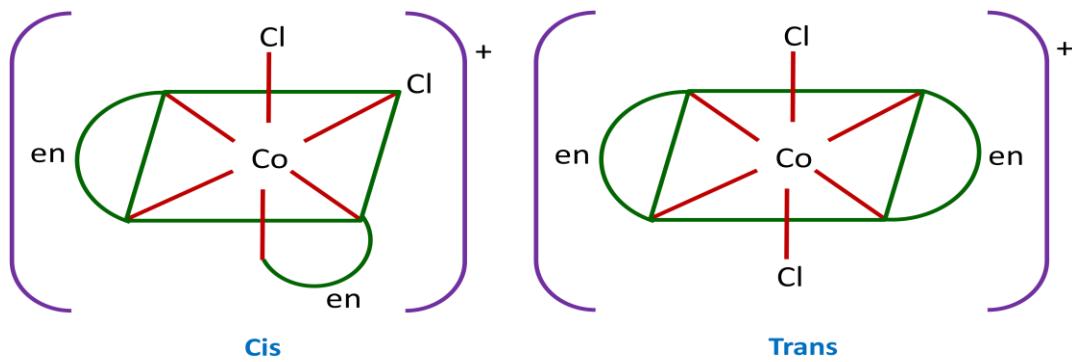
3.  $[\text{Ma}_3\text{b}_3]$  type of complexes can exhibit geometrical isomerism.

**Example:**  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  gives Cis – trans isomers.



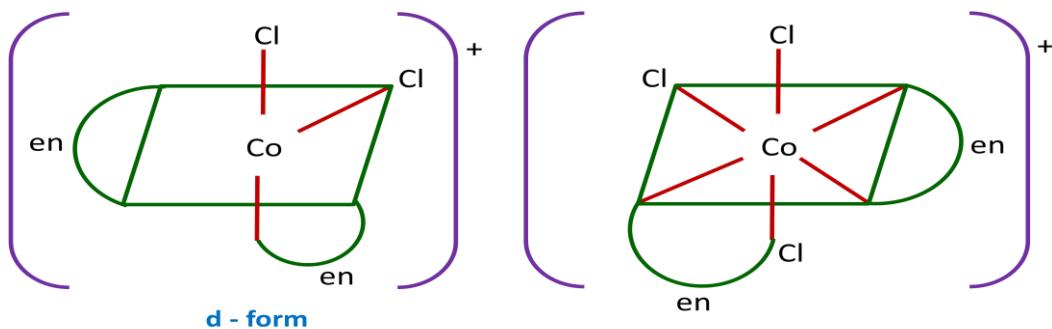
4.  $[M(aa)_2b_2]$  (where aa = bidentate ligand) type of complexes having two bidentate ligands, can exhibit geometrical isomerism.

**Example:**  $[Co(en)_2Cl_2]^+$  gives cis and trans isomers.



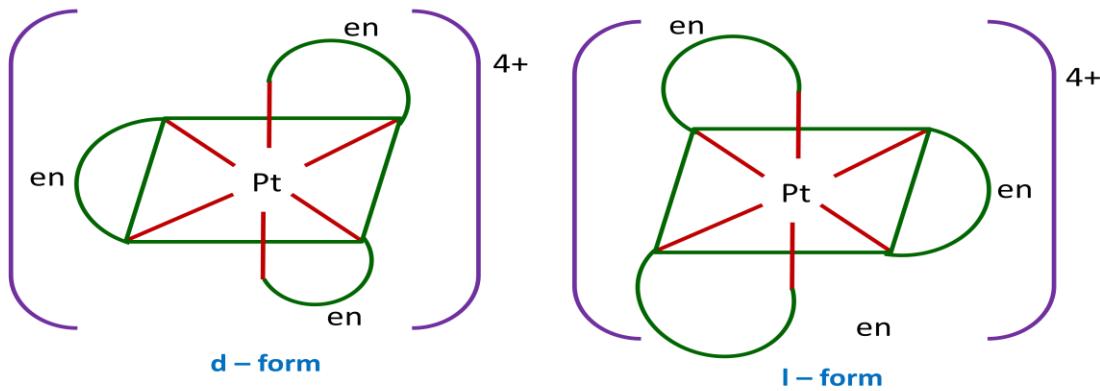
### Optical isomerism in co-ordination number 6 compounds::

1. The cis isomer of  $[M(aa)_2b_2]$  type complexes has no plane of symmetry. So it can give two isomers (d and l)



2. Complexes of  $[M(aa)_3]$  type having three bidentate ligands are also unsymmetrical and gives optical isomerism.

**Example:**  $[Pt(en)_3]^{4+}$  gives optical isomers.



### Stereo isomerism in co-ordination numbers 4 compounds:

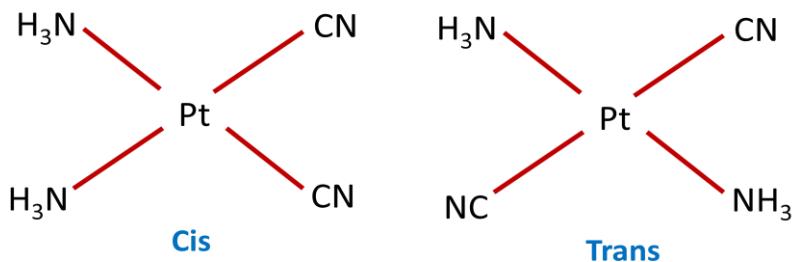
Complex compounds with co-ordination number 4 give either tetrahedral or square planar structure.

1. No isomers are possible  $[Ma_4]$ ,  $[Ma_3b]$  types complexes (square planar or tetrahedral)

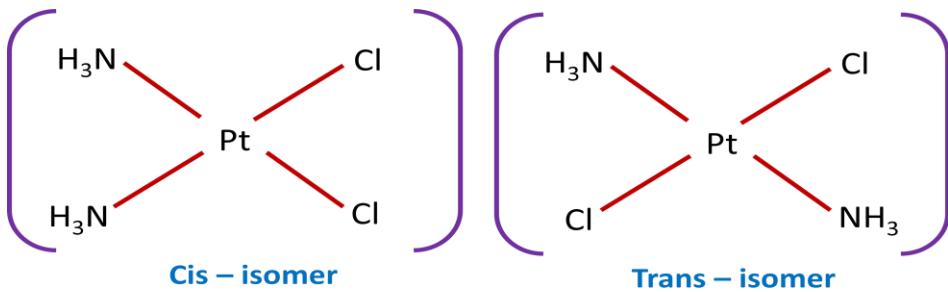
**Example:**  $\text{Ni}(\text{CO})_4$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

2.  $[\text{Ma}_2\text{b}_2]$  and  $[\text{Ma}_2\text{bc}]$  complexes of some metals like Pt (II), Pd (II), Ni (II), Cu (II) give square planar structure having  $d\text{sp}^2$  hybridization.

**Example:**  $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$  gives cis, trans isomers

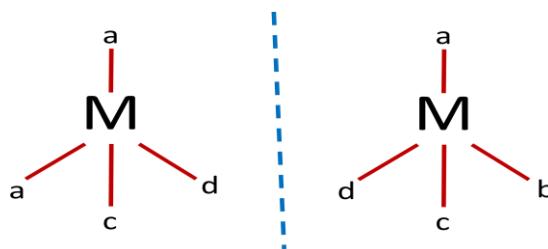


The geometrical isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  are

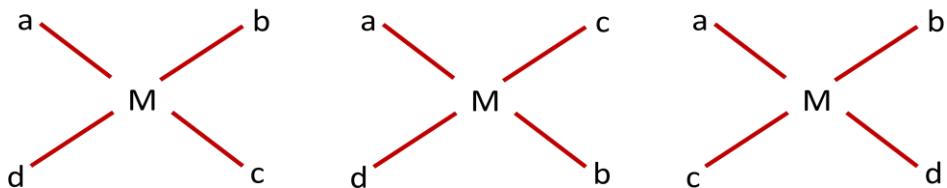


Some complex compounds of Cu, Zn, Ni can give tetrahedral structure. These metals undergo  $sp^3$  hybridisation

$[M_{abcd}]$  type of complex gives optical isomerism, if it has tetrahedral structure.



Three geometrical isomers are possible, if they have square planar structures.



