CHEMISTRY

Part 2

Class 12

CONTENTS

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Physical Chemistry

Organic Chemistry

11. CHEMICAL KINETICS-II

LEARNING OBJECTIVES

- *To study about the order and rate of reactions. To derive the expression for rate constant of first and pseudo-first order reactions.*
- *To derive half life period and rate constant relations for n^{th} order reaction.*
- *To know the experimental methods of determination of order of reaction. Graphical method of determination of order and rate constant of a reaction is also to be studied.*
- *To learn about the effect of temperature on the rates and rate constants of reaction. To know about Arrhenius equation and Arrhenius parameters (E_a and A).*
- *To differentiate between simple and complex reactions. To learn about consecutive, opposing and parallel reactions.*

The knowledge of rate of chemical reactions is valuable to understand the chemistry and mechanism of reactions. The study of chemical kinetics includes the experimental determination of rate or speed of a reaction, the rate laws and the effects of temperature, pressure, concentration, catalyst on the rates of reaction. It is possible to deduce the mechanism of the reaction from the chemical kinetic data.

11.1 RATE AND ORDER OF A REACTION

For any reaction, the rate expression (or) the rate law equates the rate of the reaction to the product of its rate constant and the concentrations of the reactants raised to certain exponential powers. The rate law for a reaction and the power (exponent) of the concentration terms involved in it must be determined by experiment only.

In a general reaction, $aA + bB \longrightarrow$ products, the overall rate expression can be written as, rate = $k[A]^p [B]^q$ ... (11.1)

p = a or less than a

q = b or less than b

where k = rate constant of the reaction, p and q are the exponents or also known as the orders with respect to reactants A and B respectively.

Therefore the term order can be defined as the sum of the powers of the exponential powers to which each concentration term is raised in the experimentally determined rate law of a chemical reaction.

In the rate expression (11.1),

rate = $k[A]^p$, $[B]^q$, p and q are called the orders of the reaction with respect to reactants A and B respectively. The total order of the reaction, $n = p + q$. Order with respect to A only p and order with respect to B only is q.

It is found that the overall rate of a reaction, depends on the exponential powers to which each concentration term is raised in the rate law. For example, for a reaction with a rate law as rate $= k[A]^2$, when the concentration of A is doubled, the rate is increased by four times the initial rate. Thus, chemical reactions and the over all rates are classified and studied according to the magnitude of the order of their reactions.

Example

From the rate equations for the reactions given below determine the order with respect to the overall reaction

(i) $2HCrO_4^- + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$

$r = k\,[HCrO_4^-]\,[I^-]^2\,[H^+]^2 \qquad \therefore$ Order = 1 + 2 + 2 = 5

(ii) $H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$

$r = k\,[H_2O_2]\,[I^-] \qquad \therefore$ Order = 1 + 1 = 2

Characteristics of order of a reaction

(i) The magnitude of order of a reaction may be zero, or fractional or integral values. For an elementary reaction, its order is never fractional since it is a one step process.

(ii) Order of a reaction should be determined only by experiments. It cannot be predicted interms of stoichiometry of reactants and products.

(iii) Simple reactions possess low values of order like $n = 0,1,2$, Reactions with order greater than or equal to 3.0 are called complex reactions. Higher order reactions are rare.

(iv) Some reactions show fractional order depending on rate.

(v) Higher order reactions may be experimentally converted into simpler order (pseudo) reactions by using excess concentrations of one or more reactants.

11.2 Rate equation for first order reactions

The reactions in which, the overall rate of the reaction is proportional to the first power of concentration of one of the reactants only are called as first order reactions. Consider the reaction

$$\text{A} \xrightarrow{k_1} \text{products}$$

$$\text{Rate of reaction} = \frac{-d[\text{A}]}{dt} = k_1[\text{A}]^{1.0}$$

where k_1 is the rate constant of the first order reaction.

At the beginning of the reaction, time 't' = 0, let the concentration of A be 'a' mole.lit^{-1}. After the reaction has proceeded for some time 't', let the concentration of A that has reacted be x mole.lit^{-1}. The concentration of unreacted A remaining at time 't' will be $(a - x)$ mole.lit^{-1}. The rate of the reaction will be dx/dt. For a first order reaction,

$$\text{rate} = dx/dt = k_1 (a - x) \qquad \text{... (11.2.)}$$

upon integrating, equation 11.2 becomes,

$$\int \frac{dx}{(a-x)} = k_1 \int dt$$

which is, $-ln(a - x) = k_1 t + c$ ... (11.3)

c = integration constant

at time, $t = 0$, $x = 0$.

$\therefore$ in equation 11.3,

$$-\ln (a - 0) = k_1 \times 0 + C$$

$$\text{or } C = -\ln a.$$

Substituting C value in equation 11.3

$$-\ln (a - x) = k_1 t - \ln a$$

Rearranging, $k_1 = \frac{1}{t} \ln \frac{a}{a-x}$

$$\text{(or)} \quad k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{... (11.4)}$$

Unit of k_1 is sec^{-1}.

This equation is known as the first order rate constant equation.

This equation can be used for determining the rate constant of a first order reaction based on the experimental data of (a) and ($a - x$) at different periods of time 't'. Sometimes, the following expression is also used.

$k_1 = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$ where x_1 and x_2 are the amounts reacted in t_1 and t_2 periods of time.

Characteristics of first order reaction

(i) When the concentration of the reactant is increased by '*n*' times, the rate of reaction is also increased by n times. That is, if the concentration of the reactant is doubled, the rate is doubled.

(ii) The unit of rate constant of a first order reaction is $\sec^{-1}$ or time^{-1}.

$$k_1 = \frac{\text{rate}}{(a-x)} = \frac{\text{mol.lit}^{-1}\sec^{-1}}{\text{mol.lit}^{-1}} = \sec^{-1}$$

(iii) The time required to complete a definite fraction of reaction is independent of the initial concentration, of the reactant if $t_{1/u}$ is the time of one 'u'th fraction of reaction to take place then from equation 11.4,

$$x = \frac{a}{u} \quad \text{and} \quad t_{1/u} = \frac{2.303}{k_1}\log\frac{a}{a-\frac{a}{u}}$$

$$\therefore\ t_{1/u} = \frac{2.303}{k_1}\ \log\frac{u}{(u-1)}$$

since k_1 = rate constant, $t_{1/u}$ is independent of initial concentration 'a'.

Examples of first order reactions

1. All radioactive transformations follow first order kinetics. For example,

$$_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}$$

2. Decomposition of sulphuryl chloride in the gas phase proceed by first order kinetics.

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

3. Inversion of sucrose in acidic aqueous medium follows first order reaction.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

4. Decomposition of nitrogen pentoxide in CCl_4 medium also exhibits first order kinetics.

$$N_2O_5 \longrightarrow 2NO_2 + ½\,O_2$$

There are many other reactions that proceed by first order kinetics. We shall study some of the reactions that are experimentally followed by first order kinetic expressions including the parameters that change with concentration of the reactants or products which change with time of progress of the reaction.

Let us consider some of the first order reactions in detail :

1. Decomposition of nitrogen pentoxide in CCl_4

$$N_2O_5 \xrightarrow{k_1} 2NO_2 \quad + \quad ½O_2$$

At time $t = 0$, the volume of oxygen liberated is zero. Let V_t and V_∞ be the measured volumes of oxygen liberated after the reactant has reacted in 't' time and at completion ($t = \infty$). Initial concentration of N_2O_5 is proportional to total volume of oxygen liberated (i.e.,) (V_∞).

(V_∞-V_t) is proportional to undecomposed N_2O_5 at time 't'.

$$\therefore \quad k_1 = \frac{2.303}{t} \log \frac{V_\infty}{(V_\infty - V_t)} \sec^{-1}$$

Example : From the following data on N_2O_5 decomposition in CCl_4, at 298 K, show that the reaction is first order. Also evaluate the rate constant of the reaction.

time (min)	10	15	20	∞
Vol. of O_2 (cc)	6.3	8.95	11.4	34.75

The first order rate constant k_1 is given as,

$$k_1 \quad = \quad \frac{2.303}{t} \log \frac{V_\infty}{(V_\infty - V_t)} \sec^{-1}$$

V_∞ = 34.75 cc 1 min = 60 secs

$t_{(min)}$	$(V_\infty - V_t)$	$k_1 = \frac{2.303}{t \times 60} \log \frac{V_\infty}{V_o - V_t}$ sec^{-1}
10	28.45	$\frac{2.303}{10 \times 60} \log \frac{34.75}{28.45} = 2.079 \times 10^{-4}\, sec^{-1}$
15	25.8	$\frac{2.303}{15 \times 60} \log \frac{34.75}{25.8} = 1.530 \times 10^{-4}\, sec^{-1}$
20	23.35	$\frac{2.303}{20 \times 60} \log \frac{34.75}{23.35} = 1.267 \times 10^{-4}\, sec^{-1}$

Mean value = 1.6253×10^{-4} sec^{-1}

$k_1 = 1.625 \times 10^{-4}\, sec^{-1}$ is the rate constant of reaction. Since k_1 values are nearly constant at different timings, this is a first order reaction.

2. Decomposition of H_2O_2 in aqueous solution

$$H_2O_2 \xrightarrow{Pt} H_2O + \tfrac{1}{2}O_2$$

The decomposition of H_2O_2 in aqueous medium in the presence of Pt catalyst follows a first order reaction. The progress of the reaction is followed by titrating equal volumes of the reaction mixture at regular time intervals against standard $KMnO_4$ solution.

Since volume of $KMnO_4$ used in the titration is a measure of concentration of undecomposed H_2O_2, volume of $KMnO_4$ consumed at $t = 0$ is 'V_o' which proportional to 'a', the initial concentration of H_2O_2. V_t is proportional to unreacted H_2O_2 which is similarly $(a - x)$. Similarly $(V_o\text{-}V_t)$ is proportional to 'x', the concentration of H_2O_2 reacted in time interval 't'. V_t is the volume of $KMnO_4$ consumed after time 't' of the reaction.

$\therefore$ The first order rate constant 'k_1' of the reaction is,

$$k_1 = \frac{2.303}{t} \log \frac{V_o}{V_t}\ sec^{-1}.$$

Example : From the following data, show that decomposition of H_2O_2 in aqueous solution follows a first order reaction. What is the value of the rate constant?

time (min)	0	10	20	30	40
vol of $KMnO_4$ (CC)	25	20	15.6	12.7	9.4

$\text{time}_{\text{(min)}}$	V_t	$k_1 = \dfrac{2.303}{t \times 60} \log \dfrac{V_o}{V_t}$ sec^{-1}
10	20	$\dfrac{2.303}{10\times60} \log \dfrac{25}{15.6} = 2.68 \times 10^{-4}$ sec^{-1}
20	15.6	$\dfrac{2.303}{20\times60} \log \dfrac{25}{15.6} = 1.72 \times 10^{-4}$ sec^{-1}
30	12.7	$\dfrac{2.303}{30\times60} \log \dfrac{25}{12.7} = 1.42 \times 10^{-4}$ sec^{-1}
40	9.4	$\dfrac{2.303}{40\times60} \log \dfrac{25}{9.4} = 1.43 \times 10^{-4}$ sec^{-1}

Mean value $= 1.81 \times 10^{-4}$ sec^{-1}

Since all the k_1 are nearly constant. This is a first order reaction $k_1 = 1.81 \times 10^{-4}$ sec^{-1}.

Half life period '$t_{1/2}$'

Half life period, '$t_{1/2}$', of a reaction is defined as the time required to reduce the concentration of a reactant to one half of its initial value. $t_{1/2}$ values are calculated by using the integrated rate equation of any order of a reaction.

For first order reaction,

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}$$

if amount reacted $x = \frac{a}{2}$ then $t = t_{½}$

$$\therefore \quad t_{½} = \frac{2.303}{k_1}\log\frac{a}{a-a/2}$$

$$t_{½} = \frac{2.303 \log 2.0}{k_1}$$

$$t_{½} = \frac{0.693}{k_1} \text{ secs.}$$

Thus half life period of a first order reaction is independent of the initial concentration of the reactant and also, inversely proportional to the rate constant of the reaction.

Example : Compound A reacts by first order kinetics. At 25°C, the rate constant of the reaction is 0.45 sec^{-1}. What is the half life of A at 25°C. What is the time required to have 12.5% unreacted A for first order reaction,

$$t_{½} = \frac{0.693}{k_1} = \frac{0.693}{0.45}$$

$$= 1.54 \text{ secs}$$

No. of $t_{½}$	**Amount unreacted from 100%**
1	50%
2	25%
3	12.5%

$$\therefore \text{ Time of three half-life periods } = 3 \times 1.54$$

$$= 4.62 \text{ secs}$$

Example : Show that for a first order reaction time required for 99% completion is twice the time required for 90% completion of the reaction.

$$t_{99\%} = \frac{2.303}{k_1}\log\frac{100}{100-99} = \frac{2.303}{k_1}\log 100$$

$$t_{90\%} = \frac{2.303}{k_1}\log\frac{100}{100-90} = \frac{2.303}{k_1}\log 10$$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\log 100}{\log 10} = \frac{2.0}{1.0} = 2.0$$

$$\therefore\ t_{99\%} = 2.0\ t_{90\%}$$

Example : In the thermal decomposition of N_2O at 764°C, the time required to decompose half the reactant was 263 seconds, when the initial pressure was 290 mm of Hg and 212 seconds at an initial pressure of 360 mm of Hg. What is the order of this reaction ?

Solution : $$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

a_1 = 290 mm of Hg t_1 = 263 seconds

a_2 = 360 mm of Hg t_2 = 212 seconds

$$\frac{263}{212} = \left(\frac{360}{290}\right)^{n-1}$$

$$1.24 = (1.24)^{n-1}$$

$$n - 1 = 1$$

$$n = 1 + 1 = 2$$

Hence, the reaction is of second order.

Example : In a first-order reaction, it takes the reactant 40.5 minutes to be 25% decomposed. Find the rate constant of the reaction.

Solution : Since the reactant is 25% decomposed in 40.5 min, the remaining reactants is 75%, i.e. $(a - x) = 0.75$ a t 40.5 min.

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40.5\,\text{min}}\log\frac{a}{0.75a}$$

$$= 0.05686 \log 1.33 \text{ min}^{-1}$$

$$= 0.05686 \times 0.1249 \text{ min}^{-1}$$

$$= 7.1 \times 10^{-3} \text{ min}^{-1}$$

Example : Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50% completion.

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$t_{99.9\%} = \frac{2.303}{k}\log\frac{100}{100-99.9}$$

$$= \frac{2.303}{k}\log_{10}\frac{100}{0.1}$$

$$= \frac{2.303}{k}\log_{10} 1000 \qquad \text{... (1)}$$

$$t_{(50\%)} = \frac{2.303}{k}\log_{10}\frac{100}{100-50}$$

$$= \frac{2.303}{k}\log_{10}\frac{100}{50}$$

$$= \frac{2.303}{k}\log_{10} 2 \qquad \text{... (2)}$$

$$\frac{(1)}{(2)} = \frac{t_{(99.9\%)}}{t_{(50\%)}} = \frac{\frac{2.303}{k}\log_{10}1000}{\frac{2.303}{k}\log_{10}2}$$

$$= \frac{3.000}{0.3010} = 10$$

Example : The rate constant for a first order reaction is $1.54\times10^{-3}\text{sec}^{-1}$. Calculate its half-life period.

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{1.54\times10^{-3}\,\text{sec}^{-1}} = 450 \text{ seconds.}$$

11.3 PSEUDO-FIRST ORDER REACTIONS

In a chemical reaction involving more than one reactant, the overall order of the reaction when experimentally determined by taking excess concentrations of all the reactants except any one of the reactant, will be found lower in magnitude than the overall order determined in presence of smaller concentrations of all the reactants. The altered and the reduced order of the reaction is called as the pseudo order of the reaction.

Thus in a second order reaction, when one of the reactants concentration is in excess (10 to 100 times) of the other reactant, then the reaction follows a first order kinetics and such a reaction is called pseudo-first order reaction. In a reaction of the type,

$$A + B = \xrightarrow{k_2} \text{products} \quad \ldots (11.5)$$

Rate = k_2 [A] [B] where k_2 is the rate constant of the second order reaction. If concentration of A is very large compared to concentration of B, then during the reaction amount of A consumed will be equal to the amount of B reacting with A. Since B concentration is smaller than that of

A, change in the concentration of A after the completion of reaction is assumed to be negligible. Hence concentration of A is considered to remain constant even after the completion of reaction. Hence equation 11.5 becomes,

Rate’ = k_2'[B] ... (11.6)

where Rate’ = rate of the reaction with excess [A].

k_2' = pseudo first order rate constant

= k_2 [A] = second order rate constant × concentration of A.

Thus rate of the pseudo first order reaction alters when concentration of B is altered, and shows a first order kinetics.

Determination of rate constant of acid catalysed hydrolysis of an ester

The hydrolysis reaction of an ester in pure water is a slow reaction and when a mineral acid like hydrochloric acid is added, the rate of the reaction is enhanced since the H^+ ions from the mineral acid acts as the catalyst. The acid catalysed hydrolysis of an ester follows pseudo first order kinetics. The reaction can be represented as :

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The overall rate of the reaction depends on the concentrations of reactants and also on the catalyst concentration.

Rate = k_3 [ester] [H_2O] [H^+] ... (11.7)

k_3 = rate constant of the third order reaction.

Therefore the true order of the reaction is 3.0. Since water is used as the solvent, its concentration is excess.

Weight of 1 lit (1000 cc) of water = 1000 gm = 1 kg

($\therefore$ density of water = 1 gm/cc)

$\therefore$ No. of moles of water in 1 lit = $\frac{1000}{18}$

$\therefore$ Concentration of pure water = 55.55 moles

If 1 molar aqueous solution of ester is used then, 1 mole of water will be consumed for its complete hydrolysis. After the completion of hydrolysis, 55.55 – 1.0 = 54.55 moles water will be present in the medium. Therefore change in the concentration of water considered as negligible and concentration of water is assumed to be constant. Since acid acts the catalyst, there will be, no change in the catalyst concentration before initial and after the completion periods of times of the reactions. Hence $[H^+]$ is considered as a constant value. Hence the expression 11.7 can be rewritten as

Rate = k_3' [ester] where k_3' = pseudo first order rate constant = k_3 $[H^+]$ $[H_2O]$. In this rate expression rate of the reaction is directly proportional to ester concentration only.

Procedure

Initially to a definite volume of (100 ml) hydrochloric acid (0.5 N), 10 ml of ester is added and the start of the reaction corresponds to time of addition of ester. The rate of the reaction is followed by withdrawing a definite volume of the reaction mixture consisting of the ester and acid at various time intervals and arresting the further progress of reaction by adding ice. The whole cold mixture is titrated with standard NaOH (0.1 N) using phenolphthalein as the indicator.

Let the volume of alkali consumed at $t = 0$ be V_o cc which is equivalent to the amount of hydrochloric acid present in the definite volume of the reaction mixture drawn out at regular intervals of time. If V_t cc is the volume of alkali consumed for the same definite volume of the reaction mixture drawn out after reaction time '*t*', then $(V_t - V_o)$ cc is equivalent to the acetic acid produced by the hydrolysis of ester in time '*t*'. A final titration is done after about 8 hours or after refluxing the solution for 45 mins to complete the hydrolysis which is V_∞ cc. $(V_\infty - V_o)$ cc is equivalent to acetic acid produced from complete hydrolysis of ester.

Calculations

The initial concentration of ester = $a \propto (V_\infty - V_o)$ cc

Concentration of ester reacted at '*t*' = $x \propto (V_t - V_o)$ cc

$\therefore$ Concentration of ester remaining at time '*t*' = $(a - x) \propto (V_\infty - V_t)$

$$\therefore \frac{a}{(a-x)} = \frac{(V_\infty - V_o)}{(V_\infty - V_t)}$$

∴ The first order rate expression for the hydrolysis of ester can be written as

$$k = \frac{2.303}{t} \log_{10} \frac{(V_\infty - V_o)}{(V_\infty - V_t)}$$

By substituting V_t values for various 't' values, k is determined. These values are found to be constant indicating k as the rate constant of the reaction.

Example : A certain amount of methyl acetate was hydrolysed in the presence of excess of 0.05 M HCl at 25°C. 20 mL of reaction mixture were removed and titrated with NaOH solution, the volume V of alkali required for neutralisation after time 't' were as follows :

t (min)	0	20	40	60	∞
v (mL)	20.2	25.6	29.5	32.8	50.4

Show that the reaction is the first order reaction.

Solution : $k = \frac{2.303}{t} \log \frac{(V_\infty - V_o)}{(V_\infty - V_t)}$

$$V_\infty - V_o = 50.4 - 20.2 = 30.2$$

when t = 20 mts. $k = \frac{2.303}{20} \log \frac{50.4-20.2}{50.4-25.6}$

$$= 0.1151 \log \frac{30.2}{24.8}$$

$$= 0.1151 \log 1.2479$$

$$= 0.1151 \times 0.0959 = 11.03 \times 10^{-3} \text{ min}^{-1}$$

when t = 40 mts

$$k = \frac{2.303}{40} \log \frac{50.4-20.2}{50.4-29.5}$$

$$= 0.0576 \times \log \frac{30.2}{20.9} = 0.0576 \times 0.1596$$

$$= 9.19 \times 10^{-3} \text{ min}^{-1}$$

when t = 60 mts

$$k = \frac{2.303}{60} \log \frac{50.4-20.2}{50.4-32.8} = 0.03838 \times \log \frac{30.2}{17.6}$$

$$= 0.03838 \times 0.2343 = 8.99 \times 10^{-3} \text{ min}^{-1}$$

The constant values of k show that the reaction is of first order.

11.4 TEMPERATURE DEPENDANCE OF RATE CONSTANT

It is a common observation that rates of reactions increase with increase in temperature of the reaction mixture. Keeping the concentration of the reactants constant, the rate is found to be two times its initial value, when measured at a temperature 10 K greater than the initial temperature. However, the exact value of the rate constant determined at various temperature is predicted by using Arrhenius equation. This expression is obeyed by most of the reactions. Arrhenius equation is given as

$$k = \text{A } e^{-\text{Ea/RT}}$$

where k = rate constant, E_a = activation energy, A = frequency factor, R = gas constant, T = temperature in Kelvin. If k_1 and k_2 are the rate constants measured at two different T_1 and T_2 temperatures respectively, then E_a can be determined as follows :

Arrhenius equation for two different temperatures T_1 and T_2 are :

$$\log k_1 = \log \text{A} - \frac{\text{E}_a}{2.303\text{R}\text{T}_1} \quad \text{... (1)}$$

$$\log k_2 = \log \text{A} - \frac{\text{E}_a}{2.303\text{R}\text{T}_2} \quad \text{... (2)}$$

where k_1 and k_2 are the rate constants at temperature T_1 and T_2 respectively.

(2) – (1)

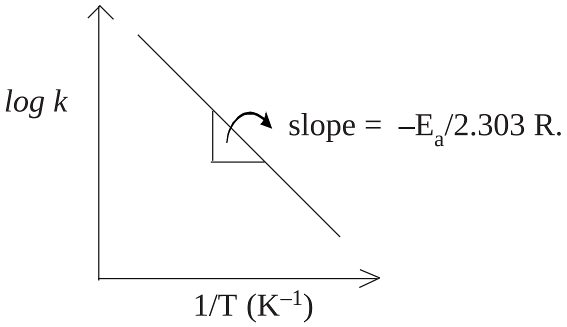
$$\log k_2 - \log k_1 = -\frac{E_a}{2.303RT_2} + \frac{E_a}{2.303RT_1}$$

$$= -\frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$$

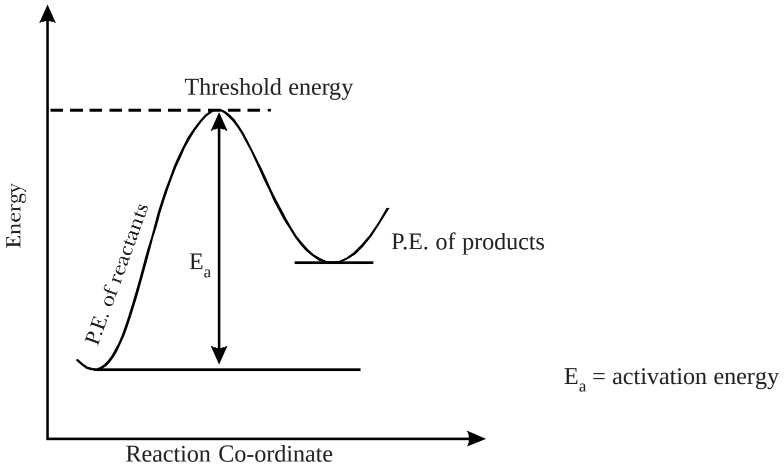
$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

If $R = 1.987$ cals.mol^{-1}, then unit of E_a is 10^{-3} k.cal.

Also, a plot of log k against 1/T values gives a straight line with slope value equals to $-E_a/2.303$ R and intercept value equals to log A. When E_a is a positive value, and if $T_2 > T_1$ then $k_2 > k_1$. That is, rate constant value at higher temperature is greater than rate constant value at lower temperature. Under such conditions, plot of log k against 1/T gives a negative slope straight line. From the slope of the straight line, E_a can be calculated.



Reactant molecules come into contact through collisions for transformation into product molecules. Since, not all collisions are successful in producing the product molecules, all colliding molecules must possess certain minimum energy called as the **threshold energy** which is needed to make the collisions effective and successful. The additional energy required by the molecules to attain the threshold energy in addition to the energy of colliding molecules is called as activation energy 'E_a'. Thus, **activation energy = threshold energy - Energy of colliding molecules**. Generally, this E_a value is higher than the potential energies of reactants and products. Thus, E_a is considered as an energy barrier that must be crossed by the reactant molecules before getting converted to actual product molecules.



Potential energy diagram of a reaction. The molecular state present at the Ea position in the potential energy diagram, is considered as the intermediate product (or) the transition state. Thus Ea, is also the energy required to form the activated state or the intermediate, which is necessary to form the products. Ea is a characteristic value of a reaction. The rate, rate constant, and their temperature dependance are determined by the value of Ea. Higher the value of Ea, slower is the rate of the reaction.

Example : The following values for the first order rate constant were obtained for a certain reaction :

Temp (°C)	$k \times 10^{-5}$ sec^{-1}
25	3.46
35	13.50

Calculate the Arrhenius frequency factor and activation energy 'E_a'.

Solution : $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

$k_1 = 3.46 \times 10^{-5}\ \text{sec}^{-1} \quad T_1 = 298\text{K}$

$k_2 = 1.35 \times 10^{-4}\ \text{sec}^{-1} \quad T_2 = 308\ \text{K}$

$$\log \frac{1.35\times10^{-4}}{3.46\times10^{-5}} = \frac{E_a}{2.303\times1.987}\left(\frac{308-298}{308\times298}\right)$$

$$E_a = \frac{2.303\times1.987\times308\times298}{10}\log\frac{1.35\times10^{-4}}{3.46\times10^{-5}}$$

$$= 2.4830\ \text{cals.}$$

$$\log k_1 = \frac{E_a}{2.303\times RT} + \log A$$

$$\log 3.46\times 10^{-5} = \frac{-24830}{2.303\times1.987\times298} + \log A$$

$$\therefore \quad \log A = 13.7491$$

$$\therefore A = 5.611\times10^{13}\ \text{sec}^{-1}$$

Examples : The activation energy of a certain reaction is 100 KJ/mole what is the change in the rate constant of the reaction if the temperature is changed from 25°C to 35°C ? Let the rate constants at 25°C be k_1 and at 35°C be k_2 respectively.

$$\log\frac{k_1}{k_2} = \frac{E_a}{2.303R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

$$\therefore \frac{k_1}{k_2} = \frac{100000\,\text{J/mol}}{2.303\times8.314\,\text{JK}^{-1}\text{mol}^{-1}}\left[\frac{1}{308}-\frac{1}{298}\right]$$

$$= -0.5745$$

$$\therefore \frac{k_1}{k_2} = \text{antilog}\,(-0.5745)$$

$$= 0.2664$$

$$k_2 = \frac{1}{0.2664} k_1 = 3.75 \text{ times } k_1.$$

$\therefore$ k_2, the rate constant at 35°C will be 3.75 times the rate constant at 25°C.

Example : Decomposition of ethyl bromide and propyl bromide follow first order kinetics, and have the same frequency factor 'A'. The rate constant for decomposition of ethylbromide at 390°C is same as that for propylbromide at 320°C. If the E_a of ethyl bromide reaction is 230 KJ/mole, what is the E_a of propylbromide reaction ?

For ethyl bromide decomposition at 390°C

$$\log k = \log A - \frac{230000}{2.303 \times 8.314 \times 663} \qquad \ldots (1)$$

For propyl bromide decomposition at 320°C

$$\log k = \log A - \frac{E_a}{2.303 \times 8.314 \times 593} \qquad \ldots (2)$$

equations (1) and (2) are equal.

$$\therefore \frac{230000}{2.303 \times 8.314 \times 663} = \frac{E_a}{2.303 \times 8.314 \times 593}$$

$$\therefore E_a = \frac{230000 \times 593}{663}$$

$$E_a = 205.7 \text{ kJ/mole.}$$

11.5 SIMPLE AND COMPLEX REACTIONS

A simple reaction takes place in a single step. Simple reactions are also known as elementary reactions. One step reactions are elementary reactions. In some reactions many side reactions occur along with the main reaction involving product formation.

Reactions which do not take place in a single step but take place in a sequence of a number of elementary steps are called as complex reactions.

Simple reactions	Complex reactions
1. Occurs in single step	Occurs in multi (or) many steps.
2. Overall order values are small. Total and pseudo order values lie between 0,1,2 and 3.	Overall order values are large and greater than 3.0. Sometimes fractional orders such as 1/2, 1/3, 3/2 etc. are seen.
3. No side reactions	Many side reactions are present.
4. Products are formed directly from the reactants	In some complex reactions products are not formed in steps directly involving the reactants.
5. Experimental rate constant values agree with the calculated values. Theories of reaction rates apply well on simple reactions.	Experimental overall rate constant values differ from the calculated values. Theories of reaction rates do not agree well on complex reactions.

Types of Complex reaction

(i) Consecutive reactions

The reactions in which the reactant forms an intermediate and the intermediate forms the product in one or many subsequent reactions are called as consecutive or sequential reactions. In such reactions the product is not formed directly from the reactant. Various steps in the consecutive reaction are shown as below :

$$A \xrightarrow{k_1} B \quad \xrightarrow{k_2} \quad C$$

A = reactant ; B = intermediate ; C = product. Initially only the reactant A will be present. As the reaction starts, A produces an intermediate B through k_1 rate constant. As and when B is formed, it produces the product C through k_2 rate constant. After the completion of reaction only ‘C’ is present and concentrations of A and B will be zero.

Example of consecutive reactions

Saponification of a diester in presence of an alkali :

$$R'OOC\text{–}(CH_2)_n\text{–}COOR \xrightarrow{k_1} R'OOC\text{–}(CH_2)_n\text{–}COOH \xrightarrow{k_2} HOOC-(CH_2)_n-COOH$$

(ii) Parallel reactions

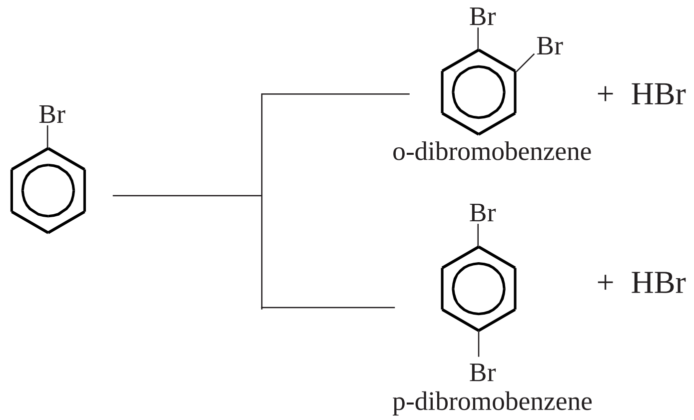
In these group of reactions, one or more reactants react simultaneously in two or more pathways to give two or more products. The parallel reactions are also called as side reactions.

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[r, "k_2"] \arrow[dr, "k_3"'] & C \\ & D \end{tikzcd}$$

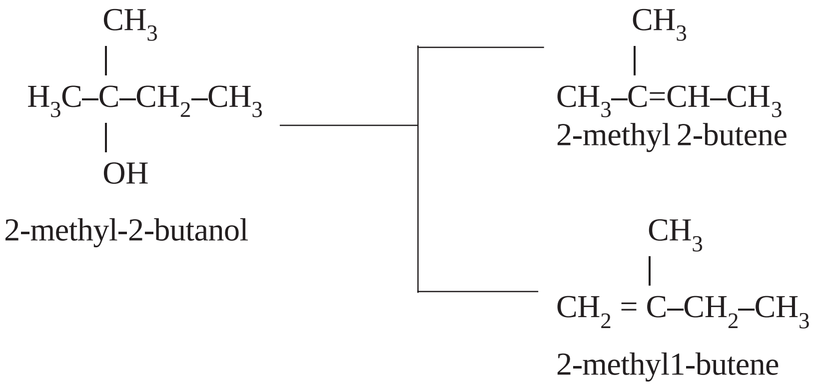
The reactant A reacts to give products B,C,D separately by following three different reaction pathways involving different k_1, k_2, k_3 rate constants respectively. Among the many side reactions, the reaction in which maximum yield of the product obtained is called as the main or major reaction while the other reactions are called as side or parallel reactions.

Examples of parallel reaction :

(i) Bromination of bromobenzene :



(ii) Dehydration of 2-methyl-2-butanol



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 \;;\; CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$$

2-methyl-2-butanol

2-methyl 2-butene

2-methyl1-butene

(iii) Opposing reactions

In opposing reactions the products formed react back simultaneously to form the reactants. These reactions are also called as reversible reactions.

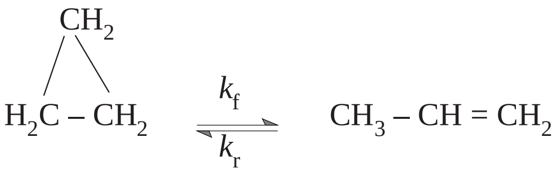
$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D,$$

Examples of opposing reactions

(i) Reaction between CO and NO_2 gases

$$CO_{(g)} + NO_{2(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CO_{2(g)} + NO_{(g)}$$

(ii) Isomerisation of cyclopropane to propene



(iii) Dissociation of hydrogen iodide in gas phase

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

SELF EVALUATION

(A) Choose the correct answer :

1. Hydrolysis of an ester by dilute HCl is an example for

   (a) second order reaction (b) zero order reaction
   (c) pseudo first order reaction (d) first order reaction

2. The unit of zero order rate constant is

   (a) litre mol^{-1} sec^{-1} (b) mol $litre^{-1}$ sec^{-1}
   (c) sec^{-1} (d) $litre^{2}$ sec^{-1}

3. The excess energy which a molecule must posses to become active is known as

   (a) kinetic energy (b) threshold energy
   (c) potential energy (d) activation energy

4. Arrhenius equation is

   (a) $k = Ae^{-1/RT}$ (b) $k = Ae^{-RT/Ea}$ (c) $k = Ae^{-Ea/RT}$ (d) $k = Ae^{Ea/RT}$

5. The term A in Arrhenius equation is called as

   (a) Probability factor (b) Activation of energy
   (c) Collision factor (d) Frequency factor

6. The sum of the powers of the concentration terms that occur in the rate equation is called

   (a) molecularity (b) order (c) rate (d) rate constant

7. Reactions in which the reacting molecules react in more than one way yielding different set of products are called

   (a) consecutive reactions (b) parallel reactions
   (c) opposing reactions (d) chain reactions

8. The half life period of a first order reaction is 10 minutes. Then its rate constant is

   (a) 6.93×10^{2} min^{-1} (b) 0.693×10^{-2} min^{-1}
   (c) 6.932×10^{-2} min^{-1} (d) 69.3×10^{-1} min^{-1}

9. For a reaction : $aA \longrightarrow bB$, the rate of reaction is doubled when the concentration of A is increased by four times. The rate of reaction is equal to

(a) $k\ [A]^a$ (b) $k\ [A]^{½}$ (c) $k\ [A]^{1/a}$ (d) $k\ [A]$

10. $2N_2O_5 \longrightarrow 4NO_2 + O_2$, $\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$,

$\frac{d[NO_2]}{dt} = k_2\,[N_2O_5]$ and $\frac{d[O_2]}{dt} = k_3\,[N_2O_5]$, the relation between k_1, k_2 and k_3 is

(a) $2k_1 = 4k_2 = k_3$ (b) $k_1 = k_2 = k_3$

(c) $2k_1 = k_2 = 4k_3$ (d) $2k_1 = k_2 = k_3$

11. For a reaction, $E_a = 0$ and $k = 4.2 \times 10^5\ sec^{-1}$ at 300K, the value of k at 310K will be

(a) $4.2 \times 10^5\ sec^{-1}$ (b) $8.4 \times 10^5\ sec^{-1}$

(c) $8.4 \times 10^5\ sec^{-1}$ (d) unpredictable

(B) Answer in one or two sentences :

1. Define order of a reaction.
2. Derive the relationship between half-life period and rate constant for a first order reaction.
3. What is activation energy ?
4. What is meant by zero order reaction ? What is the rate constant of such a reaction ?
5. Write the Arrhenius equation and explain the terms.
6. Define half life period.
7. Give examples for first order reaction.
8. What are simple and complex reactions ?
9. Give examples for opposing reactions.

(C) Answer not exceeding sixty words :

1. Explain the experimental determination of rate constant of acid hydrolysis of methyl acetate.
2. Write an account of the Arrhenius equation for rates of chemical reactions.

3. Write notes on (i) consecutive reactions, (ii) parallel reactions and (iii) opposing reactions.
4. State the characteristics of order of reaction.
5. Explain the experimental determination of rate constant for decomposition of H_2O_2 is aqueous solution.

(D) Solve the problems :

1. The specific reaction rates of a chemical reaction are 2.45×10^{-5} sec^{-1} at 273 K and 16.2×10^{-4} sec^{-1} at 303 K. Calculate the activation energy. (**Ans.** 96.101 kJ/mole)
2. Rate constant of a first order reaction is 0.45 sec^{-1}, calculate its half life.
3. (a) What are zero order reactions? (**Ans.** 1.5 sec)
   (b) Give the units of first, third and zero order rate constants.
4. A first order reaction completes 25% of the reaction in 100 mins. What are the rate constant and half life values of the reaction? (**Ans.** $k = 2.8773 \times 10^{-3}$ min^{-1}, t½ = 240.85 mins)
5. If 30% of a first order reaction is completed in 12 mins, what percentage will be completed in 65.33 mins? (**Ans.**85.62%)
6. Show that for a first order reaction the time required for 99.9% completion is about 10 times its half life period.
7. The half life period of a first order reaction is 10 mins, what percentage of the reactant will remain after one hour? (**Ans.** 1.563%)
8. The initial rate of a first order reaction is 5.2×10^{-6} $mol.lit^{-1}.s^{-1}$ at 298 K. When the initial concentration of reactant is 2.6×10^{-3} $mol.lit^{-1}$, calculate the first order rate constant of the reaction at the same temperature. (**Ans.** 2×10^{-3} s^{-1})

SUMMARY :

- Order is defined as the exponential power of the concentration term in the experimentally determined rate expression :

$$\text{rate} = \text{rate constant } [A]^p [B]^q [C]^r.$$

$$\text{Total order} = p + q + r$$

- Units of k and $t_{½}$ depend on the order '*n*'.

  Unit of k $= \text{lit}^{(n-1)}\ \text{mole}^{(1-n)}\ \text{sec}^{-1}$

  $t_{½} \propto (a)^{(1-n)}$.

- Experimental determination of the pseudo first order rate constant from the acid hydrolysis of ester is studied.
- Temperature dependance on the rate constant, Arrhenius equation and the parameters, their significances and determinations are also learnt.
- Determination of activation energy E_a value from the plot of log k against 1/T and the analysis of the potential energy diagram to know the significance of E_a are also learnt.
- Differences between simple and complex reactions are understood. Consecutive, parallel and opposing studied.

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12. SURFACE CHEMISTRY

LEARNING OBJECTIVES

- *To study the adsorption, classification of adsorption and factors affecting adsorption.*
- *To study the catalysis and types of catalysis*
- *To learn the theories of catalysis*
- *To study the preparation and properties of colloids*
- *To understand about emulsions*

12.1 ADSORPTION

Adsorption is a surface phenomenon. It is observed at the surface of the solution. Adsorption is a phenomenon of concentration of substance on the surface of a liquid or solid.

"The condition in which concentration of a substance in the interfacial layers between two phases is greater than in the bulk of either phase, then the substance is said to be adsorbed at the interface and the phenomenon is known as adsorption".

The process of adsorption of gases by solids is a common phenomenon. The charcoal specially coconut charcoal has a great capacity of the adsorption of gases. Silica gel is also utilised for the adsorption of number of gases. The solid that takes up gas or vapour or solute from a given solution is called **adsorbent** and the solute or gas which is held to surface of solid is known as **adsorbate**.

Classification of adsorption of gases on solids

The adsorption of gases on solids has been divided in to two types based on the nature of forces holding the gas molecules to the solids.

1. Physical adsorption (or) Vander waal's adsorption
2. Chemical adsorption (or) chemisorption.

1. Physical adsorption

This adsorption is due to the operation of forces between solid surface and the adsorbate molecules that are similar to vander waal's forces between molecules. These forces are generally undirected and relatively non specific. Physical adsorption can also be defined as that type of adsorption where physical forces hold the gas molecules to the solids.

2. Chemical adsorption

Chemical adsorption is defined as a type of adsorption in which chemical bonds serve the function of holding gas molecules to the surface. It occurs due to the stronger binding forces, comparable with those leading to formation of chemical compounds. It is generally an irreversible process.

The main differences can be summarised as follows:-

Physical adsorption	Chemical adsorption
1. It is due to intermolecular Vander waal's force.	1. It is due to chemical bond formation.
2. Depends on the nature of gas. Easily liquefiable gases are adsorbed readily.	2. More specific than the physical adsorption.
3. Heat of adsorption is small.	3. Heat of adsorption is large.
4. Reversible.	4. Irreversible.
5. If occurs rapidly at low temperature and decreases with increase of temperature.	5. Increases with increase of temperature.
6. Increase of pressure increases adsorption.	6. Change of pressure has no effect.
7. Forms multimolecular layers on adsorbent surface.	7. Forms unimolecular layer

Factors affecting adsorption

The magnitude of gaseous adsorption depends upon the following factors:

i. Temperature
ii. Pressure
iii. Nature of the gas and
iv. Nature of the adsorbent.

Effect of temperature and pressure

Adsorption is invariably accompanied by evolution of heat. Therefore, in accordance with Le chatelier's principle, the magnitude of adsorption increases with decrease in temperature. Further, since adsorption of a gas leads to decrease of pressure, the magnitude of adsorption increases with increase in pressure. Thus, decrease of temperature and increase of pressure both tend to cause increase in the magnitude of adsorption of a gas on a solid.

Nature of the gas

It is observed that the more readily soluble and easily liquefiable gases such as ammonia, chlorine and sulphur dioxide are adsorbed more than the hydrogen, nitrogen and oxygen. The reason is that Vander waal's or intermolecular forces which are involved in adsorption are more predominant in the former than in the latter.

Nature of the adsorbent

Adsorption is a surface phenomenon. Therefore, the greater the surface area per unit mass of the adsorbent, the greater is its capacity for adsorption under the given conditions of temperature and pressure.

12.2 CATALYSIS

A catalyst is a substance which alters the speed of a chemical reaction without itself undergoing any chemical change and the phenomenon is known as catalysis.