**Example:**  $[Pt(NH_3)(Py)ClBr]$  gives three isomers.

### Assignment Questions:

1. Draw the structures of optical isomers of
  - $[Pt(en)_3]^{4+}$
  - $[Co(en)_2Cl_2]^+$

### Example Set:

1. Which one of the following square planar complexes will show cis – trans isomerism

- a.  $Ma_4$
- b.  $Ma_3b$
- c.  $Ma_2b_2$
- d.  $M_{abcd}$

**Solution:** c)

2. The number of isomers possible for square planar complex  $K_2[PdClBr_2(SCN)]$
- a. 2
  - b. 4
  - c. 5
  - d. 6

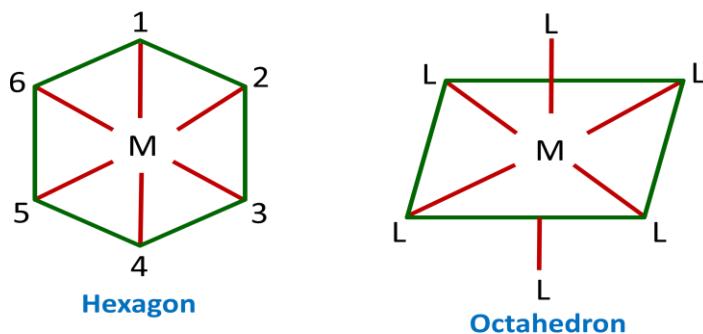
**Solution:** a)

3. Write an account on geometrical isomerism in complexes giving examples.

**Solution:**

#### Geometrical isomerism in co-ordination number 6 compounds:

The arrangement of six ligands in a complex around central metal ion is possible in two different ways. Those are regular hexagon and regular octahedron.



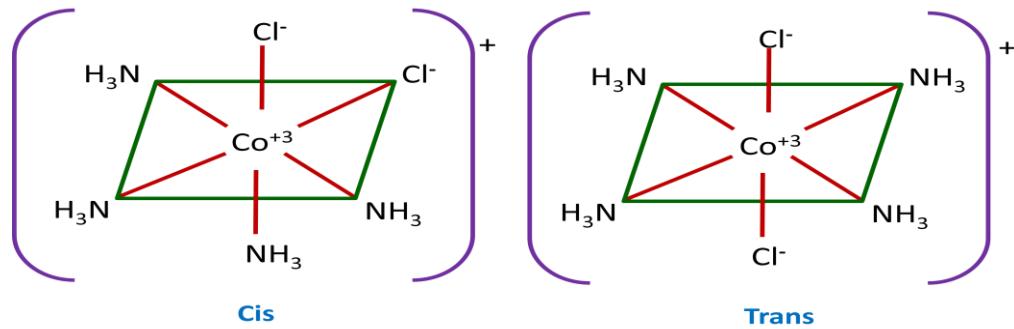
If the complex  $Ma_4b_2$  (where M = central metal atom; a = ligand) has hexagonal structure it can give three isomers corresponding to (1, 2), (1, 3) and (1, 4) positions of a and b, while octahedral arrangement can give only two isomers. X – ray analysis confirmed that co-ordination number 6 complexes exhibit octahedral arrangement by giving two isomers of  $Ma_4b_2$  type. Hence co-ordination number 6 complexes have octahedral structure.

- No isomerism is possible in  $[Ma_6]$  or  $Ma_5b$  of complexes

**Example:**  $[Co(NH_3)_6]^{3+}$ ;  $[Co(NH_3)_5Cl]^{2+}$

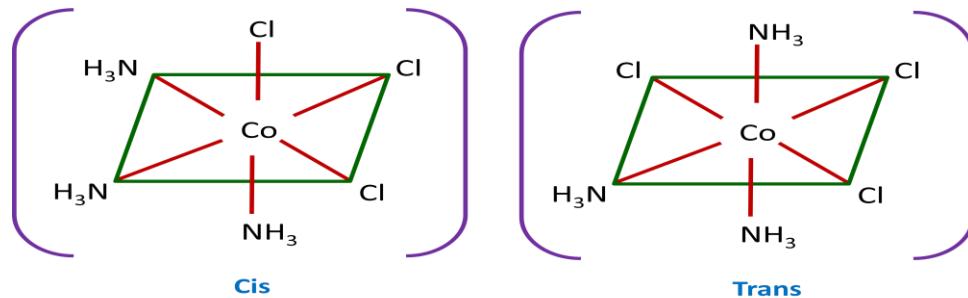
- $[Ma_4b_2]$  and  $[Ma_4bc]$  type complexes can give two isomers. Those are cis and trans – isomers.

**Example:**  $[Co(NH_3)_4Cl_2]^+$  gives cis and trans isomers.



- $[Ma_3b_3]$  type of complexes can exhibit geometrical isomerism.

**Example:**  $[Co(NH_3)_3Cl_3]$  gives cis – trans isomers.



### Problem Set:

- Geometrical isomerism would be expected from?
  - $[Zn(NH_3)_2(H_2O)_2]^{2+}$
  - $[Cu(CN)_4]^{3-}$
  - $[Pt(NH_3)_2Cl_2]$
  - $[Ag(NH_3)_2]^+$

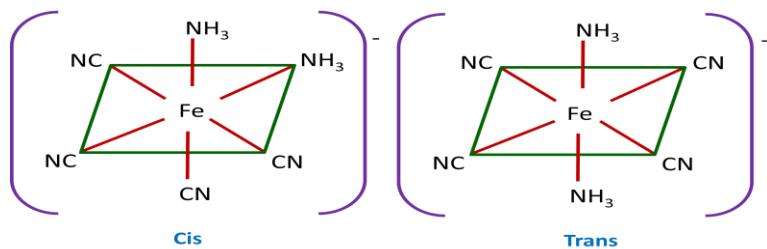
**Solution:** c)

2. Which of the following octahedral complexes does not show geometrical isomerism (a and b are monodentate ligands)?
- $\text{Ma}_3\text{b}_3$
  - $\text{Ma}_4\text{b}_2$
  - $\text{Ma}_5\text{b}$
  - $\text{Ma}_2\text{b}_4$

**Solution:** c)

3. Draw structures of the geometrical isomers of  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]$ .

**Solution:**

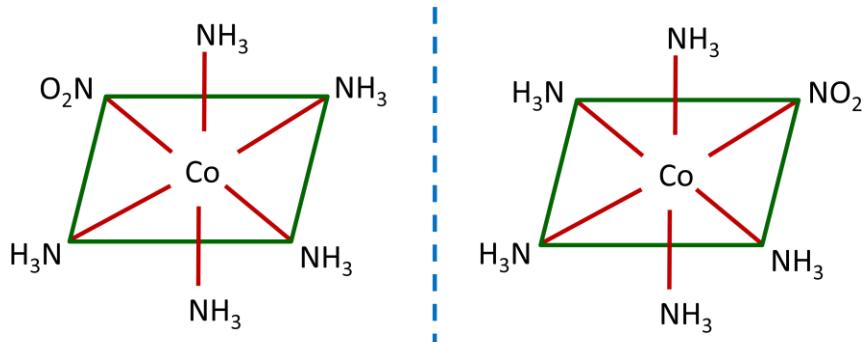


### Exercise Questions:

- Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands?
- Give evidence that  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  are ionization isomers?
- Platinum (II) forms square planar complexes and platinum (IV) forms octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Draw their structures.
  - $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
  - $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$
  - $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
  - $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^{+2}$

## Solutions to Exercise Questions:

1. b
2. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same w.r.t each other.
3.
  - a. A pair of optical isomers



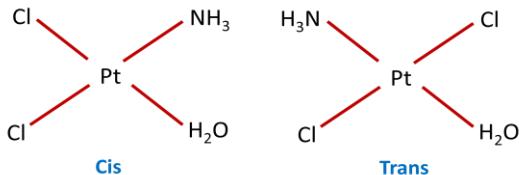
It can also show linkage isomerism



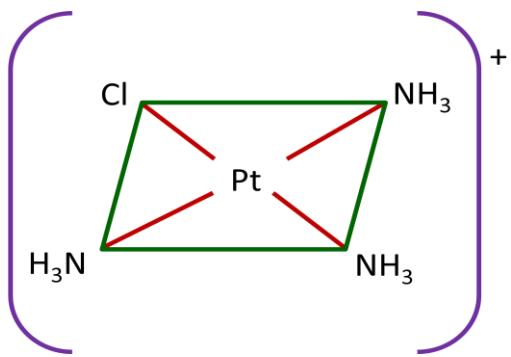
It can also show ionization isomerism



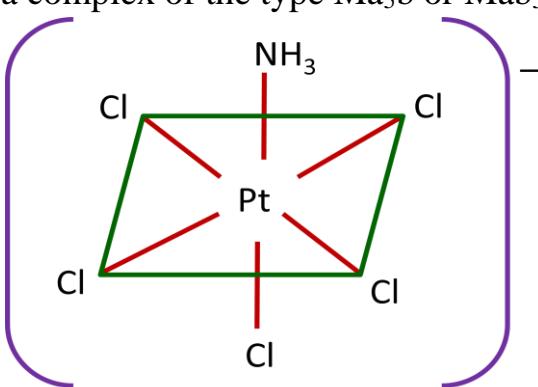
- b. Geometrical (cis-, trans-) isomers of  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$  can exist