Example,

$$2KClO_3 \xrightleftharpoons{MnO_2} 2KCl + 3O_2$$

In the above reaction, MnO_2 acts as a catalyst.

General characteristics of catalytic reactions

The following characteristics are generally common to most of the catalytic reactions.

1. The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.
2. Only a small quantity of catalyst is generally needed.
3. A catalyst cannot initiate a reaction. The function of a catalyst is only to alter the speed of the reaction which is already occurring at a particular rate.
4. A catalyst does not alter the position of equilibrium in a reversible reaction.
5. The catalyst is generally specific in its action.

Types of catalytic reactions

Catalytic reactions are classified into two broad types;

1. Homogeneous catalysis
2. Heterogeneous catalysis

1. Homogeneous Catalysis

In these reactions, the reactants and catalyst remain in the same phase. The following are some of the examples of homogeneous catalysis.

i. Oxidation of SO_2 to SO_3 with oxygen in the presence of nitric oxide as the catalyst in the lead chamber process.

$$2SO_{2(g)} + O_{2(g)} \overset{NO_{(g)}}{\rightleftharpoons} 2SO_3$$

ii. Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid.

$$CH_3\ COO\ CH_{3(l)} + H_2O_{(l)} \overset{HCl_{(l)}}{\rightleftharpoons} CH_3COOH + CH_3OH$$

2. Heterogeneous Catalysis

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below.

i. Oxidation of SO_2 to SO_3 in the presence of Pt metal or V_2O_5 as catalyst in the contact process for the manufacture of sulphuric acid.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_3$$

The reactants are in gaseous phase while the catalyst is in solid phase.

ii. Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in Haber's process.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_3$$

The reactants are in gaseous phase while the catalyst is in solid phase.

Types of catalysts

The catalysts have been divided into different types according to their behaviour and pattern of action.

1. Positive catalyst

A catalyst which enhances the speed of the reaction is called positive catalyst and the phenomenon is known as positive catalysis. Various examples are given below :

i. Decomposition of H_2O_2 in presence of colloidal platinum

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

ii. Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

2. Negative Catalyst

There are certain substances which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called negative catalysts or inhibitors and the phenomenon is known as negative catalysis. The examples are given below.

i. The oxidation of sodium sulphite by air is retarded by alcohol.

$$2\ Na_2SO_3 + O_2 \xrightarrow{\text{Alcohol}} 2\ Na_2SO_4$$

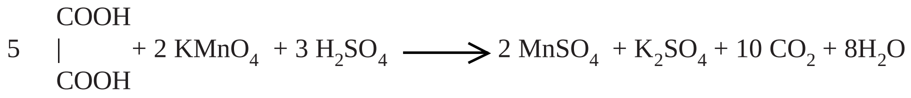
ii. The decomposition of hydrogen peroxide decreases in presence of glycerine.

$$2\ H_2O_2 \xrightarrow{\text{Glycerine}} 2\ H_2O + O_2$$

3. Auto catalyst

In certain reactions, it is observed that one of the products formed during the reaction acts as a catalyst for that reaction. Such type of catalyst is called auto catalyst and the phenomenon is known as auto catalysis.

In the oxidation of oxalic acid by potassium permanganate, one of the products $MnSO_4$ acts as a auto-catalyst because it increases the speed of the reaction.



$$5\ \begin{array}{c} COOH \\ | \\ COOH \end{array} + 2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8H_2O$$

4. Induced Catalyst

When one reactant influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. Thus sulphite has induced the arsenite and hence is called induced catalyst.

Promoters

The activity of a catalyst can be increased by addition of a small quantity of a second material. A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter. Some examples of the promoters are given below.

i. In the Haber's process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst.

$$N_2 + 3\,H_2 \underset{+\,\text{Mo}}{\overset{\text{Fe}}{\rightleftharpoons}} 2\,NH_3$$

Catalytic Poisons

A substance which destroys the activity of the catalyst is called a poison and the process is called catalytic poisoning. Some of the examples are

(i) The platinum catalyst used in the oxidation of SO_2 in contact process is poisoned by arsenious oxide.

$$SO_2 + O_2 \underset{\substack{\text{Poisoned} \\ \text{by } As_2O_3}}{\overset{\text{Pt}}{\rightleftharpoons}} 2\,SO_3$$

(ii) The iron catalyst used in the synthesis of ammonia in Haber process is poisoned by H_2S

$$N_2 + 3\,H_2 \underset{\substack{\text{Poisoned} \\ \text{by } H_2S}}{\overset{\text{Fe}}{\rightleftharpoons}} 2\,NH_3$$

Active Centres

The catalytic surface has unbalanced chemical bonds on it. The reactant gaseous molecules are adsorbed on the surface by these free bonds. This accelerates the rate of the reaction. The distribution of free bonds on the catalytic surface is not uniform. These are crowded at the peaks, cracks and corners of the catalyst. The catalytic activity due to adsorption of reacting molecules is maximum at these spots. These are, therefore, referred to as the active centres. If a catalyst has more active centres, then its catalytic activity is increased.

12.3 THEORIES OF CATALYSIS

There are two main theories to explain catalysis.

1. Intermediate compound formation theory

2. Adsorption theory

In general, the intermediate compound formation theory applies to homogeneous catalytic reactions and the adsorption theory applies to heterogeneous catalytic reactions.

The Intermediate Compound Formation Theory

According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

For example, a reaction of the type

$$A + B \xrightarrow{C} AB$$

which occurs in presence of a catalyst C, may take place as

$$A + \underset{\text{Catalyst}}{C} \longrightarrow \underset{\text{Intermediate compound}}{AC}$$

$$AC + B \longrightarrow \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{C}$$

Many catalytic reactions can be explained on the basis of this theory.

The catalytic oxidation of SO_2 to SO_3 in the lead chamber process probably takes place as;

$$\underset{\text{Catalyst}}{2\,NO} + O_2 \longrightarrow \underset{\text{Intermediate compound}}{2NO_2}$$

$$NO_2 + SO_2 \longrightarrow \underset{\text{Product}}{SO_3} + \underset{\text{Catalyst}}{NO}$$

Adsorption Theory

This theory explains the mechanism of heterogeneous catalysis. Here, the catalyst functions by adsorption of the reacting molecules on its surface.

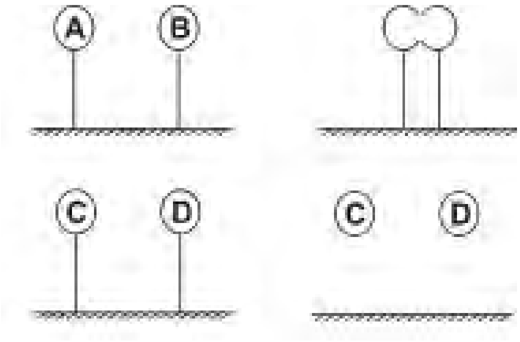


Fig. 12.1 Adsorption

In general, there are four steps involved in the heterogeneous catalysis.

$$A_{(g)} + B_{(g)} \xrightarrow{\text{Catalyst}} C_{(g)} + D_{(g)}$$

Step - 1. Adsorption of reactant molecules

The reactant molecules A and B strike the surface of the catalyst. They are held up at the surface by weak vanderwaal's forces or by partial chemical bonds.

Step - 2. Formation of Activated complex

The particles of the reactants adjacent to one another join to form an intermediate complex (A-B). The activated complex is unstable.

Step - 3. Decomposition of Activated complex

The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.

Step - 4. Desorption of Products

The particles of the products are desorbed or released from the surface.

Applications of catalysis

The applications of catalysis are summarised as follows.

Process	Catalyst
1. Haber's process for the manufacture of ammonia.	Finely divided iron. Molybdenum as promoter.
2. Ostwald's process for the manufacture of nitric acid.	Platinished asbestos
3. Lead chamber process for the manufacture of sulphuric acid.	Nitric oxide.
4. Contact process for the manufacture of sulphuric acid.	Platinised asbestos or vanadium pentoxide (V_2O_5).
5. Deacon's process for the manufacture of chlorine.	Cupric chloride ($CuCl_2$)
6. Bosch's process for the manufacture of hydrogen.	Ferric oxide (Fe_2O_3). Chromic oxide as a promoter.
7. Hydrogenation of vegetable oils Oil + $H_2 \longrightarrow$ Vanaspati ghee	Nickel (finely divided).
8. Bergius process for the synthesis of petrol from coal.	Ferric oxide (Fe_2O_3)

12.4 COLLOIDS

Thomas Graham, in 1861, during his work on diffusion, found that while certain substances, such as sugars, salts, acids and bases diffused readily through a parchment membrane, others, such as gelatin, albumen and glue, diffused at a very slow rate. The substances belonging to the former category which generally exist in crystalline state, were called crystalloids while the substances belonging to the second category were given the name colloids. These observations led to the development of a new branch known as colloidal science.

In a true solution as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules or ions. Thus the diameter of the dispersed particles ranges from 1A° to 10A°. On the other hand, in a suspension as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order of 2000A° or more. The colloidal solutions are intermediate between true solutions and suspensions. When the diameter of the particles of a substance dispersed in a solvent ranges from about 10A° to 2000A°, the system is termed a colloidal solution.

Types of Colloids

A colloidal system is made up of two phases. The substance distributed as the colloidal particles is called the **dispersed phase.** The second continuous phase in which the colloidal particles are dispersed is called the **dispersion medium.** Depending upon the physical state of dispersed phase and dispersion medium, the following types of colloidal solutions are possible.

Dispersed phase	Dispersion medium	Name	Examples
Solid	Solid	Solid-sol	Ruby glass, alloys
Solid	Liquid	Sol	paint, ink
Solid	Gas	Aerosol	Smoke, haze
Liquid	Solid	Gel	Curd, cheese
Liquid	Liquid	Emulsion	Milk, Cream
Liquid	Gas	Liquid Aerosol	Cloud, mist
Gas	Solid	Solid form	Cork, pumice stone
Gas	Liquid	Foam	Froths of air

A colloidal solution of gas in gas is not possible as gases are completely miscible and always form true solutions.

Lyophobic and Lyophilic Colloids

Colloidal solutions in which the dispersed phase has very little affinity for the dispersion medium are termed as lyophobic (solvent hating) colloids. Colloidal solutions of metals which have negligible affinity for solvents and sulphur in water are examples of this type.

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium are called lyophilic (solvent loving) colloids. Gelatin, protein and starch are examples of this type.

12.5 PREPARATION OF COLLOIDS

1. **Preparation of lyophilic sols:** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either in cold or on warming.
2. **Preparation of lyophobic sols :** Lyophobic sols are prepared by special methods. These methods fall into two categories.

i. Dispersion methods: By splitting coarse aggregates of a substance into a colloidal size.

ii. Condensation methods: By aggregating very small particles into the colloidal particles.

Dispersion method	**Condensation methods**
1. Mechanical dispersion	1. Exchange of solvents
2. Electro-dispersion	2. Change of physical state
3. Ultrasonic dispersion	3. Chemical methods
4. Peptization	i. Double decomposition
	ii. Oxidation
	iii. Reduction
	iv. Hydrolysis

Dispersion Methods

1. Mechanical dispersion using colloidal mill

The solid along with the liquid is fed into a colloidal mill. The colloidal mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed. The solid particles are ground down to colloidal size and then dispersed in the liquid. Colloidal graphite and printing inks are made by this method.

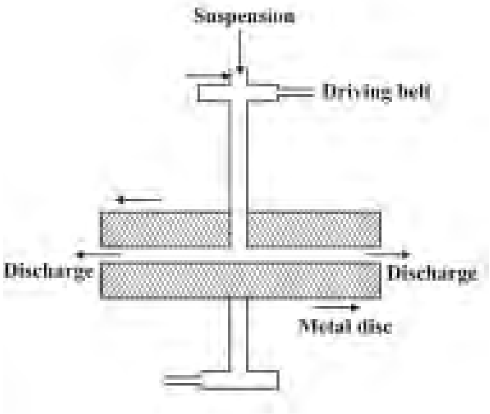


Fig. 12.2 Colloid mill

2. Electro-dispersion method: (Bredig's Arc Method)

This method is suitable for the preparation of colloidal solution of metals like gold, silver, platinum etc. An arc is struck between the metal electrodes under the surface of water containing some stabilising agent such as trace of alkali. The water is cooled by immersing the container in a cold bath. The intense heat of the arc vapourises some of the metal which condenses under cold water.

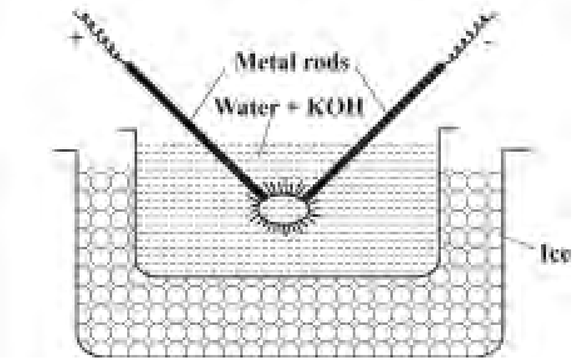


Fig. 12.3 Electro-dispersion

3. Ultra-sonic dispersion :

The sound waves of high frequency are usually called ultra-sonic waves. Ultrasonic waves are passed through the solution containing larger particles. They break down to form colloidal solution.

4. Peptisation :

The dispersion of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptisation. The electrolyte used is called a peptizing agent.

A few examples are

i. Silver chloride can be converted into a sol by adding hydrochloric acid

ii. Ferric hydroxide yields a sol by adding ferric chloride

II. Condensation methods

1. By exchange of solvent

If a solution of sulphur or phosphorus in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water.

2. By change of physical state

Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabiliser.

3. Chemical Methods

The chemical methods involve chemical reaction in a medium in which the dispersed phase is sparingly soluble. Some of the methods are

(i) **Double decomposition**: An Arsenic sulphide sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide. This is continued till the yellow colour of the sol attains maximum intensity.

$$As_2O_3 + 3\,H_2S \longrightarrow \underset{\text{Yellow}}{As_2S_3} + 3\,H_2O$$

Excess hydrogen sulphide is removed by passing in a stream of hydrogen

(ii) **Oxidation :** A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3\ S$$

(iii) **Reduction:** Silver sols and gold sols can be obtained by treating dilute solution of silver nitrate or gold chloride with organic reducing agents like tannic acid or formaldehyde.

$$AgNO_3 + \text{tannic acid} \longrightarrow \text{Ag Sol}$$

$$AuCl_3 + \text{tannic acid} \longrightarrow \text{Au Sol}$$

(iv) **Hydrolysis:** Colloidal solutions of the hydroxides of Fe, Cr, Al etc can be prepared by hydrolysis of their salts. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

PURIFICATION OF SOLS

In the methods of preparation stated above, the resulting sol frequently contains besides colloidal particles appreciable amounts of electrolytes. To obtain the pure sol, these electrolytes have to be removed. This purification of sols can be accomplished by three methods:

(a) Dialysis
(b) Electrodialysis and
(c) Ultrafiltration

Dialysis

Animal membranes (bladder) or those made of parchment paper and cellophane sheet, have very fine pores. These pores permit ions (or small molecules) to pass through but not the large colloidal particles.

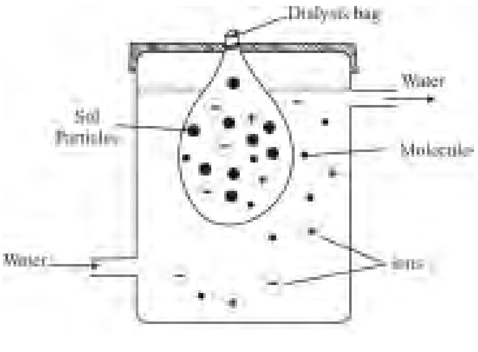


Fig. 12.4 Dialysis of a sol containing ions and molecule

When a sol containing dissolved ions (electrolyte) or molecules is placed in a bag of semipermeable membrane dipping in pure water, the ions diffuse through the membrane. By using a continuous flow of fresh water, the concentration of the electrolyte outside the membrane tends to be zero. Thus diffusion of the ions into pure water remains brisk all the time. In this way, practically all the electrolyte present in the sol can be removed easily. The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is called **Dialysis**. The apparatus used for dialysis is called a **Dialyser.**

Electrodialysis

In this process, dialysis is carried under the influence of electric field. Potential is applied between the metal screens supporting the membranes. This speeds up the migration of ions to the opposite electrode. Hence dialysis is greatly accelerated. Evidently electrodialysis is not meant for non-electrolyte impurities like sugar and urea.

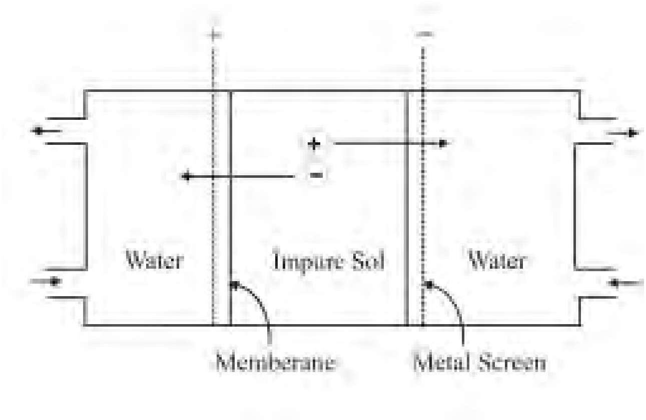


Fig. 12.5 Electrodialysis

Ultrafiltration

Sols pass through an ordinary filter paper. Its pores are too large to retain the colloidal particles. However, if the filter paper is impregnated with collodion or a regenerated cellulose such as cellophane or visking, the pore size is much reduced. Such a modified filter paper is called an ultrafilter.

The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called ultrafiltration.

Ultrafiltration is a slow process. Gas pressure (or suction) has to be applied to speed it up. The colloidal particles are left on the ultrafilter in the form of slime. The slime may be stirred into fresh medium to get back the pure sol. By using graded ultrafilters, the technique of ultrafiltration can be employed to separate sol particles of different sizes.

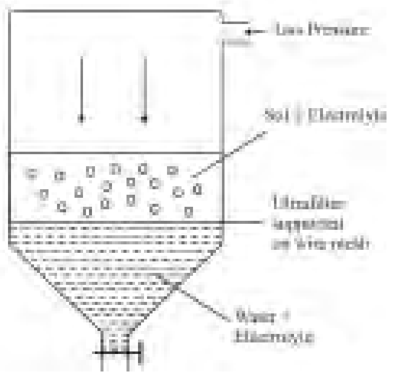


Fig. 12.6 Ultra filtration

12.6 PROPERTIES OF COLLOIDS

The properties of colloids are discussed under three types

i. Kinetic property

ii. Optical property

iii. Electrical property

(i) Kinetic property

When sol is examined with an ultramicrosope, the suspended particles are seen as shining specks of light. By following an individual particle, it is observed that the particle is undergoing a constant rapid motion. It moves in a series short straight line paths in the medium, changing direction abruptly.

The continuous rapid zig-zag chaotic random and ceaseless movement executed by a colloidal particle in the dispersion medium is called brownian movement. This is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

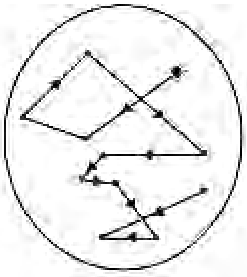


Fig. 12.7 Brownian movement

(ii) Optical property

When a strong beam of light is passed through a sol and viewed at right angles, the path of light shows up as a hazy beam. This is due to the fact that sol particles absorb light energy and then emit it in all directions. This scattering of light illuminates the path of the beam. The phenomenon of the scattering of light by the sol particles is called Tyndall effect.

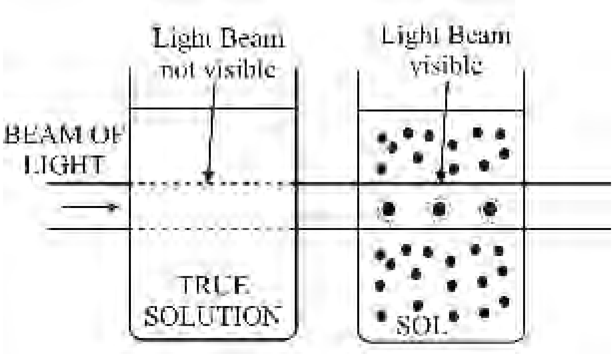


Fig. 12.8 Tyndall effect

III. ELECTRICAL PROPERTIES

(i) Charge on Colloidal particles

The important property of colloidal dispersions is that all the suspended particles possess either a positive or negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol.

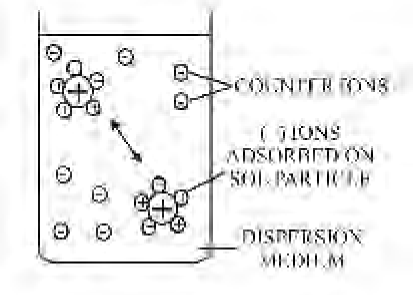


Fig. 12.9 Adsorption of ions from dispersion medium gives charge to sol particles which do not settle on account of mutual repulsions

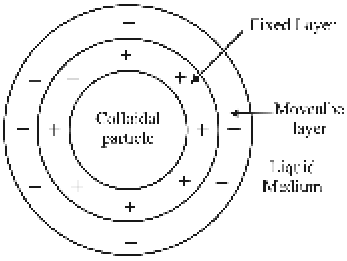


Fig. 12.10 Helmholtz Double layer

The surface of colloidal particle acquires a positive charges by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which form a second layer of negative charges. The combination of the two layers of charges around the sol particle is called **Helmholtz double layer.**

(ii) Electrophoresis

If electric potential is applied across two platinum electrodes immersed in a hydrophilic sol, the dispersed particles move toward one or the other electrode. The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis. If the sol particles here negatively charged, they migrate toward the positive electrode. On the other hand, if they have positively charged they move toward the negative electrode. From the direction of movement of the sol particles, we can determine the charge of the sol particles.

The phenomenon of electrophoresis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of about 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side (Fig.) This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged.