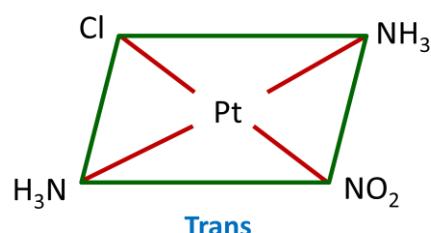
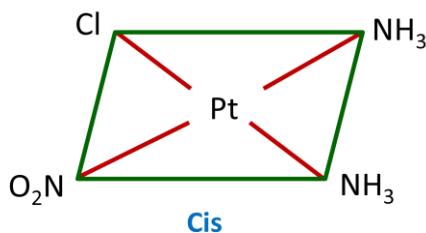
4.
  - a. No isomers are possible for a square planar complex of the type  $\text{Ma}_3\text{b}$ . It is  $[\text{Ma}_3\text{b}]$  type of a complex



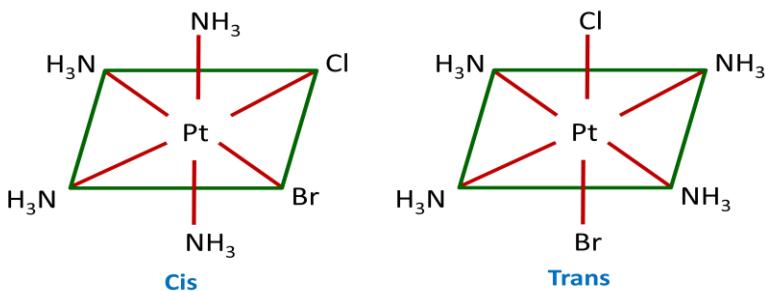
- b. No isomers are possible for an octahedral complex of the type  $\text{Mab}_5$ . This is a complex of the type  $\text{Ma}_5\text{b}$  or  $\text{Mab}_5^-$



- c. cis and trans isomers are possible for a square planar complex of the type  $\text{Ma}_2\text{bc}$



- d. cis and trans isomers are possible for an octahedral complex of the type  $\text{Ma}_4\text{bc}$



5. A, B and C are three complexes of chromium (III) with the empirical formula  $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively , on treatment with concentrated  $\text{H}_2\text{SO}_4$  identify A , B and C.

**Solution:**

The compound A does not react with concentrated  $\text{H}_2\text{SO}_4$  implying that all water molecules are coordinated with  $\text{Cr}^{3+}$  ion. Hence, its structure would be  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ . The compound B loses 6.75% of its original mass when treated with concentrated  $\text{H}_2\text{SO}_4$ . This loss is due to the removal of water molecules which is/are not directly coordinated to  $\text{Cr}^{3+}$  ion.

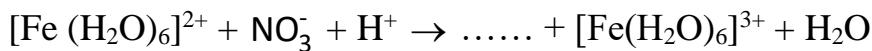
The mass of water molecules removed per mole of the complex

$$\begin{aligned}
 &= \frac{6.75}{100} \times \text{molar mass of the complex} \\
 &= \frac{6.75}{100} \times 266.5 \text{ g} = 17.98 \text{ g} \text{ (one mole H}_2\text{O)}
 \end{aligned}$$

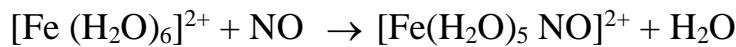
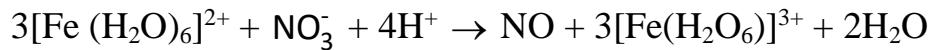
Compound B will be  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}](\text{H}_2\text{O})\text{Cl}_2$

The compound C loses 13.5 % of its mass when treated with concentrated  $\text{H}_2\text{SO}_4$  which is twice of the mass lost by the compound B. Hence compound C will be  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{H}_2\text{O})_2\text{Cl}$ .

7. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of  $\text{NO}_3^-$  , by the following two steps. Complete and balance the equations.

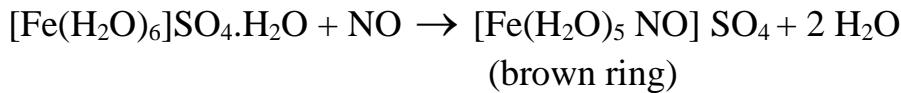
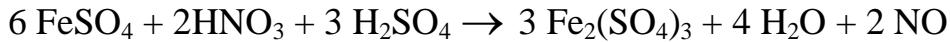
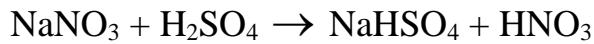


**Solution:**



8. Write the chemical reaction associated with the brown ring test.

**Solution:**

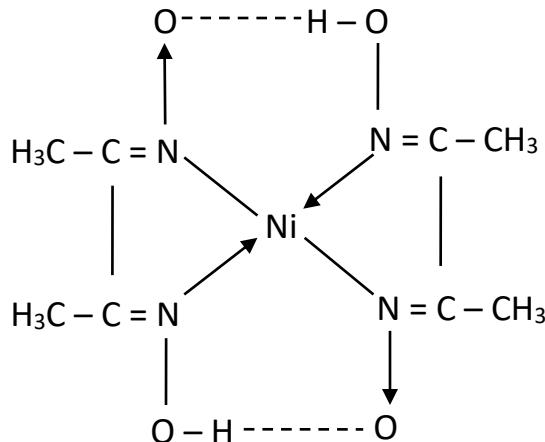


9. Nickel chloride, when treated with dimethyl gyloxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following.

- Draw the structure of the complex showing H- bonds
- Give oxidation state of nickel and its hybridization
- Predict the magnetic behavior of the complex.

**Solution:**

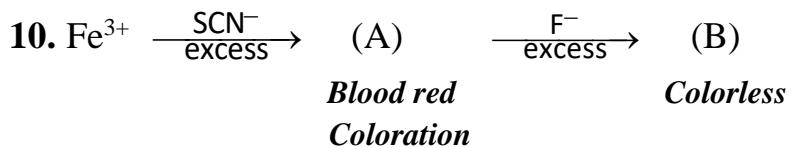
(a)



Bis(dimethylglyoximato) nickel (II).

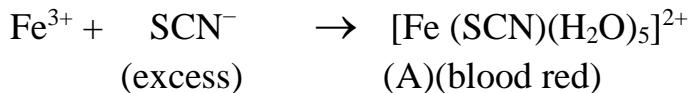
(b) Charge on Ni in the complex is +2 and it is  $dsp^2$  hybridized.

(c) Since number of unpaired electrons in  $Ni^{2+}$  is zero, the complex is diamagnetic.



What are (A) and (B)? Give IUPAC Name of (A). Find the spin only magnetic moment of (B).

**Solution:**



IUPAC name of A is pentaquaquathiocyanato ferrate (III) ion

IUPAC name of B is hexafluoroferrate (III)

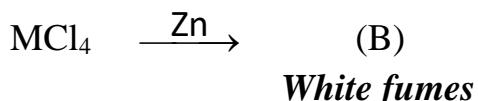
In  $[FeF_6]^{3-}$  co-ordination no.of Fe = 6

In  $[FeF_6]^{3-}$  oxidation state of Fe = +3

∴ It has 3 unpaired electrons, n = 5

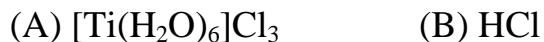
Magnetic moment =  $\sqrt{35} = 5.92$  B.M.

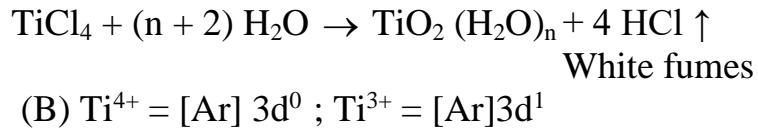
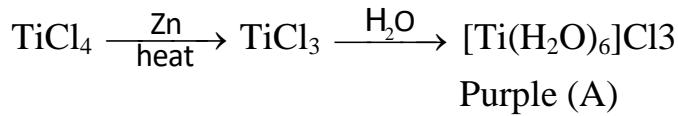
11.(Colourless liquid)  $MCl_4 \xrightarrow{Zn}$  Purple color compound ; M = Transition metal



Identify (A), (B) and  $MCl_4$ . Explain color difference between  $MCl_4$  and (A).

**Solution:**



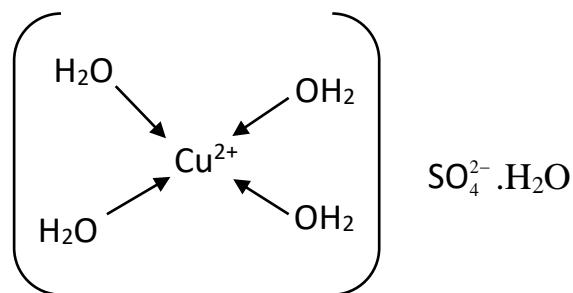


$\text{TiCl}_4$  is colorless since  $\text{Ti}^{4+}$  has no d electrons. Hence d-d transition is impossible. On the other hand,  $\text{Ti}^{3+}$  is colored due to d-d transition.  $\text{Ti}^{3+}$  absorbs greenish yellow compound of white light, hence its aqueous solution is purple which is complementary color of greenish yellow in white light.

- 12.** The number of water molecules (s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is

**Solution:**

The number of water molecules directly bonding to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is 4



- 13.** Total number of geometrical isomers for the complex

$[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is

**Solution:**

Four different ligands and hence three different arrangements.

## Module – 37.1 & 37.2

### Polymers - I

#### Introduction:

The word polymer has been derived from Greek (**Poly = many; mer = part**).

Polymers are macro – sized molecules of relatively high molecular masses, some of which find extensive use in our daily life.

Polymers are large but single chained molecules. In these molecules the repeating unit is derived from small molecules called monomers and these are covalently linked.

Structurally, they are characterized by linear chains or a cross – linked network.

Common examples of materials made of polymers are plastic dishes, cups, non – stick pans, automobile tyres, plastic bags, rain coats, television and computer cabinets, flooring materials and materials for biomedical and surgical operations.

#### Some Important Terms:

##### Polymer:

Polymer is a compound of high molecular mass formed by a repeated combination of small molecules called monomers.

##### Monomers:

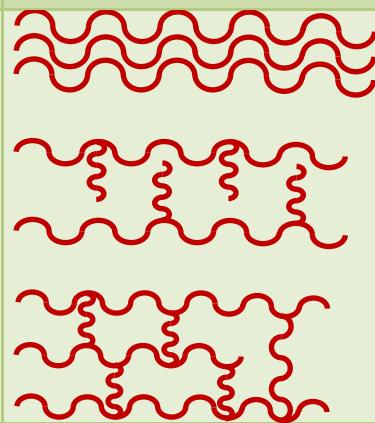
Monomers are small units, which constitute the repeating units in polymers.

##### Polymerization:

The repeated addition of similar or dissimilar simple units to form a giant molecule is known as polymerization. In the process monomers are transformed into polymers.

#### Classification of polymers:

S.NO (1)	Basis of classification (2)	Nature of polymers (3)	Common examples (if any) (4)	Some simple structures (5)
1.	Source of polymer	a. Natural polymers  b. Semisynthetic polymers	Cotton, silk, wool and rubber etc  Cellulose rayon; cellulose nitrate	

		c. Synthetic polymers	Polyethylene, PVC, nylon, terylene	
2.	Structure of polymers	a. Linear polymer  b. Branched polymer  c. Cross linked or network polymers	Polythene, PVC  Low density polythene  Bakelite; melamine	
3.	Mechanism of polymerization	a. Condensation polymers  b. Addition polymers	Terylene; Nylon – 6, 6  Bakelite  Neoprene;  polyvinyl pyrrolidone (PVP), PVC	$\begin{array}{c} \text{H} \\   \\ \text{N} - (\text{CH}_2)_6 - \text{N} - \text{H} \end{array} \quad n$  $\text{C} - (\text{CH}_2)_4 - \text{C}$  $\left[ \begin{array}{c} \text{O} \\    \\ \text{C} - \text{C} \\    \\ \text{O} \end{array} \right]_n$  $\begin{array}{c} \text{CH}_2 - \text{C} = \\   \\ \text{CH} - \text{C} - \text{CH}_2 \end{array} \quad n$

				$\left[ \begin{array}{c} \text{CH}_2 - \\   \\ \text{C} \end{array} \right]_n$
4.	Heat treatment	a. Thermoplastic polymers  b. Thermosetting polymers	Polyethylene, PVC, Nylon and sealing wax  Bakelite, polysiloxanes	$\left[ \begin{array}{c} \text{CH}_2 - \\   \\ \text{CH}_2 \end{array} \right]_n$  $\left[ \begin{array}{c} \text{Si} - \text{O} \\   \\ \text{Si} \end{array} \right]$
5.	Polarity	a. Cationic polymerization polymers  b. Anionic polymerization polymers	Polystyrene;  Polyvinyl ethers, poly isobutene  Buna type synthetic rubbers  Polyacrylonitrile  Poly isoprene	$\left[ \begin{array}{c} \text{CH}_2 - \\   \\ \text{C}_6 \text{H}_5 \end{array} \right]_n$  $\left[ \begin{array}{c} \text{C} \\   \\ \text{CH}_2 \text{N} \end{array} \right]_n$ CH

				$\left[ \begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C} - \text{CH}_2 \end{array} \right]_n$
6.	Molecular forces	a. Elastomers	Buna – N  Buna – S  Neoprene	$\left[ \text{ } \right]$
		b. Fibres	Polyamides; Nylon 6, 6; Polyesters Terylene (or) dacron	$\left[ \begin{array}{c} \text{CH}_2 - \text{C} = \text{CH} \\   \\ - \text{CH}_2 \end{array} \right]_n$
		c. Thermoplastic polymers	Polythene; Polystyrene; Polyvinyl	$\left[ \text{ } \right] \text{---} \text{C}_6\text{H}_5\text{---} \text{C}$
		d. Thermosetting polymers	Bakelite Urea – HCHO resins	They soften on heating and harden on cooling  They undergo extensive cross – linking in moulds and become infusible afterwards
7.	Organic and inorganic substances	a. Organic polymers	Leather; cellulose; rayon	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$
		b. Inorganic polymers	Glass, silicone rubbers etc	

## General Methods of Polymerization:

A few major methods that are generally used for preparing polymers are:

- a. Condensation polymerization.
  - b. Addition polymerization.
  - c. Co-polymerization

#### a. Condensation polymerization method:

Condensation polymers are formed when the monomers containing active functional groups (generally two), react together with the elimination of a small molecule like water, ammonia, alcohol etc.

**Examples:** Nylon-66, polyester, bakelite etc.

Nylon – 66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:



### b. Addition polymerization method:

Addition polymers are formed when monomer units are separately added to form long chains without elimination of any molecules. These polymers are formed by reactions between monomer molecules having multiple bonds.

**Example:** Ethylene undergoes polymerization to form polythene.



The empirical formula of the monomer and polymer are the same.

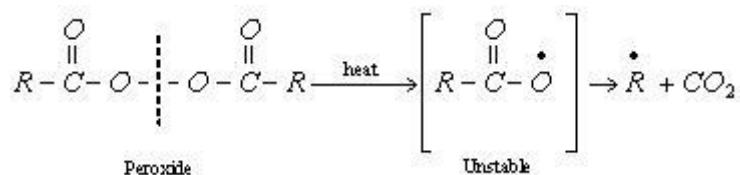
Addition polymerization reactions take place. The mechanisms of these processes are of two types. They are:

- a. Free Radical mechanism and
- b. Ionic Addition Polymerization.

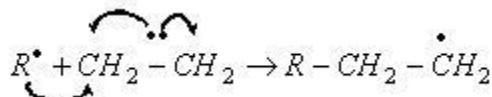
**a. Free-radical mechanism of polymerization:**

Free-radical polymerisation is initiated by organic peroxide or other reagents. These reagents decompose to give free radicals. Following steps are involved.

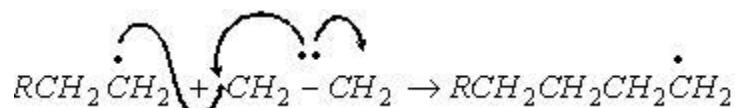
- i. Chain initiation:** Organic peroxides undergo homolytic fission to form free radicals.



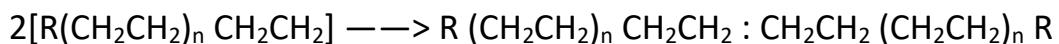
- ii. Chain propagation:** Free radical adds to the monomer (i.e. an alkene) molecule to form a new free radical.



The free radical formed attacks another alkene molecule and the process continues in building a long chain.



- iii. Chain termination:** The chain reaction comes to halt when two free radicals (either chains or monomer units) combine.



Benzoyl or t – Butyl peroxide is common initiators, used.

Free radical polymerisation can also be initiated by a mixture of ferrous sulphate and hydrogen peroxide ( $\text{FeSO}_4 + \text{H}_2\text{O}_2$ ).

**b. Ionic Addition Polymerization:**

Vinylic monomers can undergo addition polymerization through the formation of ionic intermediates instead of free radicals. Here the initiator is an ion, and not a free radical. Ionic polymerization may be:

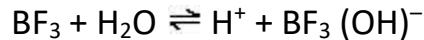
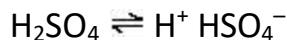
- a. Cationic addition polymerization
- b. Anionic addition polymerization

**a. Cationic mechanism:**

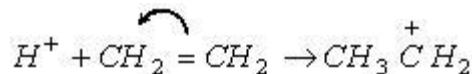
Cationic polymerisation is initiated by use of acids such as  $H_2SO_4$ ,  $HF$  or  $BF_3$  in  $H_2O$ .