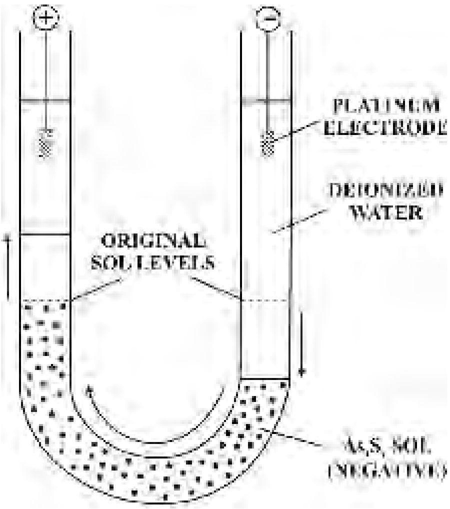


Fig. 12.11 Electrophoresis of a sol

(iii) Electro osmosis

In a sol, the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus, the medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movement of the dispersion medium under the influence of applied potential is known as electro-osmosis.

The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction.

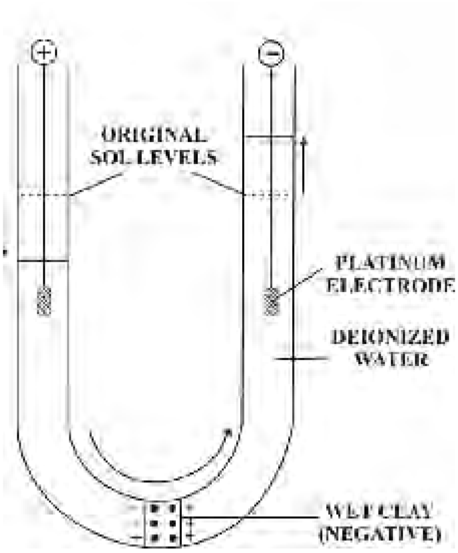


Fig. 12.12 Electro-osmosis

12.7 APPLICATIONS OF COLLOIDS

Most of the substances, we come across in our daily life, are colloids. The meal we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

The applications of colloid chemistry are limitless. These can be divided mainly into two classes:

1. Natural applications and
2. Technical applications

1. Natural applications

(i) Blue colour of the sky : Colloidal particles scatter blue light. Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) Fog, mist and rain : When a large mass of air, containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in the air in the form of mist or fog.

Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositively charged clouds meet.

It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

(iii) Food articles : Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) Blood : Blood is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(v) Soils : Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.

(iv) Formation of delta : River water is colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay which get deposited with the formation of delta.

2. Technical Applications

(i) Electrical precipitation of smoke : Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called **Cottrell precipitator.**

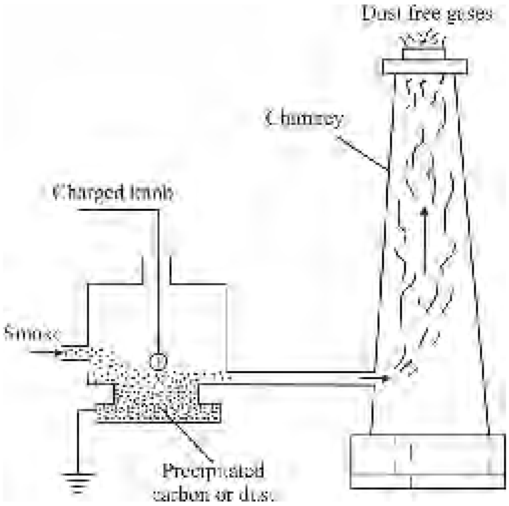


Fig. 12.13 Cottrell smoke precipitator

(ii) Purification of drinking water : The water obtained from natural sources often contains bacteria and suspended impurities. Alum is added to such water so as to destroy the bacteria as well as to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) Medicines : Most of the medicines in use are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because these are easily assimilated.

(iv) Tanning : Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place, which results in the hardening of leather. The process is termed as **tanning.** Chromium salts have been used in place of tannin.

(v) Photographic plates and films : The photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(vi) Rubber industry : Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(vii) Industrial products : Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions..

12.8 EMULSIONS

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called **emulsion**. Generally, one of the two liquids is water. There are two types of emulsions.

(i) Oil dispersed in water (O/W type),

(ii) Water dispersed in oil (W/O type).

In the first system water acts as dispersion medium. Examples of this type of emulsions are milk and vanishing cream. In milk, liquid fat is dispersed in water.

In the second system oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For the stabilization of an emulsion, a third component called **emulsifying agent** is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed, forms at once a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

SELF EVALUATION

(A) Choose the correct answer :

1. The migration of colloidal particles under the influence of an electric field is known as

   (a) electroosmosis (b) cataphoresis
   (c) electrodialysis (d) electrophoresis

2. Which one is the correct factor that explains the increase of rate of reaction by a catalyst

   (a) shape selectivity (b) particle size
   (c) increase of free energy (d) lowering of activation energy

3. Fog is a colloidal solution of

   (a) gas in liquid (b) liquid in gas
   (c) gas in solid (d) solid in gas.

4. The phenomenon of Tyndall's effect is not observed in

   (a) emulsion (b) colloidal solution
   (c) true solution (d) None

5. The Tyndall's effect associated with colloidal particles is due to

   (a) presence of charge (b) scattering of light
   (c) absorption of light (d) reflection of light

6. In case of physical adsorption, there is desorption when

   (a) temperature increases (b) temperature decreases
   (c) pressure increases (d) concentration increases

7. Colloidal medicines are more effective because

   (a) they are clean
   (b) they are easy to prepare
   (c) the germs more towards, them
   (d) they are easily assimilated and adsorbed

8. Oil soluble dye is mixed with emulsion and emulsion remains colourless then, the emulsion is

   (a) O/W (b) W/O (c) O/O (d) W/W

9. For selective hydrogenation of alkynes into alkene the catalyst used is
   (a) Ni at 250°C
   (b) Pt at 25°C
   (c) Pd, partially inactivated by quinoline
   (d) Raney nickel

10. For chemisorption, which is wrong
   (a) irreversible
   (b) it requires activation energy
   (c) it forms multimolecular layers on adsorbate
   (d) surface compounds are formed

11. An emulsion is a colloidal solution of
   (a) two solids (b) two liquids
   (c) two gases (d) one solid and one liquid

12. Colloids are purified by
   (a) precipitation (b) coagulation
   (c) dialysis (d) filtration

(B) Answer in one or two sentences :

1. Define adsorption.
2. Define colloidal solution.
3. What is electrophoresis?
4. What is catalysis ?
5. What are the two types of catalysis?
6. What are active centers ?
7. Why colloidal system in gas in gas does not exist ?
8. Why colloids are purified ?
9. What are emulsions ?
10. What is Tyndall effect ?

(C) Answer not exceeding sixty words :

1. Distinguish between physical adsorption and chemical adsorption.
2. Discuss the factors affecting adsorption.
3. Write notes on catalytic reactions
4. Write notes on
    i. Positive catalyst
    ii. Negative catalyst
    iii. Auto catalyst
    iv. Induced catalyst
5. Write briefly about the theories of catalysis.
6. Write the applications of catalysis.
7. Write briefly about the preparation of colloids by dispersion methods.
8. Write briefly about the preparation of colloids by condensation methods.
9. Write notes on
    i. Dialysis
    ii. Electrodialysis
    iii. Ultrafiltration
10. Write notes on
    i. Brownian movement
    ii. Tyndall effect
    iii. Helmholtz double layer
11. What is electro osmosis ? Explain.
12. Write the applications of colloids.

SUMMARY :

Adsorption is a phenomenon of concentration of substance on the surface of a liquid or solid. The adsorption is classified into physical adsorption and chemical adsorption.

A catalyst is a substance which alters the speed of a chemical reaction without itself undergoing any chemical change and the phenomenon is known as catalysis. Catalytic reactions are classified into homogeneous catalysis and heterogeneous catalysis. The intermediate compound formation theory and the adsorption theory are the two main theories which explain the catalytic processes.

Colloids are intermediate between true solutions and suspensions. Colloids are classified based on dispersion medium and dispersed phase. Colloids are prepared by dispersion methods and condensation methods. Colloids are purified by dialysis, electrodialysis and ultrafiltration. The properties of colloids are discussed under the types namely, kinetic, optical and electrical properties.

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13. ELECTRO CHEMISTRY - I

LEARNING OBJECTIVES

- *To learn and differentiate among conductors, insulators and semi conductors based on the conductivity differences of various substances.*
- *To know about intrinsic and extrinsic semi conductors.*
- *To study about the theory of electrical conductance specially about the Arrhenius theory of weak electrolytes, lilmitations of Arrhenius theory of electrolytic dissociation are also understood.*
- *Onsagar equation will be known and*

  $$\lambda_C = \lambda_\infty - (A + B\lambda_\infty)\sqrt{C},$$

  the relation between equivalent conductance and concentration of strong electrolytes will be studied.
- *Statements of Faraday's laws of electrolysis and their significances will be studied. Quantitative calculations on Faraday's laws will be learnt.*
- Definitions and explanations of specific resistance, equivalent and molar conductances are to be studied.
- *Variations of conductance with dilution of strong and weak electrolytes are to be explained and studied. Graphical representations of conductance against concentrations are explained and understood.*
- *Statement of Kohlraush's law and its significances can be understood.*
- *Buffer action, the nature of acidic and basic buffers, explanation of Henderson equation, examples of buffer solutions in domestic and industrial utilities will be explained and learnt.*
- *Use of pH values, indicators with applications of different pH ranges will be studied.*

The science of electrochemistry deals with the study of interconversion of electrical and chemical energy.

13.1 CONDUCTORS , INSULATORS AND SEMI CONDUCTORS

All substances are classified into three types known as conductors, insulators and semi conductors based on their ability to allow the electrical current to pass through them.

Conductors : Those substances which allow electrical current to pass through them completely are known as **conductors.**

Examples are metals, alloys and fused electrovalent compounds.

Insulators : Those substances which do not allow electrical current to pass through them are known as insulators. Examples of insulators are wood, silk, cotton, glass, rubber, organic compounds like benzene and carbon tetra chloride.

Semiconductors : Those substances that allow the electrical current to pass through them partially (or) possess very low electrical conductivity are known as semi conductors. Examples of semi conductors are Silicon, Germanium, oxides of Manganese, Cobalt oxide, Titanium dioxide etc.

Conductors of electricity are further classified into two types depending on their mode of transport of electrical charges inside them. These are **electronic conductors** and **electrolytic conductors.**

Metallic conductors : Metals and alloys conduct electricitiy due to the movement (mobility) of delocalised outershell electrons present inside them and are known as **electronic conductors** (or) **metallic conductor.** Electrical conduction through metals do not bring about any chemical transformations.

Electrolytic conductor : Electrovalent (or) ionic compounds conduct electrical current in their dissolved state (in solutions) or in their fused state only. These compounds consists of ions of opposite charges and in aqueous solution they exist as ions. In the presence of applied electrical field, these ions migrate to respective electrodes exhibiting electrical conductivity. This mobility of ions is responsible for conduction of electricity through electrolytes and is referred as **electrolytic conduction.** Passage of current through electrolytes is accompanied by chemical changes also. The differences in the properties of electronic and electrolytic conductors are given below :

S.No.	Electronic conduction	Electrolytic conduction
1.	Pure metals and their solid solutions such as alloys are called as metallic conductors.	Electrovalent (or) ionic compounds conduct electricity through their ions present in fused state or in dissolved state.
2.	Free and mobile electrons of the metallic atoms or alloys are responsible for electrical conductance.	Ions with positive and negative charges conduct electricity and move towards cathode and anode respectively.
3.	Positive holes in the metals move in the opposite direction to electrons.	Electrolysis occurs when electrical current is passed through electrolytic solutions.
4.	There is no chemical change in the material when electricity is passed.	Chemical change occurs.
5.	There is only flow of electrical energy but there is no transfer of matter.	There is actual transfer of matter since ions move towards respective electrodes.
6.	Conductivity of metal decreases with increase in temperature due to the enhanced thermal vibration of metal atoms disrupting the movement of electrons passing through them.	The conductivity of electrolytes increases with increase in temperature. This is due to increase with ionic mobility.

Semi conductors : Certain type of solids like pure silicon and germanium which are poor conductors of electricity at normal temperature become good conductors either at high temperatures or in the presence of impurities like Arsenic or Boron. There are two types of semi conductors known as intrinsic and extrinsic semiconductors.

Intrinsic semi conductors : In the intrinsic type, these solids have very low conductivity at room temperature but at high temperatures one of the interatomic covalent bonds between Silicon (or) Germanium atoms are broken heterolytically such that free electrons and corresponding positive holes are created. When electrical field is applied these electrons migrate along the direction of the applied electricfield causing electrical conductivity in them. The positive holes move in opposite direction to that of the movement of electrons.

Extrinsic semi conductor : In the extrinsic type of semi conductors addition of impurities like Arsenic or Boron causes appreciable increase in the electrical conductivity. This effect can be obtained as follows :

N-type semi conductor : In silicon and germanium crystals, each atom is covalently bonded to four neighbours so that all its four valence electrons are tied down. Thus in the pure state these elements are poor conductors. Suppose an atom of arsenic is introduced in place of silicon or germanium in the crystal lattice. Arsenic has five valence electrons, four of which will be utilised in the formation of covalent bonds and the remaining electron is free to move through the lattice. This leads to enhanced conductivity.

p-type semi conductor : Now let a Boron atom be introduced in place of Silicon atom in the crystal lattice. A Boron atom has only three valence electrons. It can form only three of the four bonds required for a perfect lattice. Thus it is surrounded by seven electrons (one of Si) rather than eight. Thus electron vacancy or a 'positive hole' in the lattice is produced. Another electron from the bond of the adjacent Si atom moves into this hole, completing the four bonds on the B atom. This electron also leaves a hole at its original site. In this way electrons move from atom to atom through the crystal structure and the holes move in the opposite direction. Therefore the conductivity of the material improves.

Semi conductors which exhibit conductivitiy due to the flow of excess negative electrons, are called ***n*-type semiconductors** (*n* for negative).

Semiconductors which exhibit conductivity due to the positive holes, are called ***p*-type semiconductors** (*p* for positive).

13.2 THEORY OF ELECTROLYTIC CONDUCTANCE

Arrhenius theory of electrolytic conductance is also known as Arrhenius theory of ionisation since electrolytic dissociation into ions is considered here.

Postulates of Arrhenius Theory : 1. When dissolved in water, **neutral electrolyte molecules are split up into two types of charged particles.** These particles were called **ions** and the process was termed **ionisation.** The positively charged particles were called **cations** and those having negative charge were called **anions.**

The theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules *dissociate* to form separate anions and cations.

$$A^+ B^- \longrightarrow A^+ + B^-$$

For that reason, this theory may be referred to as the theory of electrolytic dissociations.

2. The ions present in solution constantly reunite to form neutral molecules. Thus there is a state of equilibrium between the undissociated molecules and the ions.

$$AB \rightleftharpoons A^+ + B^-$$

Applying the Law of Mass Action to the ionic equilibrium we have,

$$\frac{[A^+][B^-]}{[AB]} = K$$

where K is called the **Dissociation constant.**

3. The charged ions are free to move through the solution to the oppositely charged electrode. This is called as migration of ions. This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

4. The electrical conductivity of an electrolyte solution depends on the number of ions present in solution. Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte.

We know that electrolytes dissociate in solution to form positive ions (cations) and negative ions (anions).

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

As the current is passed between the electrode of the electrolytic cell, the ions migrate to the opposite electrodes. Thus in the electrolytic solution of $AgNO_3$, the cations (Ag^+) will move to the cathode and anions (NO_3^-) will move to the anode. Usually different ions move with different rates. The migration of ions through the electrolytic solution can be demonstrated by the following experiments.

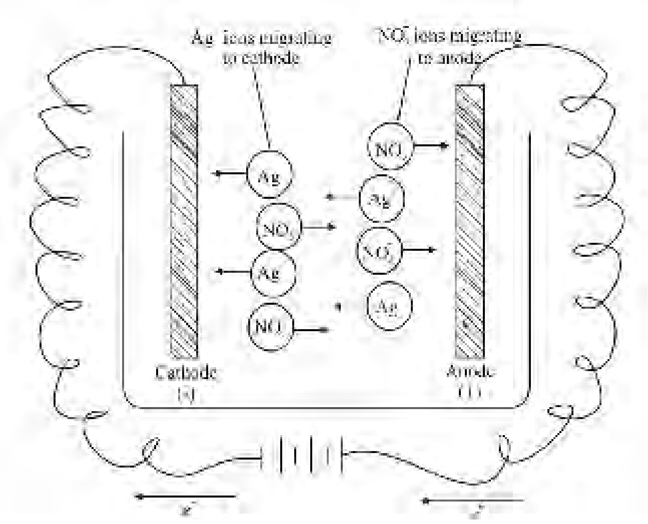


Fig. 13.1 Migration of ions through electrolytic solution to opposite electrodes

5. The properties of solution of electrolytes are the properties of ions. The solution of electrolyte as a whole is electrically neutral unless an electric field is applied to the electrodes dipped into it. Presence of hydrogen ions (H^+) renders the solution acidic while presence of hydroxide ions (OH^-) renders the solution basic.

6. There are two types of electrolytes. Strong electrolytes are those when dissolved in water are completely dissociated (ionised) into ions of

positive and negative charges. The total number of cations and anions produced are equal to those in the formula of the electrolyte.

(e.g.,) $Al_2 (SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$

NaCl, KCl, $AgNO_3$ etc., are few examples of strong electrolytes.

In the case of weak electrolytes, there is partial dissociation into ions in water and an equilibrium exists between the dissociated ions and the undissociated electrolyte.

(e.g.,) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. Acetic acid is a weak electrolyte in water and unionised acetic acid molecules are in equilibrium with the acetate anions and H^+ ions in solution.

Evidences of Arrhenius theory of electrolytic dissociation

1. The enthalpy of neutralisation of strong acid by strong base is a constant value and is equal to –57.32 kJ. $gm.equiv^{-1}$. This aspect is well explained by adopting Arrhenius theory of electrolytic dissociation. Strong acids and strong bases are completely ionised in water and produce H^+ and OH^- ions respectively along with the counter ions. The net reaction in the acid-base neutralisation is the formation of water from H^+ and OH^- ions.

$$H^+ + OH^- \longrightarrow H_2O \; ; \qquad \Delta H_r^o = -57.32 \text{ kJ.mol}^{-1}.$$

2. The colour of certain salts or their solution is due to the ions present. For example, copper sulphate is blue due to Cu^{2+} ions. Nickel salts are green due to Ni^{2+} ions. Metallic chromates are yellow due to CrO_4^{2-} ions.

3. Ostwalds dilution law, common ion effect and solubility product and other such concepts are based on Arrhenius theory.

4. Chemical reactions between electrolytes are almost ionic reactions. This is because these are essentially the reaction between oppositely charged ions. For example,

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

5. Electrolytic solutions conduct current due to the presence of ions which migrate in the presence of electric field.

6. Colligative properties depend on the number of particles present in the solution. Electrolytic solution has abnormal colligative properties. For example, 0.1 molal solution of NaCl has elevation of boiling point about twice that of 0.1 molal solution of non-electrolyte. The abnormal colligative properties of electrolytic solutions can be explained with theory of electrolytic dissociation.

Ostwald's dilution law for weak electrolytes

According to Arrhenius theory, weak electrolytes partially dissociate into ions in water which are in equilibrium with the undissociated electrolyte molecules. Ostwald's dilution law relates the dissociation constant of the weak electrolyte with the degree of dissociation and the concentration of the weak electrolyte. Consider the dissociation equilibrium of CH_3COOH which is a weak electrolyte in water.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

α is the degree of dissociation which represents the fraction of total concentration of CH_3COOH that exists in the completely ionised state. Hence $(1 - \alpha)$ is the fraction of the total concentration of CH_3COOH, that exists in the unionised state. If 'C' is the total concentration of CH_3COOH initially, then at equilibrium $C\alpha$, $C\alpha$ and $C(1 - \alpha)$ represent the concentration of H^+, CH_3COO^- and CH_3COOH respectively.

Then $K_a = \dfrac{C\alpha.C\alpha}{C(1-\alpha)} = \dfrac{\alpha^2 C}{1-\alpha}$

if α is too small, then $K_a = \alpha^2 C$ and

$$\alpha = \sqrt{\frac{K_a}{C}}. \text{ Also } [H^+] = [CH_3COO^-] = C\alpha.$$

$$[H^+] = C\left(\frac{K_a}{C}\right)^{1/2} = (K_a.C)^{1/2} = \sqrt{K_a.C}$$

$K_a = \frac{\alpha^2 C}{1-\alpha}$ is known as the Ostwald's dilution law. For weak bases,

$K_b = \frac{\alpha^2 C}{1-\alpha}$ and $\alpha = \sqrt{\frac{K_b}{C}}$ at α = small values. K_b = dissociation constant for weak base.

This law fails for strong electrolytes. For strong electrolytes, α tends to 1.0 and therefore K_a increases tremendously.

13.4 FARADAY'S LAWS OF ELECTROLYSIS

Electrolysis

When electric current is passed through an electrolyte solution, the ions of electrolyte undergoes chemical changes at the respective electrodes. The chemical reaction carried out by passing electricity is called as electrolysis.

There are two important laws of electrolysis proposed by Faraday and the relation between the amount of products liberated at the electrodes and the quantity of electricity passed through the electrolyte is established based on these laws.

Faraday's First law :

The mass of the substance (*m*) liberated at the electrodes during the electrolysis is directly proportional to the quantity of electricity (Q) that passes through the electrolyte.

Faraday's Second law :

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

Electrochemical equivalent defined in First law

If *m* is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

$$m \propto Q \qquad \text{... First law}$$

We know that $Q = I \times t$

or $m = Z \times I \times t$

where Z is the constant known as the Electrochemical equivalent of the substance (electrolyte). If I = 1 ampere and t = 1 second, then

$$m = Z$$

Thus, the electrochemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (i.e., one coulomb)

The Electrical unit Faraday

It has been found experimentally that the quantity of electricity required to liberate one gram equivalent of a substance is 96,495 coulombs. This quantity of electricity is known as **Faraday** and is denoted by the symbol F.

It is obvious that the quantity of electricity needed to deposit 1 mole of the substance is given by the expression.

$$\text{Quantity of electricity} = n \times F$$

where n is the valency of its ion. Thus the quantity of electricity required to discharge :

one mole of $Ag^+ = 1 \times F = 1F$

one mle of $Cu^{2+} = 2 \times F = 2F$

one mole of $Al^{3+} = 3 \times F = 3F$

We can represent the reactions on the cathode as :

$Ag^+ + e = Ag$

$Cu^{2+} + 2e = Cu$

$Al^{3+} + 3e = Al$

It is clear that the moles of electrons required to discharge one mole of ions Ag^+, Cu^{2+} and Al^{3+} is one, two and three respectively. Therefore it means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say that,

1 Faraday = 96,495 coulombs = 1 Mole electrons

Importance of the First law of Electrolysis

With the help of the first law of electrolysis we are able to calculate :

1. the value of electrochemical equivalents of different substances ; and
2. the mass of different substances produced by passing a known quantity of electricity through their solutions.

96495 coulomb of electricity liberates one gram equivalent weight of the element.

$$\therefore \text{ 1 coulomb current liberates} = \frac{\text{equivalent mass}}{96495} \text{ g.coulomb}^{-1}$$

$$\therefore \text{ Z } = \text{electrochemcial equivalent mass}$$

$$= \frac{\text{equivalent mass}}{96495} \times 10^{-3} \text{ kg.coulomb}^{-1}$$

Electronic charge.

1 Faraday equal the quantity of electricity produced by 1 mole of electrons.

$$\therefore \text{ Charge of an electron} = \frac{96495}{6.023 \times 10^{23}}$$

$$= 1.602 \times 10^{-19} \text{ Coulomb.}$$

Example 1. If 50 milli ampere of current is passed through copper coulometer for 60 min, calculate the amount of copper deposited.

Solution : Electrical charge input $= \mathrm{I} \times t$ coulombs

$= 50 \times 10^{-3}\ \mathrm{A} \times 60 \times 60$ sec

$= 180$ coulombs.

The chemical reaction is, $Cu^{2+} + 2e \longrightarrow Cu_{(s)}$

1 gm atom of copper requires 2F current

$\therefore$ amount of copper deposted $= \dfrac{63.5\text{g.mol}^{-1} \times 180\text{C}}{2 \times 96500\text{C}}$

$= 0.0592$ gm.

Example 2. 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrichemical equivalent of copper ?

Solution : Here, $t = 50$ minutes $= 50 \times 60$ seconds ; I = 0.2 ampere. Quantity of electricity used is

$$Q = I \times t = 0.2 \times 50 \times 60 = 600 \text{ coulombs}$$

Amount of copper deposited by 600 coulombs = 0.1978 g

Amount of copper deposited by 1 coulomb $= \dfrac{0.1978}{600}$ g = 0.0003296 g

Electrochemical equivalent of copper $= 0.0003296 = 3.296 \times 10^{-4} \text{gc}^{-1}$

$= 3.206 \times 10^{-7} \text{ kg c}^{-1}$

Example 3. What current strength in amperes will be required to liberate 10 g of iodine from potassium iodide solution in one hour ?

Solution : 127 g of iodine (1g eqvt) is liberated by = 96,500 coulomb

10 g of iodine is liberated by $= \dfrac{96{,}500}{127} \times 10$ coulomb

Let the current strength be = I

Time in seconds $= 1 \times 60 \times 60$

We know that the quantity of electricity, Q, used is given by the expression

$$Q = I \times \text{time in seconds}$$

Curernt strength, $I = \dfrac{Q}{t} = \dfrac{96{,}500 \times 10}{127 \times 60 \times 60}$

$= 2.11$ ampere.

Example 4. An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine will be liberated while 1.25 g of copper is being deposited ?

Solution : $\frac{\text{Wt. of copper}}{\text{Wt. of Iodine}} = \frac{\text{Eqvt. wt. copper}}{\text{Eqvt. wt. of Iodine}}$

or $\frac{1.25}{x} = \frac{31.7}{127}, \quad x = \frac{1.25 \times 127}{31.7}$

Hence, Wt. of Iodine $x = 5.0$ g of iodine

Also, $\frac{\text{Wt. of Copper}}{\text{Wt. of Silver}} = \frac{1.25}{y}$

$$= \frac{\text{Eqvt. wt. of Cu} (=31.7)}{\text{Eqvt. wt. of Silver} (=108)}$$

Wt. of silver (y) $= \frac{108 \times 1.25}{31.7}$

$= 4.26$ g

13.5 ELECTRICAL CONDUCTANCE QUANTITIES

The S.I. unit of electrical current is ampere. The unit of quantity of electricity is coulomb. when one ampere of current is passed for one second, then the quantity of current passed is one coulomb.

(i.e.,) $Q = I \times t$ Coulomb

Ohm's law : This law can be stated as, at constant temperature, the strength of the current flowing through a conductor is directly proportional to the potential difference and inversely proportional to the resistance of the conductor.

Thus, $I = \frac{V}{R}$, $\therefore$ V = RI, V = Volts, I = ampere, R = ohms

Specific resistance : The resistance 'R' ohms offered by the material of the conductor to the flow of current through it is directly proportional to its length (*l*) and inversely proportional to the area of cross section (*a*). Thus,

$$R \propto \frac{l}{a} \quad \text{and} \quad R = \rho \frac{l}{a}$$

ρ is called the specific resistance and it is resistance in ohms which one meter cube of material offers to the passage of electricitiy through it, unit of specific resistance is **ohm-meter.**

Specific conductance : The reciprocal of specific resistance is called as specific conductance (or) specific conductivity (κ) [κ is called 'kappa'].

κ is defined as the conductance of one metre cube of an electrolyte solution

$$\therefore \kappa = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$$

Unit of specific conductance is ohm^{-1} m^{-1} (or) $mho.m^{-1}$

Since ohm^{-1} = mho

$$\kappa = \frac{1}{\text{ohm}} \times \frac{m}{m^2} = \text{ohm}^{-1}.\text{m}^{-1}$$

Also, 1 siemen = 1 mho. $\therefore$ κ is also expressed as $S.m^{-1.}$

Conductance is the reciprocal of resistance 'R'.

$$\text{Conductance} = \frac{1}{R}$$

$\frac{l}{a}$ is called as the cell constant (m^{-1}) and is constant for a given conductance cell.

Thus specific conductance 'κ' = cell constant × conductance

$$= \frac{\text{Cell constant}}{\text{Resistance}}$$

Equivalent conductance : Equivalent conductance (λ_C) is defined as the conductance of an electrolyte solution containing one gram equivalent of the electrolyte. It is equal to the product of specific conductance (κ) of the solution and the volume (V) of the solution that contains one gram equivalent of the electrolyte.

$$(\lambda_C) = \kappa \times V$$

In general if an electrolyte solution contains N gram-equivalents in 1,000 cc of the solution the volume of the solution containing 1 gram equivalent will be $\frac{1000}{N} \times 10^{-6}$ m^3 (1 cc = 10^{-6} m^3)

$$\therefore \lambda_C = \kappa \frac{10^{-3}}{N} \text{ mho.m}^2 \text{ gm.equiv.}^{-1}$$

for 1 : 1 electrolyte normality N equals to molarity 'C'. Then

$$\lambda_C = \frac{\kappa \times 10^{-3}}{C} \text{ mho.m}^2\text{.(gm.equiv)}^{-1}$$

λ_C values depend on the type of the electrolyte, concentration of the solution and temperature.

Molar conductance : Molar conductance 'μ_C' is defined as the conductance of a solution containing one mole of the electrolyte dissolved in it.

$$\therefore \mu_C = \frac{\kappa \times 10^{-3}}{M} \text{ mho.m}^2\text{.mole}^{-1}$$

where M is the molarity of the electrolyte solution.

For 1 : 1 electrolyte like NaCl, equivalent conductance is equal to molar conductance.

Summary of electrochemical quantities.

Quantity	**Symbol**	**Unit**
Resistance	R	ohm (or) Ω
Resistivity (or) specific resistance	ρ	ohm.m.
Conductance	$\frac{1}{R}$	ohm^{-1} (or) Siemen
Specific conductivity (or) specific conductance	κ	ohm^{-1} m^{-1}
Volume (or) dilution	V	m^3
Equivalent conductance	λ_C	ohm^{-1} m^2 (gm.equiv)$^{-1}$
Molar conductance	μ_C	ohm^{-1} m^2 mole^{-1}

13.6 VARIATION OF EQUIVALENT CONDUCTANCE WITH CONCENTRATION

The effect of concentration on equivalent conductance can be studied from the plots of λ_C values versus square root of concentration of the electrolyte. By doing so, it has been found that different types of plots are obtained depending on the nature of electrolyte. For strong electrolytes λ_C decreases linearly with increase in $\sqrt{C}$ while for weak electrolytes, there is a curve type of non linear decrease of λ_C with $\sqrt{C}$.

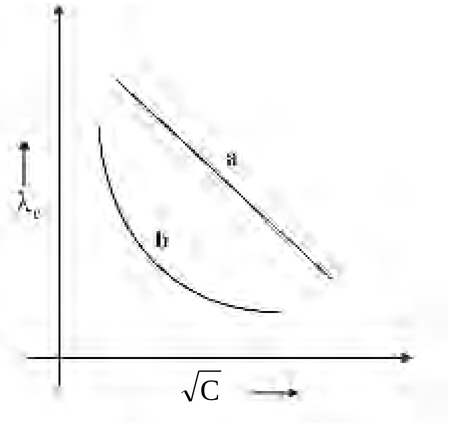


Fig. 13.2 Variation of equivalent conductivity λ_c with $\sqrt{C}$ for (a) strong electrolytes and (b) weak electrolytes.

For strong electrolytes Debye, Huckel and Onsager equation can be applied.

$\lambda_C = \lambda_\infty - (A + B\,\lambda_\infty)\sqrt{C}$ to the linear plot of λ_C versus $\sqrt{C}$ for strong electrolytes, the intercept value equals to λ_∞ value which is obtained by extrapolating the line to 'y' axis ($\sqrt{C} = 0$). The slope value equals to $(A + B\,\lambda_\infty)$. A and B are called as Debye constants for strong electrolytes.

In case of weak electrolytes, degree of dissociation (α) increases when concentration decreases. Hence, $(1 - \alpha)$ value tends to zero at infinite dilution, such that λ_C increases and tends to λ_∞ value.

λ_∞ of weak electrolytes are experimentally obtained by extrapolating the upper arm of the curve to the Y axis and the intercept value corresponds to λ_∞. In the intermediate concentration range, λ_C is lower than λ_∞ since the weak electrolyte exists in partially ionised state. The degree of dissociation α equals to the ratio of λ_C to λ_∞ value. (i.e., $\alpha = \lambda_C / \lambda_\infty$).

Example 1. The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 25°C using a conductance cell with a cell constant 0.88 cm^{-1}. Calculate the specific conductance and equivalent conductance of the solution.

Solution : R = 210 ohm ; $\frac{l}{a} = 0.88\ \text{cm}^{-1}$

$$\text{Specific conductance } \kappa = \frac{l}{a} \times \frac{1}{R}$$

$$= \frac{0.88\,\text{cm}^{-1}}{210\,\text{ohm}} = 4.19 \times 10^{-3}\ \text{mho.cm}^{-1}$$

$$= 4.19 \times 10^{-3}\ \text{mho.m}^{-1}$$

Equivalent conductance, $\lambda = \kappa \times V$

V has 1 gram equivalent dissolved given is 0.01 N in 1000 ml.

$$\therefore V = \frac{1000}{0.01} = 1{,}00{,}000 \text{ ml}$$

$$\lambda = 4.19 \times 10^{-3} \times 1{,}00{,}000$$

$$\lambda = 419.05 \text{ mho.cm}^2\text{.gm.equiv.}^{-1}$$

$$= 4.1905 \times 10^{-2} \text{ mho m}^2 \text{ (gm.equiv)}^{-1}$$

Example 2. 0.04 N solution of a weak acid has a specific conductance 4.23×10^{-4} mho.cm^{-1}. The degree of dissociation of acid at this dilution is 0.0612. Calculate the equivalent conductance of weak acid at infinite solution.

Solution : Specific conductance $\kappa = 4.23 \times 10^{-4}$ mho.cm^{-1}

$$\lambda_C = \frac{\kappa 1000}{C} = \frac{4.23 \times 10^{-4} \times 1000}{0.04}$$

$$= 10.575 \text{ mho.cm}^2\text{.eq}^{-1}.$$

$$\alpha = 0.0612 = \frac{\lambda_C}{\lambda_\infty} = \frac{10.575}{\lambda_\infty}$$

$$\therefore \lambda_\infty = 172.79 \text{ mho.cm}^2\text{.gm.equiv.}^{-1}$$

Example 3. Equivalent conductivity of acetic acid at infinite dilution is 39.7 and for 0.1 M acetic acid the equivalent conductance is 5.2 mho.cm^2.gm.equiv.$^{-1}$. Calculate degree of dissociation, H^+ ion concentration and dissociation constant of the acid.

Solution : $\alpha = \frac{\lambda_C}{\lambda_\infty} = \frac{5.2}{390.7} = 0.01333 = 1.33\%$

$$\begin{array}{cccc} CH_3COOH & \rightleftharpoons & H^+ & + \ CH_3COO^- \\ C(1-\alpha) & & C\alpha & C\alpha \end{array}$$

$$\therefore [H^+] = C\alpha = 0.1 \times 0.0133 = 0.00133 \text{ M}$$

$$K = \frac{\alpha^2 C}{1-\alpha} = \frac{0.0133^2 \times 0.1}{(1-0.0133)} = 2.38 \times 10^{-5} \text{ M}$$

13.7 KOHLRAUSH'S LAW

This law states that, ''at infinite dilution wherein the ionisation of all electrolytes is complete, each ion migrates independently and contributes a definite value to the total equivalent conductance of the electrolyte''. Consider an electrolyte AB in aqueous solution. It dissociates as

$$A_m B_n \longrightarrow mA^{n+} + nB^{m-}$$

Then at infinite dilution, according to Kohlrausch's law, the total equivalent conductance of the electrolyte, $\lambda_\infty = \frac{1}{n^+} \lambda_A{}^+ + \frac{1}{m^-} \lambda_B{}^-$ where $\lambda_\infty{}^+$ and $\lambda_\infty{}^-$ are the cationic and anionic equivalent conductances at infinite dilutions and n^+ and m^- correspond the valency of cations and anions furnished from each molecule of the electrolyte.

$$\lambda_\infty, \mathrm{NaCl} = \lambda_\infty \mathrm{Na}^+ + \lambda_\infty \mathrm{Cl}^-$$

$$\lambda_\infty, \mathrm{BaCl_2} = \frac{1}{2} \lambda_\infty \mathrm{Ba}^{2+} + \lambda_\infty \mathrm{Cl}^-$$

$$\lambda_\infty, \mathrm{AlCl_3} = \frac{1}{3} \lambda_\infty \mathrm{Al}^{3+} + \lambda_\infty \mathrm{Cl}^-$$

$$\lambda_\infty, \mathrm{Al_2(SO_4)_3} = \frac{1}{3} \lambda_\infty \mathrm{Al}^{3+} + \frac{1}{2} \lambda_\infty \mathrm{SO_4}^{2-}$$

For weak electrolytes,

$$\lambda_\infty, \mathrm{CH_3COOH} = \lambda^+_\infty \mathrm{H}^+ + \lambda_\infty^- \mathrm{CH_3COO}^-$$

$$\lambda_\infty, \mathrm{NH_4OH} = \lambda_\infty^+ \mathrm{NH_4}^+ + \lambda_\infty^- \mathrm{OH}^-$$

Application of Kohlraush's law : The important use of Kohlraush's law is to deduce the λ_∞ value of the weak electrolytes correctly by arithmetically combining the λ_∞ values of strong electrolyte in appropriate manner.

For example λ_∞ of CH_3COOH which is a weak electrolyte is deduced from λ_∞ values of NaCl, HCl, and CH_3COONa in such a manner that λ_∞ of CH_3COOH is obtained. Sodium acetate (CH_3COONa) is a strong electrolyte and it ionises to acetate (CH_3COO^-) and sodium (Na^+) ions at all concentrations in water. Applying Kohlraush's law,

λ_∞ CH_3COONa + λ_∞ HCl – λ_∞ NaCl =

$\lambda_\infty CH_3COO^- + \lambda_\infty Na^+ + \lambda_\infty H^+ + \lambda_\infty Cl^- - \lambda_\infty Na^+ - \lambda_\infty Cl^-$

$\lambda_\infty CH_3COO^- + \lambda_\infty H^+ = \lambda_\infty CH_3COOH$

This method produces agreeable values of λ_∞ for weak electrolytes.

Similarly λ_∞ NH_4OH can be deduced as,

$$\begin{aligned}\lambda_\infty NH_4OH &= \lambda_\infty NH_4^+ + \lambda_\infty OH^- \\ &= \lambda_\infty NH_4^+ + \lambda_\infty Cl^- + \lambda_\infty Na^+ + \lambda_\infty OH^- - \lambda_\infty Na^+ - \lambda_\infty Cl^- \\ &= \lambda_\infty NH_4Cl + \lambda_\infty NaOH - \lambda_\infty NaCl\end{aligned}$$

Molar conductances at infinite dilution : (μ_∞) when an electrolyte dissociates into γ_+ number of cations and γ_- number of anions then total molar conductance at infinite dilution μ_∞ of the electrolyte is given by

$$A_{\gamma+} B_{\gamma-} \longrightarrow \gamma_+ A^+ + \gamma_- B^-$$

$$\text{then} \quad \mu_\infty = \gamma_+ \mu_\infty^{\ +} + \gamma_- \mu^-_{\ \infty}$$

where $\mu^-_{\ \infty}$ and $\mu^+_{\ \infty}$ are the ionic conductances at infinite dilution.

$$\therefore \mu_\infty BaCl_2 = \mu_\infty Ba^{2+} + 2\,\mu_\infty Cl^-$$

$$\mu_\infty Na_2SO_4 = 2\,\mu_\infty Na^+ + \mu_\infty SO_4^{\ 2-}$$

Example 4 : Ionic conductances at infinite dilution of Al^{3+} and $SO_4^{\ 2-}$ are 189 ohm^{-1} cm^2 $gm.equiv.^{-1}$ and 160 ohm^{-1} cm^2 $gm.equiv.^{-1}$. Calculate equivalent and molar conductance of the electrolyte at infinite dilution.

The electrolytes $Al_2(SO_4)_3$

$$\lambda_\infty Al_2(SO_4)_3 = \frac{1}{3}\lambda_\infty Al^{3+} + \frac{1}{2}\,\lambda_\infty SO_4^{\ 2-}$$

$$\lambda_\infty Al_2(SO_4)_3 = \frac{189}{3} + \frac{160}{2} = 63 + 80 = 143 \text{ mho cm}^2 \text{ gm.equi}^{-1}$$

$$\mu_\infty Al_2(SO_4)_3 = 2 \times 189 + 3 \times 160 = 858 \text{ mho cm}^2 \text{ mol}^{-1}$$

The common ion effect

When a soluble salt (say A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A+), the dissociation of AB is suppressed.

$$AB \rightleftharpoons A^+ + B^-$$

By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to Le Chatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ ions or the degree of dissociation of AB will be reduced.

The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the Common-ion effect.

Let us consider a few examples to illustrate the common-ion effect.

Example 1. In a saturated solution of silver chloride, we have the equilibrium

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

When sodium chloride is added to the solution, the concentration of Cl^- ions will increase. The equilibrium shown above will be shifted to the left to form more of solid AgCl. Thus the solubility of AgCl, a typical sparingly soluble salt, will decrease.

Example 2. When solid NH_4Cl is added to NH_4OH solution, the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

shifts to the left. Thereby the equilibrium concentration of OH^- decreases. This procedure of reducing the concentration of OH^- ions is used in qualitative analysis.

Example 3. The common-ion effect can also be applied to the ionic equilibrium of a weak acid as HF.

$$HF \rightleftharpoons H^+ + F^-$$

NaF is added to the equilibrium mixture. The concentration of F^- (common ion) is increased. Thus the equilibrium shits to the left. In other words, the degree of dissociation of HF decreases. It was found by experiment that the degree of dissociation HF in 1M solution is 2.7 while the value reduces to 7.2×10^{-4} after the addition of 1 M NaF.

Example 4. Find the degree of dissociation of HF in 1 M aqueous solution. The value of K for the ionic equilibrium $HF = H^+ + F^-$ is 7.2×10^{-4}.

Solution : HF dissociates in water to form H^+ and F^- ions. On reaching the equilibrium we have

$$HF \rightleftharpoons H^+ + F^-$$

Thus one mole of HF taken initially dissociates to yield 1 mole of H^+ and 1 mole of F^-.

If x be the degree of dissociation, the concentration terms at equilibrium are :

$$[HF] = (1 - x) \text{ mol/L}$$

$$[F^-] = x \text{ mol/L}$$

$$[H^+] = x \text{ mol/L}$$

Substituting these values in the equilibrium expression, we have

$$K = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{(1-x)}$$

If x is very small compared to 1, we can write :

$$7.2 \times 10^{-4} = \frac{x^2}{1.00}$$

$$\therefore x = (7.2 \times 10^{-4})^{1/2}$$

$$= 2.7 \times 10^{-2}$$

Thus the degree of dissociation of HF in 1 M solution is 2.7×10^{-2}.

13.8 IONIC PRODUCT OF WATER

Water is a weak electrolyte. The dissociation equilibrium of water can be considered as,

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

According to law of mass action,

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since water as a solvent is always in excess and change in concentration due its dissociation is negligible. Hence water concentration is assumed to be constant.

$$\therefore \quad K_{eq}\,[H_2O]^2 = [H_3O^+]\,[OH^-] = K_w$$

The constant K_w is called as the ionic product of water and its value is given by the product of concentrations of hydronium (H_3O^+) and hydroxide (OH^-) ions. At 298 K, $K_w = 1 \times 10^{-14}$ mol^2.dm^{-6}.