The following steps are involved:

- i. **Chain initiation:** The acid furnishes proton.

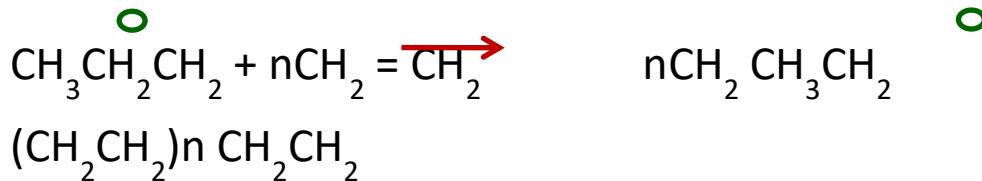


The proton adds to the carbon of the double bond of the monomer (alkene) to form a carbonium ion.

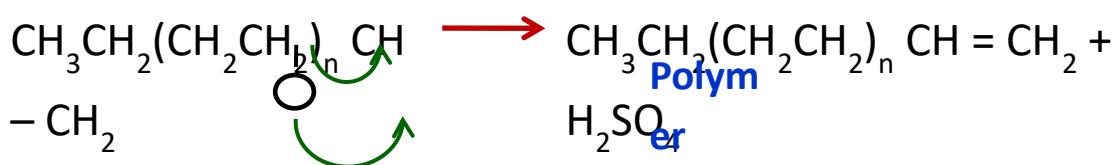


- ii. **Chain propagation:** The carbonium ion combines with another molecule of alkene to form a new carbonium ion and the process continues to form a long chain.





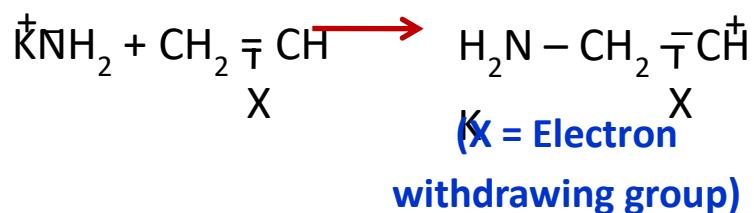
- iii. **Chain termination:** The chain may be halted by combination with negative ion or loss of a proton.



### b. Anionic Addition Polymerization:

An anionic initiator will generate a carbanion as an intermediate and thus the polymerization is of anionic addition type. Here the active centre of the propagating species is negatively charged. Hence it occurs easily with monomers containing electron withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species.

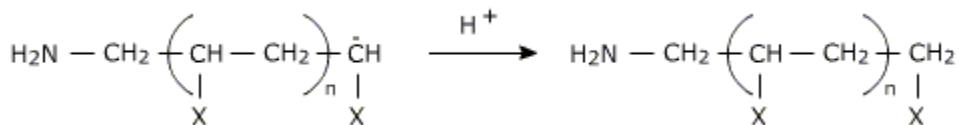
- i. **Chain initiation:** Initiation can be brought about by reagents such as n-butyl lithium or potassium amide. In the initiation step, the base adds to a double bond to form a carbanion.



- ii. **Chain propagation:** In the chain propagation, this carbanion adds to the double bond and the process repeats to form a long chain.



**iii. Chain termination:** The chain reaction can be terminated by addition of an acid.



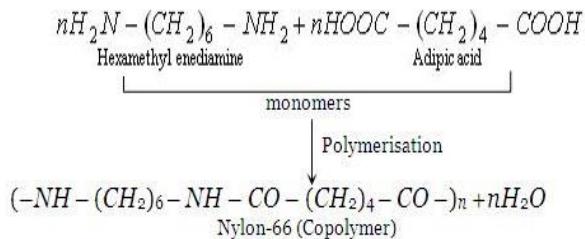
The formation of polystyrene from styrene in the presence of potassium amide is another example of this type of polymerization.

#### Difference between Addition and Condensation polymers:

Addition polymers	Condensation polymers
Formed by addition reaction. No elimination takes place.	Formed by condensation process with elimination of small molecules like $\text{H}_2\text{O}$ .
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involves identical monomer unit.	Generally involves more than one different monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
Generally chain growth polymers.	Generally step growth polymers.

#### c. Co-polymerization:

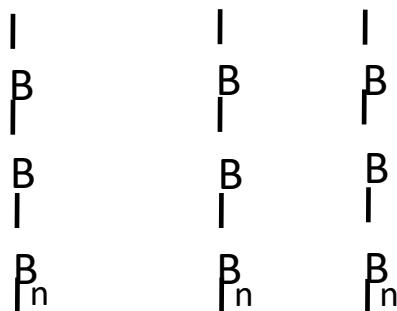
A polymer formed from two or more different monomers is called **copolymer** or **mixed polymer**. For example, nylon-66 is a polymer of two types of monomers : hexamethylenediamine and adipic acid.



It may be noted that many types of copolymers can be obtained depending upon the distribution of monomer units in the chain. Two monomers can combine in either regular fashion (although this is rare) or random fashion. For example, if monomer A is copolymerised with monomer B, the resultant product may have a random distribution of the two units throughout the chain or it might have alternating distribution.

$(-A-B-A-B-A-B-A-B-)$  **Alternating copolymer**

$(-A-A-A-B-A-B-B-A-B-)$  **Random copolymer**



### Assignment questions:

1. How are polymers classified? Give one example to each type
2. What is polymerisation? Give examples for different kinds of polymerization

### Review questions:

### Example set:

1. A high molecular weight molecule built from a large number of simple molecules is called a
  - a. Mesomer
  - b. Isomer
  - c. Polymer
  - d. Tautomer

**Solution:** c)

2. Terylene; nylon – 6, 6 and Bakelite are all examples of
  - a. Addition polymers
  - b. Condensation polymers
  - c. Thermoplastic polymers
  - d. Inorganic polymers

**Solution:** d)

3. Cationic polymerization is initiated by
  - a.  $\text{BF}_3$
  - b.  $\text{NaNH}_2$
  - c. Base
  - d. Both b) and c)

**Solution:** a)

4. In the propagation step of radical polymerization the reaction intermediate is
  - a. Carbocation
  - b. Carbanion
  - c. Free radical
  - d. Both a) and b)

**Solution:** c)

5. Write a note on
  - a. Anionic polymerisation
  - b. Cationic polymerization

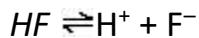
**Solution:**

### a. Cationic mechanism:

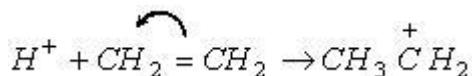
Cationic polymerisation is initiated by use of acids such as  $H_2SO_4$ ,  $HF$  or  $BF_3$  in  $H_2O$

The following steps are involved:

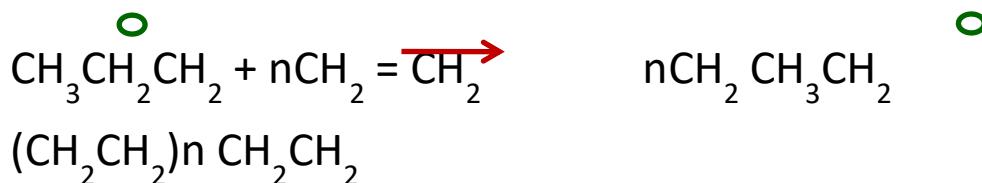
- i. **Chain initiation:** The acid furnishes proton.



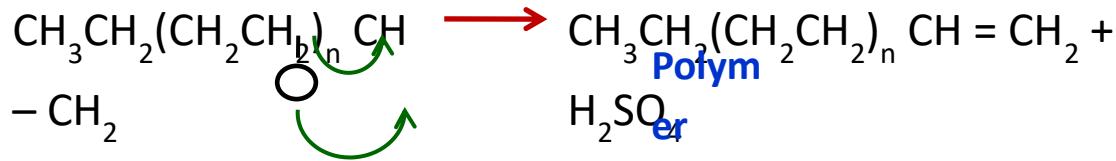
The proton adds to the carbon of the double bond of the monomer (alkene) to form a carbonium ion.



- ii. **Chain propagation:** The carbonium ion combines with another molecule of alkene to form a new carbonium ion and the process continues to form a long chain.



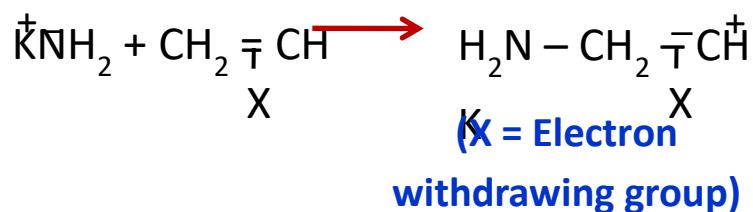
- iii. **Chain termination:** The chain may be halted by combination with negative ion or loss of a proton.