The pH of solutions

A knowledge of the concentration of hydrogen ions (more specifically hydronium ions) is of the greatest importance in chemistry. Hydrogen ion concentrations are typically quite small numbers. Therefore, chemists report the hydrogen ion concentration of a solution in terms of pH. It is defined as **the negative of the base-10 logarithm (log) of the H^+ concentration.** Mathematically it may be expressed as

$$pH = -\log_{10}[H^+]$$

where $[H^+]$ is the concentration of hydrogen ions in moles per litre

Alternative and more useful forms of pH definition are :

$$pH = \log \frac{1}{[H^+]}$$

and $$[H^+] = 10^{-pH}$$

The pH concept is very convenient for expressing hydrogen ion concentration. It was introduced by Sorensen in 1909. It is now used as a general way of expressing other quantities also, for example.

(a) Concentration of OH^- ions in aqueous solution of a base is expressed as

$$p\,[OH^-] = -\log_{10}[OH^-]$$

(b) Equilibrium constant for water is written as

$$pK_w = -\log_{10}[K_w]$$

For any quantity X, we can write

$$pX = -\log X$$

The 'p' in these expressions means ''–log of the quantity''.

The pH of a given solution can be measured with the help of an apparatus called pH meter.

Knowing the pH of the solution its hydrogen ion concentration can be calculated.

pH Scale

In order to express the hydrogen ion concentration or acidity of a solution, a pH scale was evolved. The pH is defined as

$$pH = -\log[H^+] \quad \text{or} \quad [H^+] = 10^{-pH}$$

The hydrogen ion concentrations of different acidic solutions were determined experimentally. These were converted to pH values using the above relations. Then these pH values were computed on a scale taking water as the reference substance. **The scale on which pH values are computed is called the pH scale.**

Water dissociates to H^+ and OH^- ions to a very small degree so that we have the equilibrium.

$$H_2O \rightleftharpoons H^+ + OH^-$$

Since $K_w = 1 \times 10^{-14}\ mol^2.dm^{-6}$.

$$[H_3O^+] = [H^+] = [OH^-] = \sqrt{1\times10^{-14}} = 1 \times 10^{-7}\ mol.dm^{-3}$$

Thus the H^+ ion and OH– ion concentrations in pure water are both 10^{-7} mol.dm^{-3} at 25°C and it is said to be neutral. In acidic solution, however, the concentration of H^+ ions must be greater than 10^{-7} mol. L^{-1}. Similarly in a basic solution, the concentration of OH^- ions must be greater than 10^{-7} mol L^{-1}. Thus we can state :

neutral solution $[H^+] = [OH^-]$

acidic solution $[H^+] > [OH^-]$

basic solution $[H^+] < [OH^-]$

Expressing the $[H^+]$ in terms of pH for the different solutions cited above, we get what we call the pH scale. On this scale the values range from 0 to 14. Since pH is defined as –log $[H^+]$ and the hydrogen ion concentration of water is 10^{-7}, the pH of water is 7. All solutions having pH less than 7 are acidic and those with pH greater than 7 are basic.

As shown by the pH scale, pH decreases with the increase of $[H^+]$. The lower the pH, higher is the $[H^+]$ or acidity.

To calculate $[H^+]$ and $[OH^-]$ from K_w. In any aqueous solution, the product of $[H^+]$ and $[OH^-]$ always equal to Kw. This is so irrespective of the solute and relative concentrations of H^+ and OH^- ions. However, the value of Kw depends on temperature. At 25°C it is 1.0×10^{-14}. Thus,

$$[H^+]\ [OH^-] = 1.0 \times 10^{-14}$$

Each of $[H^+]$ and $[OH^-]$ in pure water at 25°C is 10^{-7}. The concentrations of $[H^+]$ and OH^- ions are expressed in gram moles per litre.

The concentrations $[H^+]$ and $[OH^-]$ ions can be calculated from the expressions :

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[OH^-] = \frac{K_w}{[H^+]}$$

Relation between pH and pOH

pH concept can be used to express small quantities as $[OH^-]$ and K_w. Thus

$$pOH = -\log_{10} [OH^-]$$

$$pK_w = -\log_{10} K_w$$

Let us consider the log form of the expression

$$K_w = [H^+][OH^-]$$

That is $\log K_w = \log [H^+] + \log [OH^-]$

or $-\log K_w = -\log [H^+] - \log [OH^-]$

Thus $pK_w = pH + pOH$

Since $K_w = 1.0 \times 10^{-14}$

$$pK_w = -\log (1.0 \times 10^{-14}) = 14.00$$

Hence, for any aqueous solution at 25°C, pH and pOH add up to 14.00. That is,

$$pH + pOH = 14.00$$

In general, the pH problems may be of the following tpes :

Example 1. The hydrogen ion concentration of a fruit juice is 3.3×10^{-2} M. What is the pH of the juice ? Is it acidic or basic ?

Solution : The definition of pH is

We are given $[H^+] = 3.3 \times 10^{-2}$

Substituting into the definition of pH, we get

$$\begin{aligned} pH &= -\log(3.3 \times 10^{-2}) \\ &= -(-1.48) \quad = 1.48 \end{aligned}$$

Since the pH is less than 7.00, the solution is acidic.

Example 2. If a solution has a pH of 7.41, determine its H^+ concentration.

Solution :

$$\begin{aligned} pH &= -\log[H^+] \\ \therefore \quad [H^+] &= \text{antilog}[-pH] = \text{antilog}[-7.41] \\ \therefore \quad [H^+] &= 3.9 \times 10^{-8}\ M \end{aligned}$$

Example 3. pH of a solution is 5.5 at 25ºC. Calculate its $[OH^-]$

Solution :

$$\begin{aligned} pH + pOH &= 14.0 \qquad \therefore\ pOH = 14.0 - pH \\ &= 14.0 - 5.5 = 8.50 \\ pOH &= 8.5 \qquad \therefore\ \text{antilog}[-pOH] \\ \therefore\ [OH^-] &= \text{antilog}[-8.5] = 3.2 \times 10^{-9}\ M \end{aligned}$$

Example 4. Calculate the pH of 0.001 M HCl solution

$$HCl \longrightarrow H^+ + Cl^-. \qquad \text{HCl is a strong acid.}$$

$[H^+]$ from HCl is very much greater than [H+] from water which is 1×10^{-7} M.

$$\begin{aligned} \therefore \quad [H^+] &= [HCl] = 0.001\ M \\ \therefore \quad pH &= -\log(0.001) = 3.0 \end{aligned}$$

∴ That is acidic solution.

Example 5. Calculate the pH of 0.1 M CH_3COOH solution. Dissociation constant of acetic acid is 1.8×10^{-5} M.

For weak acids,

$$[H^+] = \sqrt{K_a \times C}$$

$$= \sqrt{1.8\times10^{-5}\times0.1} = \sqrt{1.8\times10^{-6}}$$

$$= 1.34 \times 10^{-3}\ M$$

$$\therefore \quad pH = -\log [H^+] = \log (1.34 \times 10^{-3})$$

$$\therefore \quad pH = 2.87$$

Example 6. Calculate the pH of 0.02 m $Ba(OH)_2$ aqueous solution assuming $Ba(OH)_2$ as a strong electrolyte.

$$Ba(OH_2) \longrightarrow Ba^{2+} + 2OH^-$$

$$\therefore \ [OH^-] = 2\,[Ba(OH)_2] = 2 \times 0.02 = 0.04\ M$$

$$\therefore \quad pOH = -\log [OH^-] = 1.398 = 1.40$$

$$\therefore \quad pH = 14 - 1.4 = 12.6$$

13.9 BUFFER SOLUTIONS

It is often necessary to maintain a certain pH of a solution in laboratory and industrial processess. This is achieved with the help of buffer solutions, buffer systems or simply buffers.

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

In other words, a buffer solution resists (or buffers) a change in its pH. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little. Two common types of buffer solutions are :

1. a weak acid together with a salt of the same acid with a strong base. These are called Acid buffers. (e.g.,) $CH_3COOH + CH_3COONa$.
2. a weak base and its salt with a strong acid. These are called Basic buffers. (e.g.,) $NH_4OH + NH_4Cl$.

Buffer action : Let us illustrate buffer action by taking example of a common buffer system consisting of a solution of acetic acid and sodium acetate (CH_3COOH/CH_3COONa).

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$$

since the salt is completely ionised, it provides the common ions CH_3COO^- in excess. The common ion effect suppresses the ionisation of acetic acid. This reduces the concentration of H^+ ions which means that pH of the solution is raised.

It is stated that a buffer solution containing equimolar amounts (0.10 M) of acetic acid and sodium acetate has pH 4.74. Now we proceed to discuss how the addition of a small amount of HCl or NaOH to the buffer solution affects its pH.

The pH of the buffer is governed by the equilibrium

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \text{... (1)}$$

The buffer solution has a large excess of CH_3COO^- ions produced by complete ionisation of sodium acetate,

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \text{... (2)}$$

1. Addition of HCl. Upon the addition of HCl, the decrease of H^+ ions is counteracted by association with the excess of acetate ions to form unionised CH_3COOH. Thus the added H^+ ions are neutralised and the pH of the buffer solution remains unchanged. However owing to the increased concentration of CH_3COOH, the equilibrium (1) shifts slightly to the right to increase H^+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl.

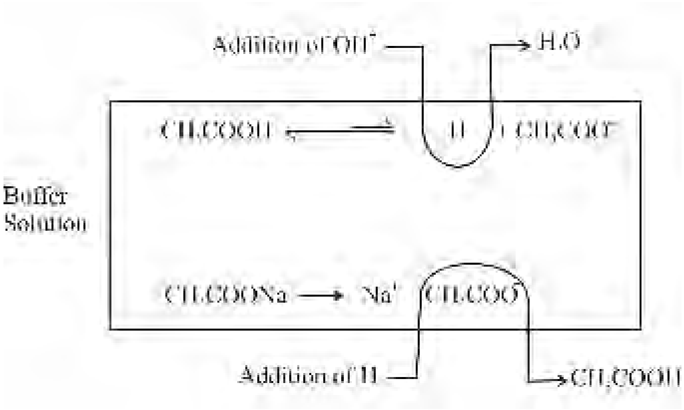


Fig. 13.3 Mechanism of Buffer action of an acid buffer.

2. Addition of NaOH. When NaOH is added to the buffer solution, the additional OH^- ions combine with CH_3COOH to give CH_3COO^- and H_2O. Thus pH of the buffer solution is maintained almost constant. The buffer NH_4OH/NH_4Cl can also be explained on the same lines as of an acid buffer upon addition of HCl the H^+ ions combine with NH_4OH to form NH_4^+ and H_2O. pH is retained. Similarly when NaOH is added, the OH^- ions combine with NH_4^+ ions present in the buffer solution to give NH_4OH and hence pH is maintained.

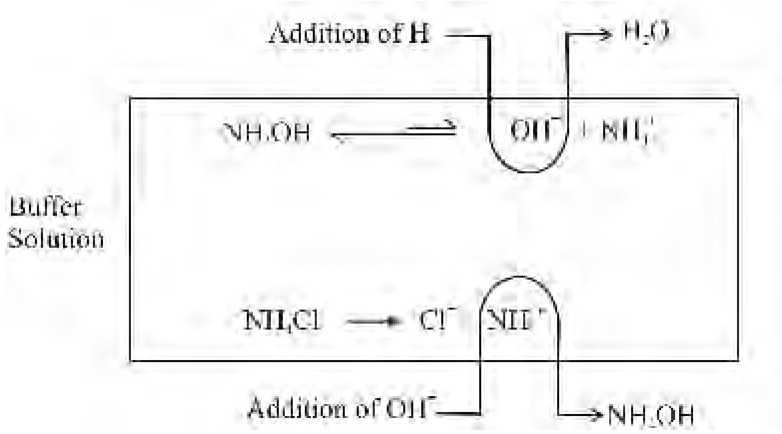


Fig. 13.4 Mechanism of buffer action of a basic buffer

Henderson equation : The pH of an acid buffer can be calculated from the dissociation constant, K_a, of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as

$$HA \rightleftharpoons H^+ + A^-$$

and $$K_a = \frac{[H^+][A^-]}{[HA]}$$

or $$[H^+] = \frac{[HA]K_a}{[A^-]} \qquad \text{... (1)}$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt ($Na^+ A^-$) which provides A^- ions (Common ion effect). As a result the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration $[A^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (1) as

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \qquad \text{... (2)}$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used.

Taking negative logs of both sides of the equation (2), we have

$$-\log [H^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]} \qquad \text{... (3)}$$

But $-\log [H^+] = pH$ and $-\log K_a = pK_a$

Thus from (3) we have

$$pH = pK_a - \log \frac{[acid]}{[salt]} = pKa + \log \frac{[salt]}{[acid]}$$

Hence, $$pH = pK_a + \log \frac{[salt]}{[acid]}$$

This relationship is called the **Henderson-Hasselbalch equation** or **simply Henderson equation.**

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

Significance of the Henderson-Hasselbalch equation. With its help

1. The pH of a buffer solution can be calculated from the initial concentrations of the weak acid and the salt provided K_a is given.

However, the Henderson-Hasselbalch equation for a basic buffer will give pOH and its pH can be calculated as (14 – pOH).

2. The dissociation constant of a weak acid (or weak base) can be determined by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Since, [salt] = [acid], $\log \frac{[salt]}{[acid]} = \log 1 = 0$

$$pK_a = pH$$

The measured pH, therefore, gives the value of pK_a of the weak acid.

Likewise we can find the pK_b of a weak base by determining the pOH of equimolar basic buffer.

3. A buffer solution of desired pH can be prepared by adjusting the concentrations of the salt and the acid added for the buffer.

It is noteworthy that buffer solutions are most effective when the concentrations of the weak acid (or weak base) and the salt are about equal. This means that pH is close to the value of pK_a of the acid (or pK_b of the base).

Example 1 : Find the pH of a buffer solution containing 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH, K_a for acetic acid is 1.8×10^{-5}

Solution :

$$K_a = 1.8 \times 10^{-5}$$

$$pK_a = -\log (1.8 \times 10^{-5}) = 4.7447$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

... Henderson - Hasselbalch equation

$$= 4.7447 + \log \frac{0.20}{0.15}$$

$$pH = 4.7447 + \log \frac{4}{3}$$

$$= 4.7447 + 0.6021 - 0.4771 = 4.8697$$

Example 2 : The K_a of propionic acid is 1.34×10^{-5}. What is the pH of a solution containing 0.5 M propionic and 0.5 M sodium proportionate ? What happens to the pH of the solution when volume is doubled by adding water ?

Solution : Ka of propionic acid = 1.34×10^{-5}

$$\therefore \quad pK_a = -\log K_a = -\log (1.34 \times 10^{-5})$$

$$= 4.87$$

By Herderson - Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.87 + \log \frac{0.5}{0.5}$$

$$pH = 4.87$$

Alternative solution : The dissociation equilibrium of propionic acid will be

$$C_2H_5COOH \longrightarrow C_2H_5COO^- + H^+$$

$$K_a = \frac{[C_2H_5COO^-][H^+]}{[C_2H_5COOH]} = \frac{0.5 \times [H^+]}{0.5}$$

$$= [H^+]$$

$$\therefore \quad pH = -\log [H^+]$$

$$= -\log K_a = -\log (1.34 \times 10^{-5})$$

$$\therefore \quad pH = 4.87$$

13.10 pH INDICATORS

An indicator is a substance which indicates the completion of a reaction by sharp colour change at the end point without taking part in the reaction. The substances which are used to indicate the end point in acid-base reactions are called as acid-base indicators. (e.g.,) phenolphthalein and methyl orange.

Those substances which change to specific colours in different pH range values of the medium are called as pH indicators. Incidentally pH indicators are used as acid-base indicators also.

Selection of pH indicators

Every pH indicator changes its colour specifically in a ranging pH which is called as indicator range. For some of the indicators, the indicator ranges are given as below.

		Colour of the indicator	
Indicator	**pH range**	**Acidic solution**	**Basic solution**
Methyl orange	3.1 - 4.4	Pink	Yellow
Methyl red	4.4 - 6.2	Red	Yellow
Phenol red	6.8 - 8.4	Yellow	Red
Phenolphthalein	8.3 - 10	Colourless	Pink

When a base is added to a solution of an acid, the H^+ ions will be slowly neutalised by the OH^- ions of the base. Hence, there is a steady decrease in the H^+ ion concentration and pH value increases uniformly. At the end point there is a steep rise in the pH value. The pH values can be plotted against the volume of the base added and the curve so obtained is called titration curve. The titration curves are useful in the choice of a suitable indicator in an acid-base titration. A suitable indicator in an acid-base titration is one whose range is well within the sharp rising portion of the titration curve. Thus the choice of a suitable indicator for any titration depends on the nature of the acid and base involved and the working range of the indicator.

1. Titration of a strong acid against a strong base : (Example, HCl vs NaOH)

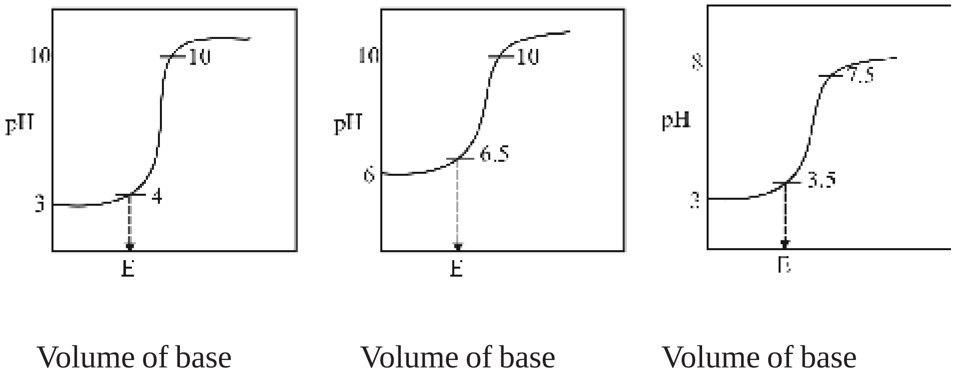
In this type of titration, the change in the pH value at the end point is roughly from 4 to 10. Therefore any indicator which changes its colour within this range may be used as a suitable indicator in the titration of strong acid against strong base and phenolphthalein can be used as indicators for this type of titrations.

2. Titration of a weak acid against a strong base : (Example, Oxalic acid vs NaOH)

There is a little change in the pH value at the end point in this type of titration. The pH value changes from 6.5 to 10. Thus phenolphthalein is the suitable indicator for this titration as its working range is 8.3 – 10. Methyl orange is not a suitable indicator. Since it has a working range below pH 5.

3. Titration of strong acid against weak base : (Example, HCl vs Na_2CO_3]

When a strong acid like HCl is titrated against a weak base like Na_2CO_3, the pH changes from 3.5 to 7.5 at the end point. The best indicator for this type of titration is methyl orange which changes its colour within this pH range.



(a) strong acid vs strong base **(b) weak acid vs strong base** **(c) strong acid vs weak base**

E-end point

4. Titration of weak acid against weak base : (Example, CH_3COOH vs NH_4OH)

In this sypte of titration there is no sharp change in the pH value at the end point. Therefore, in the titration of a weak acid against a weak base none of the indicators shown in the table are quite satisfactory.

There are two theories to explain the function of acid-base indicators.

1. Ostwald's theory

This theory was proposed by Ostwald's in 1891. It is based on Arrhenius theory. According to this theory, the acid-base indicator is either a weak acid or a weak base. They are partially ionised in solution. The ionised and unionised forms have different colours. The indicator exists predominantly in one of the two forms depending on the nature of the medium and hence there is colour change when the nature of the medium changes. Phenolphthalein is a weak acid and it is partially ionised in solutions.

$$\underset{\substack{\text{Unionised form}\\ \text{(colourless)}}}{HPh} \rightleftharpoons H^+ + \underset{\substack{\text{ionised form}\\ \text{(pink)}}}{Ph^-}$$

In acidic medium, excess H^+ ions are present which suppress the dissociation of HpH due to common ion effect. Hence the indicator exists predominantly in unionised form and it is colourless. In alkaline medium, the OH^- ion neutralises H^+ ion to form water. Consequently the dissociation of HpH is favoured and the indicator is predominantly in the ionised form and it is pink in colour.

Methyl orange is a weak base and its ionisation can be written as

$$\underset{\substack{\text{Unionised form}\\ \text{(yellow)}}}{\text{MeOH}} \rightleftharpoons \underset{\substack{\text{ionised form}\\ \text{(pink)}}}{\text{Me}^+ + \text{OH}^-}$$

In the presence of a base excess OH^- ions suppress the dissociation of MeOH due to common ion effect. Hence in basic medium, the indicator is mostly in unionised form which is yellow.

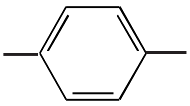
In acidic solution the H^+ ions combine with OH^- ions to form unionised water. Hence in acidic solution, the indicator is mostly in ionised form and has pink colour.

This theory also explains why phenolphthalein is not a suitable indicator in the titration of a strong acid against a weak base. The reason is the OH^- ions produced by the weak base at the end point is too low to cause the ionisation of phenolphthalein. Hence, the pink colour does not appear exactly at the equivalence point. The pink colour appears only after a sufficient excess of the weak base is added.

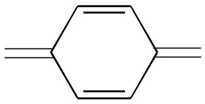
For a similar reason, methyl orange is not a suitable indicator in the titration of a strong base against a weak acid. The weak acid does not furnish sufficient H^+ ions to shift the equilibrium towards the right. A sufficient excess of the weak acid has to be added to get the colour change.

Quinonoid Theory

According to this theory the colour change of an acid-base indicator arises as a result of structural change. It is supposed that an indicator exists as an equilibrium mixture of two tautomeric forms namely, benzenoid and quinonoid forms.



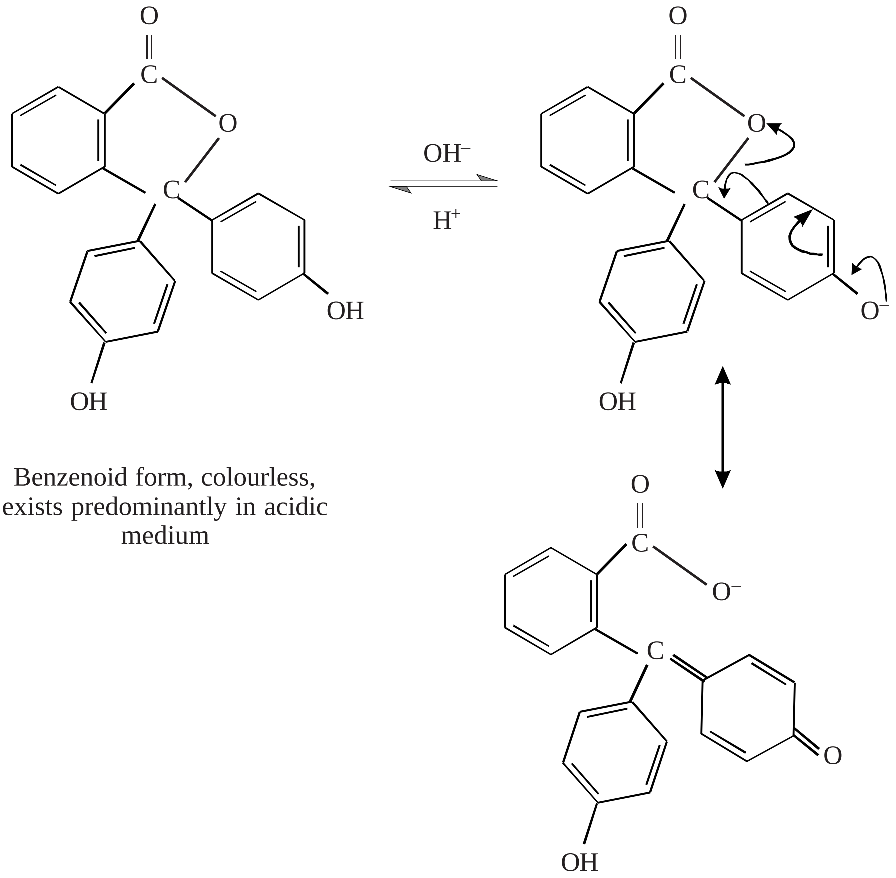
benzenoid form



quinonoid form

One form exists in acidic solution and the other form in basic solution. At least one of the tautomers is a weak acid or a weak base. The two forms possess two different colours and as the pH of the solution containing the indicator is changed, the solution shows a change of colour. The colour change is due to the fact that one tautomer changes over to the other.

For example, phenolphthalein is tautomeric mixture of the two forms.



Benzenoid form, colourless,
exists predominantly in acidic
medium

Quinonoid form, pink,
exists predominant
in basic medium

SELF EVALUATION

(A) Choose the correct answer :

1. The process in which chemical change occurs on passing electricity is termed as ....

   (a) neutralisation (b) hydrolysis
   (c) electrolysis (d) ionisation

2. The laws of electrolysis were enunciated first by ....

   (a) Dalton (b) Faraday (c) Kekule (d) Avogadro

3. When one coulomb of electricity is passed through an electrolytic solution, the mass deposited on the electrode is equal to ....

   (a) equivalent weight (b) molecular weight
   (c) electrochemical equivalent (d) one gram

4. Faraday's laws of electrolysis are related to ....

   (a) atomic number of the cation (b) atomic number of the anion
   (c) equivalent weight of the electrolyte (d) speed of the cation

5. The specific conductance of a 0.01 M solution of KCl is 0.0014 ohm^{-1} cm^{-1} at 25^{o}C. Its equivalent conductance is ....

   (a) 14 ohm^{-1} cm^2 eq^{-1} (b) 140 ohm^{-1} cm^2 eq^{-1}
   (c) 1.4 ohm^{-1} cm^2 eq^{-1} (d) 0.14 ohm^{-1} cm^2 eq^{-1}

6. The equivalent conductivity of CH_3COOH at 25^{o}C is 80 ohm^{-1} cm^2 eq^{-1} and at infinite dilution 400 ohm^{-1} cm^2 eq^{-1}. The degree of dissociation of CH_3COOH is ....

   (a) 1 (b) 0.2 (c) 0.1 (d) 0.3

7. When sodium acetate is added to acetic acid, the degree of ionisation of acetic acid ....

   (a) increases (b) decreases
   (c) does not change (d) becomes zero

8. NH_4OH is a weak base because ....

   (a) it has low vapour pressure (b) it is only partially ionised
   (c) it is completely ionised (d) it has low density

9. Which one of the following formulae represents Ostwald's dilution law for a binary electrolyte whose degree of dissociation is α and concentration C.

(a) $K = \frac{(1-\alpha)C}{\alpha}$ (b) $K = \frac{\alpha^2 C}{1-\alpha}$ (c) $K = \frac{(1-\alpha)C}{\alpha^2}$ (d) $K = \frac{\alpha^2 C}{(1-\alpha)C}$

10. Ostwald's dilution law is applicable in the case of the solution of ....

(a) CH_3COOH (b) NaCl (c) NaOH (d) H_2SO_4

11. Which one of the following relationship is correct ?

(a) $pH = \frac{1}{[H^+]}$ (b) $pH = \log_{10} [H^+]$

(c) $\log_{10} pH = [H^+]$ (d) $pH = \log_{10} \frac{1}{[H^+]}$

12. When 10^{-6} mole of a monobasic strong acid is dissolved in one litre of solvent, the pH of the solution is ....

(a) 6 (b) 7 (c) less than 6 (d) more than 7

13. When pH of a solution is 2, the hydrogen ion concentration in moles litre-1 is ....

(a) 1×10^{-12} (b) 1×10^{-2} (c) 1×10^{-7} (d) 1×10^{-4}

14. The pH of a solution containing 0.1 N NaOH solution is ....

(a) 1 (b) 10^{-1} (c) 13 (d) 10^{-13}

15. A solution which is resistant to changes of pH on addition of small amounts of an acid or a base is known as ....

(a) buffer solution (b) true solution
(c) isohydric solution (d) ideal solution

16. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its salt is given by ....

(a) $[H^+] = K_a \frac{[Acid]}{[Salt]}$ (b) $[H^+] = K_a [Salt]$

(c) $[H^+] = K_a [Acid]$ (d) $[H^+] = K_a \frac{[Salt]}{[Acid]}$

17. Indicators used in acid-base titrations are ....
   (a) strong organic acids
   (b) strong organic bases
   (c) weak organic acids or weak organic bases
   (d) non-electrolysis
18. For the titration between oxalic acid and sodium hydroxide, the indicator used in ....
   (a) potassium permanganate (b) phenolphthalein
   (c) litmus (d) methyl orange

(B) Answer in one or two sentences :

1. Differentiate between electrolytic conductor and metallic conductor.
2. Define Faraday.
3. Define electrochemical equivalent.
4. What are insulators. Give examples.
5. State Ostwald's dilution law.
6. What is common ion effect. Give examples.
7. What is a buffer action ?
8. What are indicators ?
9. Define specific and equivalent conductance. How are they related ?
10. What is Henderson equation ?

(C) Answer not exceeding sixty words :

1. Write an account of the Arrhenius theory of electrolytic dissociation.
2. Explain Faraday's laws of electrolysis.
3. Explain Ostwald's dilution law.
4. Explain buffer action with example.
5. Derive Henderson equation.
6. Write notes on (i) Ostwald's theory of indicators, (ii) Quinonoid theory of indicators.

7. Define molar, equivalent and specific conductance and describe the effect of dilution.
8. State and explain Kohlrausch's law.
9. State and explain Debye-Huckel-Onsager equation.

(D) Solve the problems :

1. What is the electrochemical equivalent of a substance when 150 gm of it is deposited by 10 ampere of current passed for 1 sec ? [**Ans.** 15.0]
2. The electrochemical equivalent of an electrolyte is 2.35 gm. amp^{-1} sec^{-1}. Calculate the amount of the substance deposited when 5 ampere is passed for 10 sec ? [**Ans.** 117.5 gm]
3. To 1 M solution of $AgNO_3$, 0.75 F quantity of current is passed. What is the concentration of the electrolyte, $AgNO_3$ remaining in the solution ?
4. 0.5 F of electric current was passed though 5 molar solutions of $AgNO_3$, $CuSO_4$ and $AlCl_3$ connected in series. Find out the concentration of each of the electrolyte after the electrolysis ? [**Ans.** $AgNO_3$, 4.5 M ; $CuSO_4$; 4.75 M ; $AlCl_3$; 4.839 M]
5. To one molar solution of a trivalent metal salt, electrolysis was carried out and 0.667 M was the concentration remaining after electrolysis. Calculate the quantity of electricity passed. [**Ans.** 1F]
6. A conductance cell has platinum electrodes, each with 5 cm^2 area and separated by 0.5 cm distance. What is the cell constant?[**Ans.** 0.1 cm^{-1}]
7. Using a conductivity cell with 0.9 cm^{-1} cell constant, the conductance was observed to be 2.5×10^{-3} mho for 0.07 M KCl solution. What is the specific conductance of the solution ? [**Ans.** 2.25×10^{-3} mho.cm^{-1}]
8. Specific conductance of 1 M KNO_3 solution is observed to be 5.55×10^{-3} mho.cm^{-1}. What is the equivalent conductance of KNO_3 when one litre of the solution is used ?[**Ans.** 5.55 mho.cm^2.gm.equiv^{-1}]
9. Explain why on dilution does the conductivity decrease whereas molar conductivity increases for an electrolytic solution.

10. The equivalent conductances at infinite dilution of HCl, CH_3COONa and NaCl are 426.16, 91.0 and 126.45 ohm^{-1} cm^2 gm.equivalent^{-1} respectively.. Calculate the λ_∞ of acetic acid.

[**Ans.** 390.71 ohm^{-1}. cm^2 gm equiv^{-1}]

SUMMARY :

- ☞ Differences between electronic, electrolytic and semiconductors are studied. Intrinsic and extrinsic semi conductors are learnt.
- ☞ Arrhenius theory of weak electrolytes and its limitations are known.
- ☞ Onsager's equation for equivalent conductors of strong electrolytes is learnt and its dependence with $\sqrt{C}$ is studied.
- ☞ Statements of Faraday's laws of electrolysis and their significances are studied.
- ☞ Quantitative calculation on amount of electricity and mass deposited at the electrodes are learnt.
- ☞ Definitions and mathematical expressions of resistance, conductance, specific, equivalent and molar conductances are learnt and studied.
- ☞ Variations of conductances with dilution for strong and weak electrolytes are leant and understood.
- ☞ Kohlrausch's law is defined and studied. It's significances are also understood.
- ☞ Buffer action, nature of acidic and basic buffers, Henderson equation are studied.
- ☞ Use of pH values, indicators with applications of different pH ranges are studied.

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14. ELECTROCHEMISTRY - II

LEARNING OBJECTIVES

- *Properties and nature of cells will be understood. The differences between electrolytic and electrochemical cells will be learnt. Interconversion of electrical and chemical energy will be emphasized.*
- *Metal - metal ion electrode and standard hydrogen electrode construction and the electrode potential will be learnt. Nernst equation will be learnt.* $\Delta G = -nFE$ *and the interconversion of change in free energy and electrode potentials will be explained.*
- *Construction of cells with specific electrodes and the EMF calculations will be studied. Daniel cell, and its representation, EMF of cell from two half cell potentials will also be calculated.*
- *Complete electrochemical cell representation and writing oxidation and reduction half cell reactions will be studied with suitable example.*

14.1 CELLS

In electrochemistry, the interconversion of chemical energy and electrical energy is an important aspect that possesses numerous applications. For example, batteries supply electrical energy stored in the form of chemical energy for the operation of torch, radio, calculators etc. Conversely, electrical energy is used to bring about certain chemical reactions which are industrially important such as purification of metals like copper, aluminium, generation of gaseous chlorine, oxygen, hydrogen, electroplating, metal coatings etc. The electrochemical or electrolytic processes are carried out in a device known as a cell. An electrolytic (or) electrochemical cell consists of two conducting metal electrodes in contact with an electrolyte solution which separates them (or) placed separately in compartments containing suitable electrolytes. The electrolyte may be an aqueous solution containing mostly the salt of the metal with which the electrode is made of (or) it may be an ionically conducting solid.

There are two types of cells known as electrolytic cell and electrochemical cell. Each of them possesses different characteristics and used in different application.

Generally at the anode oxidation reaction occurs and at the cathode reduction reaction occurs. When the electrodes are connected externally through a wire and electrons flow through them, the electrical circuit is said to be an open circuit. If the electrodes are not connected externally and the electrons do not flow from one electrode into the other, the electrical circuit is said to be a closed circuit.

Daniel cell : Daniel cell or a galvanic cell is an example of electrochemical cell. The overall reaction taking place in the cell is the redox reaction given as

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This overall reaction is made of the summation of two half reactions such as oxidation half reaction and reduction half reaction.

The oxidation half reaction occurring at the zinc electrode in contact with the aqueous electrolyte containing Zn^{2+}, accumulates the electrons at the zinc rod.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

The reduction half reaction occurring at the copper electrode in contact with the aqueous electrolyte containing Cu^{2+} ions receives the electrons from the zinc electrode when connected externally, to produce metallic copper according to the reaction as,

$$Cu^{2+} \quad + \quad 2e^- \longrightarrow \quad Cu_{(s)}$$

The decrease in the energy which appears as the heat energy when a zinc rod is directly dipped into the zinc sulphate solution, is converted into electrical energy when the same reaction takes place indirectly in an electrochemical cell. The zinc sulphate is placed in the porous pot while copper sulphate is placed in a glass vessel.

The Daniel cell is also called as the voltaic cell. However for continuous supply of current for a long period, the two half cells each comprising the metal electrode and its aqueous electrolyte kept in separate containers and can be connected externally as below :

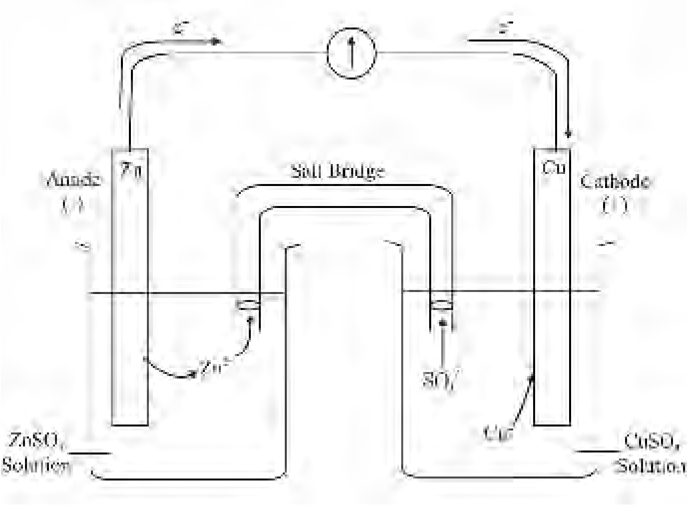

Fig. 14.3 A simple voltaic (galvanic) cell

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half cell pick up electrons and are converted to Cu atoms on the cathode.

Cell Terminology

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

Electrolyte is the salt solution in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode in contact with metal ion in solution.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

Phase Boundary

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \qquad\qquad \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

ANODE HALF-CELL **CATHODE HALF-CELL**

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

(2) A double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

(3) Anode half-cell is written on the left and cathode half-cell on the right.

(4) In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

Salt Bridge

$$\text{Zn} \mid \text{Zn}^{2+} \quad \| \quad \text{Cu}^{2+} \mid \text{Cu}$$

ANODE HALF-CELL **CATHODE HALF-CELL**

(5) The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket. For **example**,

$$\text{Mg} \mid \text{Mg}^{2+} \quad \| \quad \text{H}^{+} \mid \text{H}_2(\text{Pt})$$

Inert Electrode

ANODE HALF-CELL **CATHODE HALF-CELL**

(6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as

$$\text{Zn} \mid \text{ZnSO}_4 \quad \| \quad \text{CuSO}_4 \mid \text{Cu} \qquad E = +\,1.1\ \text{V}$$

⟶ **Direction of electron flow**

If the emf acts in the opposite direction through the cell circuit it is denoted as a negative value.

$$\text{Cu} \mid \text{CuSO}_4 \quad \| \quad \text{ZnSO}_4 \mid \text{Zn} \qquad E = -\,1.1\ \text{V}$$

⟵ **Direction of electron flow**

The negative sign also indicates that the cell is not feasible in the given direction and the reaction will take place in the reverse direction only. The overall cell reaction for E = –1.1 V of the daniel cell is

$$Cu_{(s)} + Zn_{(aq)}^{2+} \longrightarrow Cu_{(aq)}^{2+} + Zn_{(s)}$$

The reversal of the cell current is accompanied by the reversal of direction of the cell reaction. Thus a reversible cell is defined as that operates by reversal of cell reactions when the direction of flow of current is reversed. The reversible behaviour operates only for infinitesimal changes in e.m.f. of the cell on the positive and negative sides from the balance point which corresponds to the actual emf of the cell.

14.2 SINGLE ELECTRODE POTENTIAL

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (a) concentration of ions in solution ; (b) tendency to form ions ; and (c) temperature.

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard conditions are : (a) 1 M solutions of reactants and products ; and (b) temperature of 25^o C. Thus standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at 25^o C. Standard emf of a cell is represented by the symbol E^o. For gases 1 atm. pressure is a standard condition instead of concentration. For Zn-Cu voltaic cell, the standard emf, E^o is 1.10V.

$$Zn \mid Zn^{2+}_{(aq,\ 1M)} \parallel Cu^{2+}_{(aq,\ 1M)} \mid Cu \qquad E^o = 1.10\ V$$

Determination of emf of a half-cell

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. The emf of the newly constructed cell, E is determined with a voltmeter. The emf of the unknown half-cell E^o can then be calculated from the expression

$$E_{measured} \quad = \quad E_R - E_L$$

If the standard half-cell acts as anode, the equation becomes

$$E_R \quad = \quad E_{measured} \qquad (\because E_L = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L \quad = -E_{measured} \qquad (\because E_R = 0)$$

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE), is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

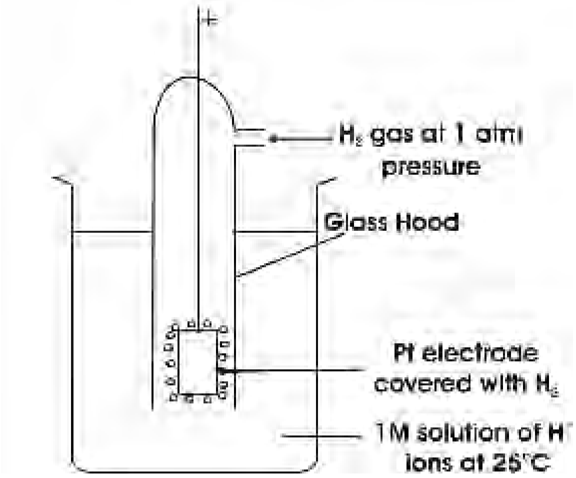

Fig. 14.4 The standard hydrogen electrode

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the emf of the zinc electrode, $Zn \mid Zn^{2+}$. It is connected with the SHE. The complete electrochemical cell may be represented as :

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2 \text{ (1 atm), Pt}$$

The emf of the cell has been found to be –0.76 V which is the emf the zinc half-cell. Similarly, the emf of the copper electrode, $Cu^{2+} \mid Cu$ can be determined by pairing it with the SHE when the electrochemical cell can be represented as :

$$\text{Pt, } H_2 \text{ (1 atm)} \mid H^+ \parallel Cu^{2+} \mid Cu$$

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$\begin{aligned} E^o_{cell} &= E^o_{Cu/Cu^{2+}} - E^o_{SHE} \\ &= 0.34 - \text{Zero} \\ &= 0.34 \text{ V} \end{aligned}$$

The two situations are explained as follows :

When it is placed on the right-hand side of the zinc electrode, the hydrogen electrode reaction is

$$2H^+ + 2e^- \longrightarrow H_2$$

The electrons flow to the SHE and it acts as the cathode.

When the SHE is placed on the left hand side, the electrode reaction is

$$H_2 \longrightarrow 2H^+ + 2e^-$$

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, the SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half-reactions are listed in Table below.

Standard Reduction Potentials at 25°C (298K)

Reduction Half - reaction	**E°V**
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$Ag^+ + e^- \longrightarrow Ag(s)$	0.80
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$	0.34
$2\,H^+ + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^- \longrightarrow Pb(s)$	–0.13
$Zn^{2+} + 2e^- \longrightarrow Zn(s)$	–0.76

Predicting Cell EMF

The standard emf E°, of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode). That is,

$$E^o_{cell} = E^o_{right} - E^o_{left}$$
$$= \text{Cathode potential} - \text{Anode potential}$$

Let us predict the emf of the cell

$$Zn_{(s)}\ |\ Zn^{2+}_{(aq)}\ ||\ Ag^+_{(aq)}\ |\ Ag$$

by using the Eo values from the table.

$$E^o_{cell} = E^o_R - E^o_L$$

$$= 0.80 - (-0.763)$$

$$= 0.80 + 0.763 = 1.563 \text{ V}$$

Predicting Feasibility of Reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, E_{cell}, can be calculated from the expression

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

In general, if E^o_{cell} = + ve, the reaction is feasible

E^o_{cell} = –ve, the reaction is not feasible.

Example 1 : Predict whether the reaction

$$2Ag_{(s)} + Zn^{2+}_{(aq)} \longrightarrow 2Ag^+_{(aq)} + Zn_{(s)}$$

is feasible or not.