### b. Anionic Addition Polymerization:

An anionic initiator will generate a carbanion as an intermediate and thus the polymerization is of anionic addition type. Here the active centre of the propagating species is negatively charged. Hence it occurs easily with monomers containing electron withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species.

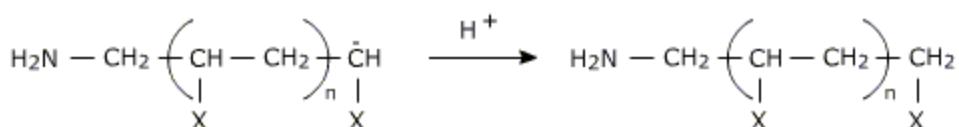
- i. **Chain initiation:** Initiation can be brought about by reagents such as n-butyl lithium or potassium amide. In the initiation step, the base adds to a double bond to form a carbanion.



- ii. **Chain propagation:** In the chain propagation, this carbanion adds to the double bond and the process repeats to form a long chain.



- iii. **Chain termination:** The chain reaction can be terminated by addition of an acid.



The formation of polystyrene from styrene in the presence of potassium amide is another example of this type of polymerization.

## 6. Distinguish between condensation polymerization and addition polymerization

### Solution: Difference between Addition and Condensation polymers:

Addition polymers	Condensation polymers
Formed by addition reaction. No elimination takes place.	Formed by condensation process with elimination of small molecules like $H_2O$ .
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involves identical monomer unit.	Generally involves more than one different monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
Generally chain growth polymers.	Generally step growth polymers.

### Problem set:

1. The structure  $\text{--CH}_2\text{--CH}_2\text{--}\overline{\text{ }}_{\text{n}}$  represents the polymer
  - a. PVC
  - b. Polyethene
  - c. Nylon – 6, 6
  - d. Bakelite

### Solution: b)

2. Which of the following monomers undergoes cationic polymerization

- a  $\text{CH}_2 = \text{CH}$
- b  $\text{CH}_2 - \text{CH}$
- c  $- \text{CN}$
- d  $(\text{CH}_3)_2\text{C} = \text{CH}_2$
- .

**Solution:** d)

3. Which of the following monomers gives the polymer neoprene on polymerization
- a.  $\text{CH}_2 = \text{CHCl}$
  - b.  $\text{CCl}_2 = \text{CCl}_2$
  - c.  $\text{CH}_2 = \text{CHCl} - \text{CH} = \text{CH}_2$
  - d.  $\text{CF}_2 = \text{CF}_2$

**Solution:** c)

4. Which of the following is a synthetic polymer
- a. Starch
  - b. Silk
  - c. Protein
  - d. Polystyrene

**Solution:** d)

5. How are polymers classified on the basis of their structures

**Solution:**

1.	<b>Structure of polymers</b>	<ul style="list-style-type: none"> <li>a. Linear polymer</li> <li>b. Branched polymer</li> <li>c. Cross linked or network polymers</li> </ul>	<ul style="list-style-type: none"> <li>Polythene, PVC</li> <li>Low density polythene</li> <li>Bakelite; melamine</li> </ul>	<p>The diagram illustrates three distinct polymer structures. The first structure, labeled 'Linear polymer', shows a single continuous zigzag line. The second structure, labeled 'Branched polymer', shows a zigzag line with several shorter, horizontal branches extending from it. The third structure, labeled 'Cross linked or network polymers', shows a complex network of interconnected zigzag lines forming a mesh-like pattern.</p>
----	------------------------------	---	---	---

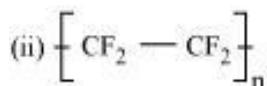
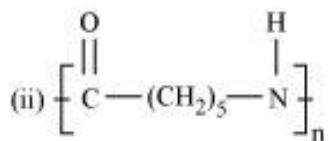
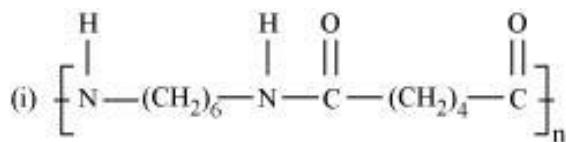
6. Give a monomer in a condensation polymerization reaction

**Solution:** Nylon – 66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:



### Exercise questions:

1. Write the names of monomers of the following polymers:



2. Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.
3. Write the free radical mechanism for the polymerisation of ethene.
4. Write the name and structure of one of the common initiators used in free radical addition polymerisation.
5. Explain the term copolymerisation and give any two examples.

### Solutions to exercise questions:

1. (i) Hexamethylenediamine  $[\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2]$  and adipic acid  $[\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}]$
- (ii)



(iii) Tetrafluoroethene ( $\text{CF}_2 = \text{CF}_2$ )

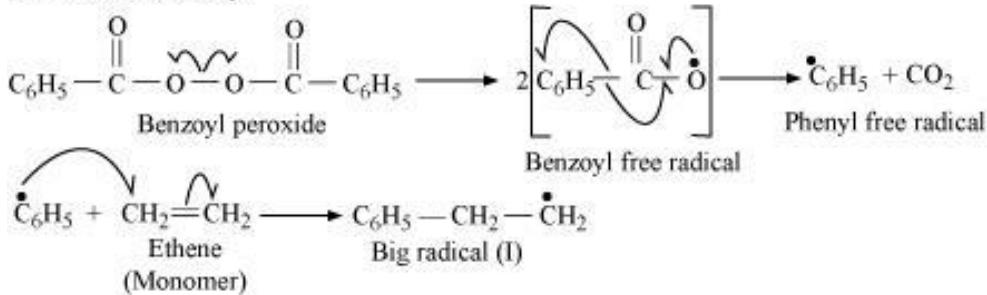
2. Addition polymers: Polyvinyl chloride, polythene

Condensation polymers: Terylene, bakelite

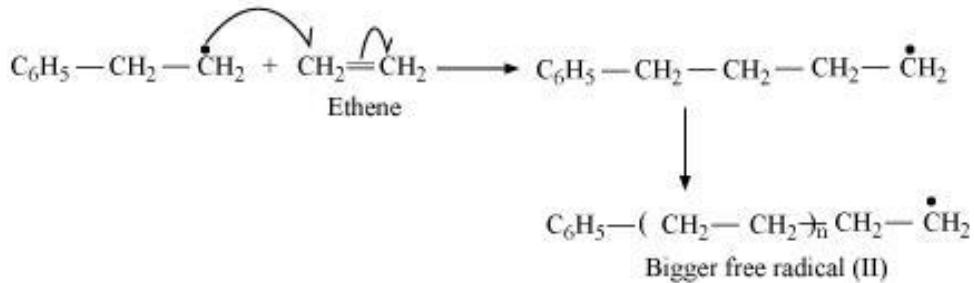
3. Polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide as the initiator.

The reaction involved in this process is given below:

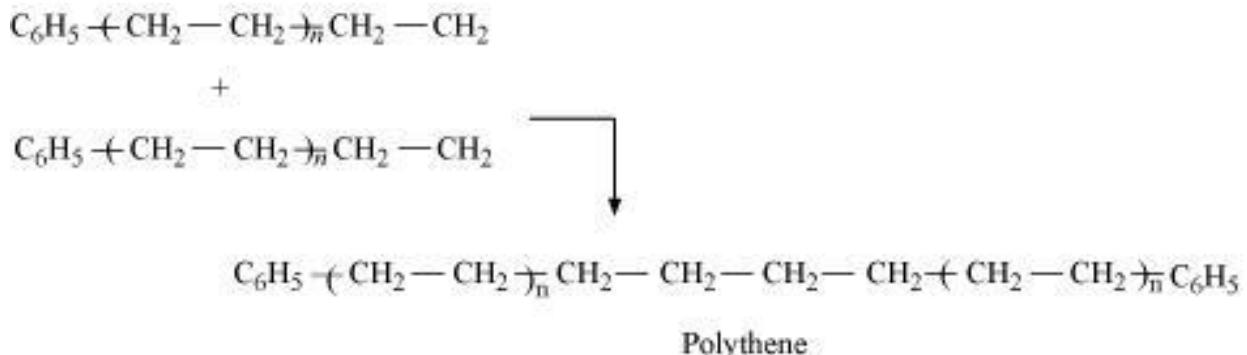
Chain initiation step



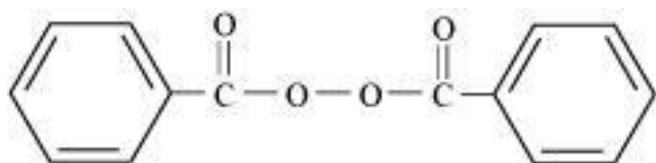
Chain Propagating step



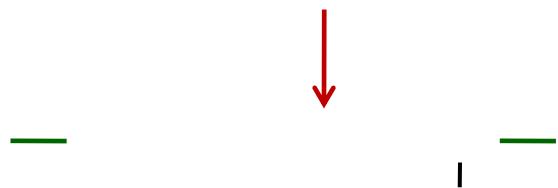
Chain Terminating step



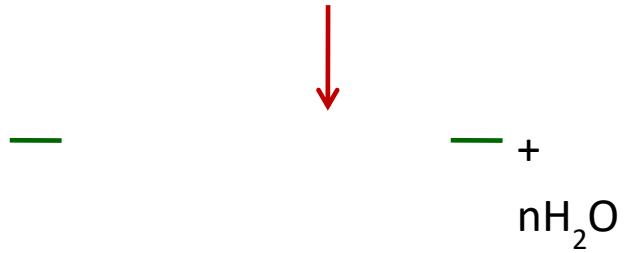
4. One common initiator used in free radical addition polymerization is benzoyl peroxide. Its structure is given below.



5. The process of forming polymers from two or more different monomeric units is called copolymerization. Multiple units of each monomer are present in a copolymer. The process of forming polymer Buna-S from 1, 3-butadiene and styrene is an example of copolymerization



Nylon 6, 6 is also a copolymer formed by the interaction of hexamethylenediamine and adipic acid.



## Module – 37.3 and 37.4

### Polymers – II

#### Rubber:

It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. It is the example of an elastomer. Rubber is of two types.

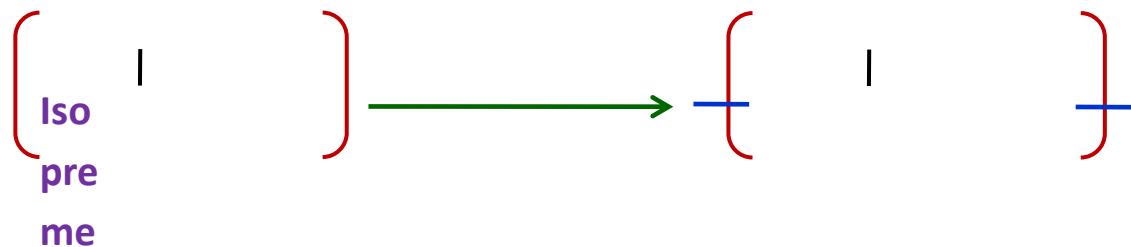
- a. Natural rubber
- b. Synthetic rubber

**a. Natural rubber:** It is obtained as latex from rubber trees. The latex is coagulated with acetic acid or formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dil. Acids and alkalies but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorbs a large amount of water. It has low elasticity and tensile strength.

Destructive distillation of natural rubber gives mainly isoprene (2-methyl butadiene).

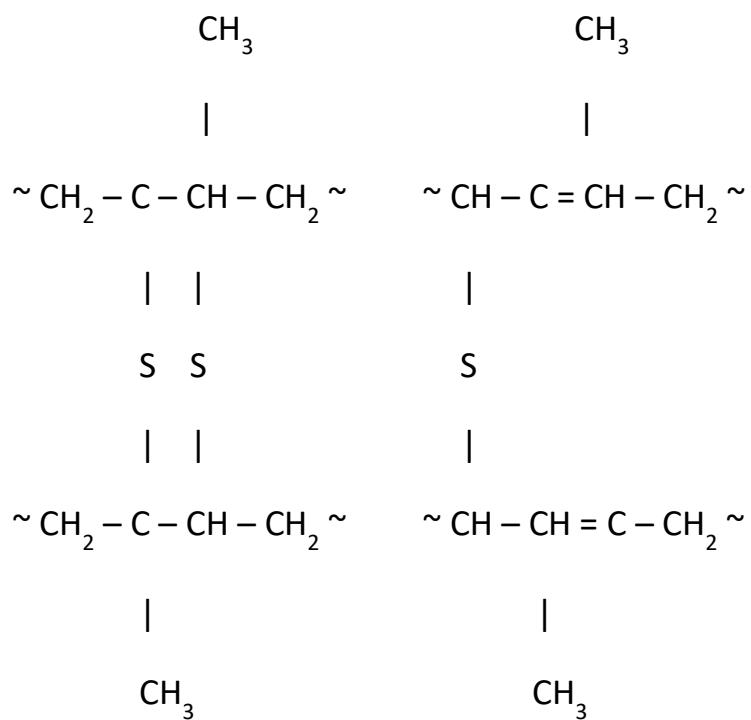
So it can be concluded that isoprene is a monomer of natural rubber. The number of isoprene units varies from 11,000 to 20,000, in rubber which are linked together in a chain.



#### Vulcanization of rubber:

The process of heating natural rubber with sulphur to improve its properties is called vulcanization. Vulcanization was introduced by Charles Goodyear.

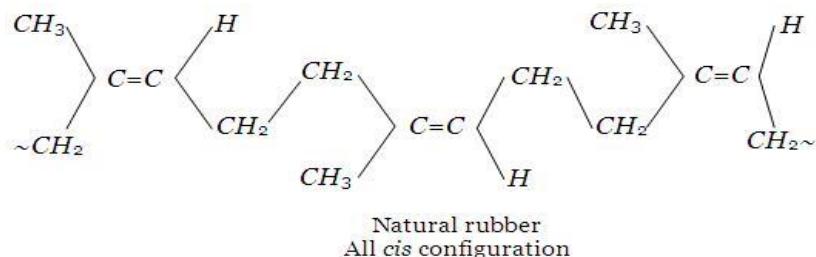
Although natural rubber is a thermoplastic substance in which there are no cross links between the polymer chain and it, on vulcanization, sets into a given shape which is retained.



The vulcanization process was found to be slow. Now a days, some additives such as zinc oxide etc. are used to accelerate the rate of vulcanization. During vulcanization, sulphur cross links are formed (given above figure) the double bonds in the rubber molecule acts as reactive sites. The allylic –  $\text{CH}_2$ , present in alpha position to double bond is also very reactive. During vulcanization, sulphur forms cross links at these reactive sites. As a result, rubber gets stiffened and intermolecular movement of rubber springs is prevented resulting in physical character of rubber. The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added. For example about 5% sulphur is used for making tyre rubber, while 30% of the sulphur is used for making battery case rubber.

In a polymer, the chains are normally tangled up with each other. When the rubber is stretched, the chains straighten out to some extent. The chains cannot

slip past each other because of the polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains try to coil up again and the rubber resumes its original shape.



The differences between the natural rubber and vulcanised rubber are briefly listed in the table that follows.

#### Differences between Natural Rubber And Vulcanized Rubber:

Natural rubber	Vulcanized rubber
a. Natural rubber is soft and sticky	Vulcanized rubber is hard and non-sticky.
b. It has low tensile strength.	It has high tensile strength.
c. It has low elasticity.	It has high elasticity.
d. It can be used over a narrow range of temperature (from 10° to 60°C).	It can be used over a wide range of temperature (- 40° to 100°C).
e. It has low resistance to wear and tear.	It has high resistance to wear and tear.
f. It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

**b. Synthetic rubber:** The synthetic rubber is obtained by polymerising certain organic compounds which may have properties similar to rubber and some desirable properties. Most of these contain carbon-carbon double bonds and

are derived from butadiene. The synthetic rubbers are either homopolymers of 1, 3 - butadiene or copolymer in which one of the monomers is 1, 3 - butadiene or its derivatives so that the polymer has the availability of double bonds for its vulcanization. Some important examples are Neoprene, styrene, butadiene rubber (SBR) Thiokol, silicones, polyurethane, rubber etc.

---

### Molecular masses of polymers:

A polymer sample contains chain of varying lengths and therefore its molecular mass is always expressed as an average. On the other hand, natural polymer such as proteins contain chain of identical length and therefore they have definite molecular mass.

The molecular mass of a polymer can be expressed in two ways.

1. Number average molecular mass ( $M_N$ )
2. Weight average molecular mass ( $M_W$ ).

1. **Number average molecular mass ( $M_N$ ) :** If  $N_1, N_2, N_3 \dots$  are the number of molecules with molecular masses  $M_1, M_2, M_3 \dots$  respectively, then the number average molecular mass is

$$M_N = [N_1M_1 + N_2M_2 + N_3M_3 + \dots] / [N_1 + N_2 + N_3 \dots]$$

This may be expressed as:  $M_N = \sum N_i M_i / \sum N_i$

Where  $N_i$  is the number of molecules of the  $i$ th type with molecular mass  $M_i$ .

2. **Weight average molecular mass ( $M_W$ ) :** If  $m_1, m_2, m_3 \dots$  are the masses of the species with molecular masses  $M_1, M_2, M_3 \dots$  respectively, then the weight average molecular mass is

$$M_w = [m_1 M_1 + m_2 M_2 + m_3 M_3 \dots] / [m_1 + m_2 + m_3 + \dots] \text{ or } = \sum m_i M_i / \sum m_i$$

$$\text{But } m_i = N_i M_i, \text{ so that } M_w = \sum N_i M_i^2 / \sum N_i M_i$$

Where  $N_i$  is the number of molecules of mass  $M_i$ .

**Polymers of Commercial Importance:** commercially important polymers along with their structures and uses are given below in the table.

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left( -CH_2 - \overset{CH_3}{ } CH \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left( -CH_2 - \overset{C_6H_5}{ } CH \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left( -CH_2 - \overset{Cl}{ } CH \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left( -NH - CO - NH - CH_2 \right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left( -OCH_2 - CH_2 OOC \begin{array}{c} \text{CO} \\ \text{C}_6\text{H}_4 \end{array} \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$\left( \text{C}_6\text{H}_4 - \overset{O-H}{ } CH_2 - \overset{O-H}{ } C_6\text{H}_4 - CH_2 \right)_n$	For making combs, electrical switches, handles of utensils and computer discs.

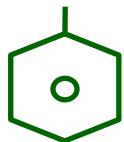
### Assignment questions:

1. Discuss the structure of natural rubber
2. What is vulcanization? Write the consequences of the vulcanization of rubber
3. Explain
  - a. Number of average molecular mass
  - b. Weight average of molecular mass

## **Review questions:**

### **Example set:**

1. Natural rubber is a polymer of
  - a.  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
  - b.  $\text{CH}_2 = \text{CH}_2$



**Solution:** d)

2. The commonly used vulcanizing agent is
  - a. Sulphur
  - b. Graphite
  - c. Carbon black
  - d.  $\text{CO}_2$

**Solution:** a)

3. The formula for calculating weight average molecular mass of a polymer is given by
  - a.  $\frac{\varepsilon Ni Mi}{\varepsilon Ni}$
  - b.  $\frac{\varepsilon Ni Mi}{\varepsilon Mi}$
  - c.  $\frac{\varepsilon Mi^2}{\varepsilon Ni}$

$$d. \frac{\varepsilon NiMi^2}{\varepsilon Ni}$$

**Solution:** d)

4. The natural rubber on vulcanization becomes
  - a. Less elastic
  - b. More elastic
  - c. Plastic
  - d. Soft

**Solution:** a)

5. What is the cross linking agent used in vulcanization

**Solution:** sulphur

6. Distinguish between natural rubber and vulcanized rubber

**Solution: Differences between Natural Rubber And Vulcanized Rubber:**

<b>Natural rubber</b>	<b>Vulcanized rubber</b>
a. Natural rubber is soft and sticky	Vulcanized rubber is hard and non-sticky.
b. It has low tensile strength.	It has high tensile strength.
c. It has low elasticity.	It has high elasticity.
d. It can be used over a narrow range of temperature (from 10° to 60°C).	It can be used over a wide range of temperature (- 40° to 100°C).
e. It has low resistance to wear and tear.	It has high resistance to wear and tear.
f. It is soluble in solvents like ether, carbon tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

7. Give the importance of polymers in commercial life

**Solution:**

Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left( \text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left( \text{CH}_2-\overset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left( \text{CH}_2-\overset{\text{Cl}}{\underset{ }{\text{CH}}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left( \text{NH}-\text{CO}-\text{NH}-\text{CH}_2 \right)_n$	For making unbreakable cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left( \text{OCH}_2-\text{CH}_2\text{OOC} \begin{array}{c} \text{CO} \\ \text{C}_6\text{H}_4 \end{array} \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	$\left( \text{O-H} \begin{array}{c} \text{CH}_2 \\   \\ \text{C}_6\text{H}_4 \end{array} \text{O-H} \begin{array}{c} \text{CH}_2 \\   \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2 \right)_n$	For making combs, electrical switches, handles of utensils and computer discs.

**Problem set:**

1. In vulcanization of rubber
  - a. Rubber reacts to form new compound

- b. Sulphur cross – links are introduced
- c. Sulphur forms very thin protective layer over rubber
- d. All statements are correct

**Solution:** b)

2. The formula for calculating number average molecular mass of a polymer is given by

- a.  $\frac{\varepsilon Ni Mi}{\varepsilon Ni}$
- b.  $\frac{\varepsilon Ni Mi^2}{\varepsilon Ni Mi}$
- c.  $\frac{\varepsilon Ni Mi}{\varepsilon Mi}$
- d.  $\frac{\varepsilon Mi^2}{\varepsilon Ni}$

**Solution:** a)

3. In order to give strength and elasticity, natural rubber is heated with

- a. Sulphur
- b. Oxygen
- c. Nitrogen
- d. Chlorine

**Solution:** a)

4. Which of the following relations is true for macro molecules?

- a.  $\bar{M}_n < \bar{M}_w$
- b.  $\bar{M}_n > \bar{M}_w$
- c.  $\bar{M}_n = \bar{M}_w$
- d.  $\bar{M}_n > \sqrt{\bar{M}_w}$

**Solution:** a)

5. Equal numbers of polymer molecules with  $M_1 = 10,000$  and  $M_2 = 40,000$  are mixed to give a polymer mixture. Calculate the number average and mass average molar masses.

**Solution:**

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$\bar{M}_m = \frac{n_1 M_1^2 + n_2 M_2^2}{n_1 M_1 + n_2 M_2}$$

Here  $n_1 = n_2$ ;  $M_1 = 10,000$  and  $M_2 = 40,000$

$$\text{Hence, } \bar{M}_n = \frac{1 \times 10,000 + 1 \times 40,000}{(1+1)}$$

$$= 25,000$$

$$\bar{M}_m = \frac{1 \times (10,000)^2 + 1 \times (40,000)^2}{1 \times 10,000 + 1 \times 40,000}$$

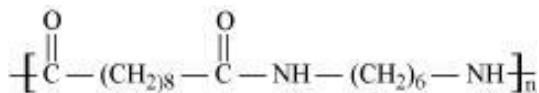
$$= \frac{(1+16) \times 10^8}{(1+4) \times 10^4} = \frac{17}{5} \times 10^4$$

$$= 34,000$$

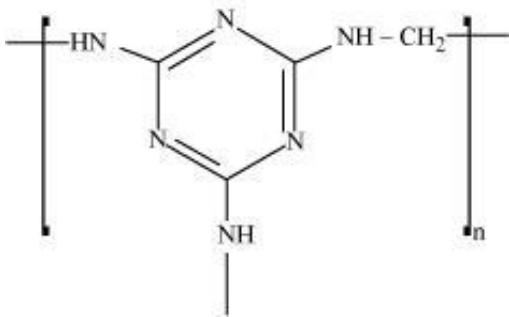
**Exercise questions:**

1. How does the presence of double bonds in rubber molecules influence their structure and reactivity?
2. Discuss the main purpose of vulcanisation of rubber.
3. Identify the monomer in the following polymeric structures.

(i)

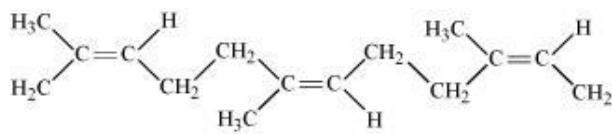


(ii)



### **Solutions to exercise questions:**

1. Natural rubber is a linear cis-polyisoprene in which the double bonds are present between  $C_2$  and  $C_3$  of the isoprene units.



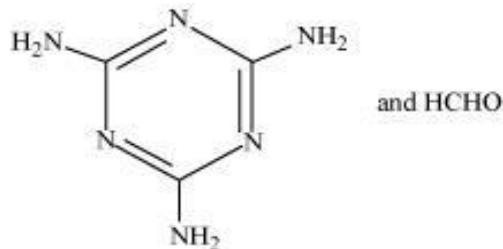
Natural rubber      Cis –  
polyisoprene

Because of this cis-configuration, intermolecular interactions between the various strands of isoprene are quite weak. As a result, various strands in natural rubber are arranged randomly. Hence, it shows elasticity.

2. Natural rubber, though useful, has some problems associated with its use. These limitations are discussed below:
  - a. Natural rubber is quite soft and sticky at room temperature. At elevated temperatures ( $> 335$  K), it becomes even softer. At low temperatures ( $< 283$  K), it becomes brittle. Thus, to maintain its elasticity, natural rubber is generally used in the temperature range of 283 K-335 K.
  - b. It has the capacity to absorb large amounts of water.
  - c. It has low tensile strength and low resistance to abrasion.
  - d. It is soluble in non-polar solvents.
  - e. It is easily attacked by oxidizing agents.

Vulcanization of natural rubber is done to improve upon all these properties. In this process, a mixture of raw rubber, with sulphur and appropriate additive like ZnO, is heated to a temperature range between 373 K and 415 K.

3. (i) The monomers of the given polymeric structure are decanoic acid [ $\text{HOOC} - (\text{CH}_2)_8 - \text{COOH}$ ] and hexamethylene diamine [ $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ ].
- (ii) The monomers of the given polymeric structure are



and  $\text{HCHO}$