Solution : The cell half reactions are

Anode : $2Ag_{(s)} \longrightarrow 2Ag^+_{(aq)} + 2e^-$ $E^o = 0.80$ V

Cathode : $Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ $E^o = -0.763$ V

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = -0.763 \text{ V} - 0.80 \text{ V}$$

$$= -1.563 \text{ V}$$

Since E^o_{cell} is negative, the given reaction is not feasible.

Example 2 : Determine the feasibility of the reaction

$$2Al_{(s)} + 3Sn^{4+}_{(aq)} \longrightarrow 2Al^{3+} + 3Sn^{2+}_{(aq)}$$

Solution : The given reaction consists of the following half reactions

Anode : $2Al_{(g)} \longrightarrow 2Al^{3+} + 6e^-$

Cathode : $3Sn^{4+} + 6e^- \longrightarrow 3Sn^{2+}$ $E^o = -1.66$ V

$E^o_{cell} = 0.15 - (-1.66)$ $E^o = +0.15$ V

$= 1.81$ V

Since E^o_{cell} is positive, the reaction is feasible.

Metal displacement : (Predicting whether a metal will displace another metal from its salt solution or not).

As already shown, the metals near the bottom of the electrochemical series are strong reducing agents and are themselves oxidised to metal ions. On the contrary, the metal lying higher up in the series are strong oxidising agents and their ions are readily reduced to the metal itself. For **example**, zinc lying down below the series is oxidised to Zn^{2+} ion, while copper which is higher up in the series is produced by reduction of Cu^{2+} ion.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$$

Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated. In general we can say that a metal lower down the electrochemical series can precipitate the one higher up in the series.

Silver cannot precipitate Cu from $CuSO_4$ solution, since both metals have positions higher up in the series and are strong oxidising agents.

Hydrogen displacement : (Predicting whether a metal will displace hydrogen from a dilute acid solution.)

Any metal above hydrogen in the electrochemical series is a weaker reducing agent than hydrogen and will not convert H^+ to H_2. This explains why Zn lying below hydrogen reacts with dil. H_2SO_4 to liberate H_2, while Cu lying above hydrogen does not react.

$$Zn + 2H^+ (dil.H_2SO_4) \longrightarrow Zn^{2+} + H_2\uparrow$$

$$Cu + 2H^+ (dil.\ H_2SO_4) \not\longrightarrow Cu^{2+} + H_2$$

Example 1 : Calculate the standard e.m.f. of the cell : Cd, $Cd^{2+} \| Cu^{2+}$, Cu and determine the cell reaction. The standard reduction potentials of Cu^{2+}, Cu and Cd^{2+}, Cd are 0.34V and –0.40 volts respectively. Predict the feasibility of the cell reaction.

E^o_{cell} = Standard EMF of the cell

$= E^o_{right} - E^o_{left}$

= [Std. reduction potential of Cu^{2+}, Cu]
– [Std. reduction potentials of Cd^{2+}, Cd]

$= E^oCu^{2+},Cu - E^o_{Cd^{2+},Cd}$

= 0.34 V – (– 0.4 V)

= + 0.74 Volts.

Left hand electrode (oxidation half cell) reaction is

$$Cd_{(s)} \longrightarrow Cd^{2+} + 2e$$

Right hand electrode (reduction half cell) reaction is

$$Cu^{2+} + 2e \longrightarrow Cu_{(s)}$$

The cell reaction is

$$Cd_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cd^{2+}_{(aq)} + Cu_{(s)}$$

E^ocell is positive. ∴ The cell reaction is feasible.

Example 2 : Determine the standard emf of the cell and predict its feasibility.

$$Ag, Ag^+ \| H^+, H_{2(g)1atm}, Pt.$$

The standard reduction potential of Ag^+, Ag is 0.80 volts.

The right hand side electrode is SHE.

$\therefore E^o_{cell} = E^o_{Right} - E^o_{Left}$

E^o_{cell} = [Std. reduction potential of SHE]
– [Std. reduction potential of Ag^+, Ag]

= 0 – (+ 0.8 V) = – 0.8 Volts.

Since E^o_{cell} is negative, the cell reaction is not feasible.

Relation between EMF and free energy

When a cell produces a current, the current can be used to do work - to run a motor, for instance. Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work, W_{max}, obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, E, through which the charge is transferred.

$$W_{max} = -\,n\,FE \qquad \ldots (1)$$

where *n* is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction. F stands for Faraday and is equal to 96,495 coulombs and E is the emf of the cell.

According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction,

$$W_{max} = \Delta G \qquad \ldots (2)$$

Therefore, from (1) and (2), we can write

$$\Delta G = -\,n\,FE \qquad \ldots (3)$$

Thus only when E has a positive value, ΔG value will be negative and the cell reaction will be spontaneous and the e.m.f. of the cell can be measured.

Here E refers to the E_{cell}.

Thus, the electrical energy supplied by the cell is (*n*FE) equal to the free energy decrease ($-\Delta G$) of the cell reaction occurring in the cell.

Example : Determine the standard emf of the cell and standard free energy change of the cell reaction.

Zn, $Zn^{2+} \| Ni^{2+}$, Ni. The standard reduction potentials of Zn^{2+}, Zn and Ni^{2+}, Ni half cells are – 0.76 V and – 0.25 V respectively.

$$E^o_{cell} = E^oR - E^oL = -0.25 - (-0.76)$$

$$= +0.51\ V \quad E^o_{cell} \text{ is + ve.} \therefore \Delta G^o = -\text{ ve.}$$

$$\therefore \Delta G^o = -n\,FE^o_{cell}$$

$$n = 2 \text{ electrons}$$

$$\therefore \Delta G^o = -2 \times 96495 \times 0.51 = -97460 \text{ Joules} = -97.46 \text{ kJ.}$$

Thermodynamics of a reversible cell

Nernst equation : Suppose the reaction occurring in a reversible cell is represented by the equation

$$A + B \rightleftharpoons C + D$$

The decrease in free energy, – ΔG, accompanying the process is given by the well known thermodynamic equation

$$-\Delta G = -\Delta G^o - RT \ln J$$

where – ΔG^o is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit activity and J stands for the reaction quotient of the activities of the products and reactants at any given stage of the reaction.

Substituting the value of J, we have

$$-\Delta G = -\Delta G^o - RT \ln \frac{a_C \times a_D}{a_A \times a_B}$$

If E is the E.M.F. of the cell in volts and the cell reaction involves the passage of '*n*' faradays (i.e.,) nF coulombs, the electrical work done by the cell is in nFE volt-coulombs or Joules. Hence free energy decrease of the system, –ΔG, is given by the expression

$$-\Delta G = nFE$$

$$nFE = -\Delta G^o - RT \ln \frac{a_C \times a_D}{a_A \times a_B}$$

$$= nFE^o - RT \ln \frac{a_C \times a_D}{a_A \times a_B}$$

$$E = E^o - \frac{RT}{nF} \ln \frac{a_C \times a_D}{a_A \times a_B}$$

where E^o is the E.M.F. of the cell in which the activity, or as an approximation, the concentration of each reactant and each product of the cell reaction is equal to unity. Eo is known as the standard E.M.F. of the cell.

$E = E^o - \frac{RT}{nF} \ln \frac{a_C \times a_D}{a_A \times a_B}$ is often referred to as the Nernst equation

Replacing activities by concentrations, as an approximation, the Nernst equation may be written as

$$E = E^o - \frac{RT}{nF} \ln \frac{[C][D]}{[A][B]}$$

where the quantities in parantheses represent the concentration of the species involved. Replacing [C] [D]/[A] [B] as equal to K, the equilibrium constant in the molar concentration units,

$$E = E^o - \frac{RT}{nF} \ln K.$$

This equation is known as Nernst equation.

$$E = E^o - 2.303 \frac{RT}{nF} \log K,$$

where E^o = standard electrode potential

R = gas constant

T = Kelvin temperature

n = number of electrons transferred in the half-reaction

F = Faraday of electricity

K = equilibrium constant for the half-cell reaction as in equilibrium law.

Calculation of Half-cell potential

For an oxidation half-cell reaction when the metal electrode M gives M^{n+} ion,

$$M \longrightarrow M^{n+} + ne^- \qquad ...(1)$$

the Nernst equation takes the form

$$E = E^o - \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]} \quad ... (2)$$

The activity of solid metal [M] is equal to unity. Therefore, the Nernst equation can be written as

$$E = E^o - \frac{2.303RT}{nF} \log [M^{n+}] ... (3)$$

Substituting the values of R, F and T at 25°C, the quantity 2.303 RT/F comes to be 0.0591. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E^o - \frac{0.0591}{n} \log [M^{n+}] \quad ... (4)$$

This is the equation for a half-cell in which oxidation occurs. In case it is a reduction, the sign of E will have to be reversed.

Example 1 : What is the potential of a half-cell consisting of zinc electrode in 0.01 M $ZnSO_4$ solution 25°C. $E^o = 0.763$ V.

Solution : The half-cell reaction is

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The Nernst equation for the oxidation half-cell reaction is

$$E = E^o - \frac{0.0591}{n} \log [Zn^{2+}]$$

The number of electrons transferred n = 2 and $E^o = 0.763$ V.

Substituting these values in the Nernst equation we have

$$\begin{aligned} E &= 0.763 - \frac{0.0591}{2} (-2) \\ &= 0.763 + 0.0591 = 0.8221 \text{ V} \end{aligned}$$

Calculation of Cell potential

The Nernst equation is applicable to cell potentials as well. Thus,

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log K$$

K is the equilibrium constant of the redox cell reaction.

Example 2 : Calculate the emf of the cell.

$$\text{Zn} \mid \text{Zn}^{2+} (0.001\ \text{M}) \parallel \text{Ag}^{+} (0.1\ \text{M}) \mid \text{Ag}$$

The standard potential of Ag/Ag^{+} half-cell is + 0.80 V and Zn/Zn^{2+} is –0.76 V.

Solution :

Step 1 : Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of E^{o}_{cell}.

Cathode : $2Ag^{+} + 2e^{-} \longrightarrow 2Ag \qquad E^{o} = +\ 0.80$

Anode : $Zn \longrightarrow Zn^{2+} + 2e^{-} \qquad E^{o} = -0.76\ V$

Cell : $Zn + 2Ag^{+} \rightleftharpoons Zn^{2+} + 2Ag \qquad E^{o} = 1.56\ V$

Step 2. K for the cell reaction = $\dfrac{[Zn^{2+}]}{[Ag^{+}]^{2}}$

Substituting the given values in the Nernst equation and solving for E_{cell}, we have

$$\begin{aligned}
E_{cell} &= E^{o}_{cell} - \frac{0.0591}{n} \log K \\
&= 1.56 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Ag^{+}]^{2}} \\
&= 1.56 - \frac{0.0591}{2} \log \frac{[10^{-3}]}{[10^{-1}]^{2}} \\
&= 1.56 - 0.02955 (\log 10^{-1}) \\
&= 1.56 + 0.02955 \\
&= 1.58955\ V
\end{aligned}$$

Calculation of Equilibrium constant for the cell reaction

The Nernst equation for a cell is

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log K$$

or $$\log K = \frac{nE^o_{cell}}{0.0591}$$

Example 3 : Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc.

Solution :

Step 1 : Write the equation for the reaction

$$2Ag^+ + Zn \rightleftharpoons Zn^{2+} + 2Ag \qquad E^o_{cell} = 1.56\ V$$

Step 2 : Substitute values in the Nernst equation at equilibrium

$$\log K = \frac{nE^o_{cell}}{0.0591}$$

$$0 = 2 \times 1.56 - 0.03 \log K$$

$$-1.56 \times 2 = -0.03 \log K$$

$$\log K = \frac{-1.56 \times 2}{-0.03} = 52.79$$

$$K = 6.19 \times 10^{52}$$

Example 4 : Calculate the E.M.F. of the zinc - silver cell at 25°C when $[Zn^{2+}] = 0.10$ M and $[Ag^+] = 10$ M. (E^o cell at 25°C = 1.56 volt]

Solution : The cell reaction in the zinc - silver cell would be

$$2Ag^+ + Zn \rightleftharpoons 2Ag + Zn^{2+}$$

The Nernst equation for the above all reaction may be written as :

$$E_{cell} \quad = \quad E^o cell - \frac{RT}{nF} \ln \frac{[Ag]^2[Zn^{2+}]}{[Ag^+]^2[Zn]}$$

(since concentrations of solids are taken as unity)

$$= \quad E^o_{cell} - \ln \frac{[Zn^{2+}]}{[Ag^+]^2}$$

Substituting the various values in Nernst equation, we have

$$E_{cell} \quad = \quad 1.56 - \frac{2.303 \times 8.314 \times 298}{2 \times 96495} \log \frac{0.1}{(10)^2}$$

$$= \quad 1.648 \text{ volts.}$$

Example 5 : Write the cell reactions for the following cells.

(i) $Zn \mid ZnO_2^{2-}, OH^- \mid HgO \mid Hg$

(ii) $Pb \mid PbSO_4 \mid H_2SO_4 \mid PbSO_4 \mid PbO_2 \mid Pt$

(iii) $Pt \mid H_2 \mid HCl \mid Hg_2Cl_2 \mid Hg \mid Pt$

Solution : (i) The electrode reactions are

$$Zn_{(s)} + 4OH^- + 2e^- \longrightarrow ZnO_2^{2-} + 2H_2O$$

$$HgO_{(s)} + H_2O + 2e^- \longrightarrow Hg_{(s)} + 2OH^-$$

Cell reaction is

$$Zn_{(s)} + HgO_{(s)} + 2OH^- \longrightarrow ZnO_2^{2-} + Hg_{(s)} + H_2O$$

(ii) The electrode reactions are

$$Pb_{(s)} + SO_4^{2-} \longrightarrow PbSO_{4(s)} + 2e^-$$

$$PbO_{2(s)} + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O$$

Cell reaction is

$$Pb_{(s)} + PbO_{2(s)} + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_{4(s)} + 2H_2O$$

(iii) The electrode reactions are

$$2H^+ + 2e^- \longrightarrow H_{2(g)}$$

$$Hg_2Cl_{2(s)} + 2e^- \longrightarrow 2Hg_{(l)} + 2Cl^-$$

The cell reaction is

$$Hg_2Cl_{2(s)} + H_2 \longrightarrow 2Hg_{(l)} + 2H^+ + 2Cl^-$$

Example 6 : Calculate the potential of the following cell at 298 K

Zn/Zn^{2+} (a = 0.1) // Cu^{2+} (a = 0.01) / Cu

$$E^o_{Zn^{2+}/Zn} = -0.762 \text{ V}$$

$$E^o_{Cu^{2+}/Cu} = +0.337 \text{ V}$$

Compare the free energy change for this cell with the free enegy of the cell in the standard state.

Solution : The overall cell reaction is

$$Zn + Cu^{2+} (a = 0.01) \longrightarrow Zn^{2+} (a = 0.1) + Cu$$

The cell potential given by nernst equation

$$E_{cell} = E^o_{cell} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}\, a_{Cu}}{a_{Zn}\, a_{Cu^{2+}}}$$

$$= E^o_{cell} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

(Since activity of a pure metal is unity)

$$E^o_{cell} = 0.337 - (-0.762) = 1.099 \text{ V}$$

$$E_{cell} = 1.099 - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$= 1.099 - \frac{0.0591}{2} \log 10$$

$$= 1.099 - 0.02956$$

$$= 1.0694 \text{ V}$$

The free energy change ΔG is given by $\Delta G = -nFE$

$$\Delta G = -\text{(2 equi/mol) (1.0694 V) (96495 coulombs equiv}^{-1}\text{)}$$

$$= -206.4 \text{ kJ mol}^{-1}$$

The standard free energy change :

$$\Delta G^o = -\text{(2 equi/mol) (1.099V) (96495 coulomb/equiv)}$$

$$= \quad -212.1 \text{ kJ/mol.}$$

Example 7 : Calculate the standard e.m.f. of the reaction

$Fe^{3+} + 3e^- \longrightarrow Fe_{(s)}$. Given the e.m.f. values of

$Fe^{3+} + e \longrightarrow Fe^{2+}$ and $Fe^{2+} + 2e \longrightarrow Fe_{(s)}$ as + 0.771V and – 0.44 V respectively.

Solution : Let $E_1 = 0.771V$ for $Fe^{3+} + e \longrightarrow Fe^{2+}$

$E_2 = -0.44V$ for $Fe^{2+} + 2e \longrightarrow Fe_{(s)}$

then $E_1 + E_2 = 0.331$ V and this e.m.f. corresponds to

$$Fe^{3+} + 3e \longrightarrow Fe_{(s)}.$$

Example 8 : The standard electrode potentials of the half cells Ag^+ / Ag and Fe^{3+}, Fe^{2+} / Pt are 0.7991 V and 0.771 V respectively. Calculate the equilibrium constant of the reaction :

$$Ag_{(s)} + Fe^{3+} \rightleftharpoons Ag^+ + Fe^{2+}$$

Solution : The cell formed is Ag / Ag^+ ; Fe^{3+}, Fe^{2+} / Pt

At anode : $Ag(s) \longrightarrow Ag^+ + e$

At cathode : $Fe^{3+} + e \longrightarrow Fe^{2+}$

Overall reaction : $Ag_{(s)} + Fe^{3+} \longrightarrow Fe^{2+} + Ag^+$

emf of the cell is given by $(E_R - E_L)$

$$E^o_{cell} = 0.771 - 0.7991 = -0.0281 \text{ V}$$

At equilibrium, $E_{cell} = E^o_{cell} - \dfrac{RT}{nF} \ln \dfrac{a_{Ag^+}\, a_{Fe^{2+}}}{a_{Fe^{3+}}}$

Since activity of solid silver is 1.0.

$$\therefore\ n = 1 \text{ and } K_{eq} = \frac{a_{Ag^+}\, a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

$$\therefore\ E^o_{cell} = \frac{0.0591}{n} \log K_{eq}$$

$$\therefore\ \log K_{eq} = \frac{0.0281 \times 1}{0.0591} = 0.4751$$

$$\therefore\ K_{eq} = 0.335$$

SELF EVALUATION

(A) Choose the correct answer :

1. The potential of a single electrode is a half cell is called the
   - (a) Reduction potential (b) Half-wave potential
   - (c) Single electrode potential (d) cell potential
2. The relationship between free energy change and e.m.f. of a cell is
   - (a) $\Delta G = -nFE$ (b) $\Delta H = -nFE$ (c) $\Delta E = nFG$ (d) $\Delta F = nEG$
3. The feasibility of a redox reaction can be predicted with the help of
   - (a) Electronegativity (b) Electrochemical series
   - (c) Electron affinity (d) Equivalent conductance
4. The metals near the bottom of the electrochemical series are
   - (a) strong reducing agents (b) strong oxidising agents
   - (c) weak reducing agents (d) weak oxidising agents
5. The emf of a cell with 1 M solutions of reactants and products in solution at 25^o C is called
   - (a) Half cell potential (b) Standard emf
   - (c) Single electrode potential (d) Redox potential
6. The relationship between equilibrium constant and standard emf of a cell is
   - (a) $E^o = 0.0591 \log K$ (b) $0.0591\, E^o = \log K$
   - (c) $nE^o = 0.0951 \log K$ (d) $nE^o = 0.0591 \log K$

(B) Answer in one or two sentences :

1. The standard reduction potentials of Fe^{3+}/Fe and Fe^{2+}/Fe electrode systems are –0.035 V and –0.44V respectively. Predict which of the two oxidations is easy : Fe^{3+}/Fe and Fe^{2+}/Fe. [**Ans.** Fe^{2+}/Fe]
2. What are the types of changes in the cathode and anode in electrolytic and electrochemical cells.
3. Write the electrochemical cell for the overall cell reaction

   $Zn_{(s)} + 2AgNO_3 \longrightarrow 2Ag_{(s)} + Zn(NO_3)_2$.
4. The standard reduction potential of Fe3+, Fe2+/Pt is + 0.771V. This half cell is connected with another half cell such that e.m.f. of the cell is 0.771V. What is the other half cell ? [**Ans.** SHE]
5. Write the cell reaction for the half cell $Cl^-_{(aq)} / AgCl_{(s)}$ Ag.

   [**Ans.** $AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-$]
6. What are two types of cells ?
7. What is single electrode potential ?
8. Define standard emf of a cell.
9. How to predict the feasibility of a cell reaction ?
10. Write the Nernst equation.

(C) Answer not exceeding sixty words :

1. Write the differences between electrolytic and electrochemical cells.
2. How emf of a cell is determined ?

(D) Solve the problems :

1. The standard reduction potential for the reaction $Sn^{4+} + 2e \longrightarrow Sn^{2+}$ is + 0.15 V. Calculate the free energy change of the reaction.

   [**Ans.** 28.95 kJ]
2. Write the Nernst equation for the half cell $Zn^{2+}_{(aq)} / Zn_{(s)}$.

   [**Ans.** $E_{Zn^{2+}/Zn} = E^o{}_{Zn^{2+}/Zn} - \frac{RT}{2F} \ln [Zn^{2+}]$]

3. The emf of the cell : $Cd/CdCl_2 . 25H_2O / AgCl_{(s)}$ Ag is 0.675 V. Calculate ΔG of the cell reaction. [**Ans.** $n = 2$; $\Delta G = -130.335$ kJ]

4. The standard free energy change of the reaction $M^+_{(aq)} + e \longrightarrow M_{(s)}$ is –23.125 kJ. Calculate the standard emf of the half cell. [**Ans.** $E^o = + 0.25$ V]

5. The emf of the half cell $Cu^{2+}_{(aq)}/Cu_{(s)}$ containing 0.01 M Cu^{2+} solution is + 0.301 V. Calculate the standard emf of the half cell. [**Ans.** $n = 2$, $E^o_{Cu^{2+}/Cu} = 0.359$ V]

   [Hint : $E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$]

6. If $E_1 = 0.5$ V corresponds to $Cr^{3+} + 3e^- \longrightarrow Cr_{(s)}$ and $E_2 = 0.41$ V corresponds to $Cr^{3+} + e \longrightarrow Cr^{2+}$ reactions, calculate the emf (E_3) of the reaction $Cr^{2+} + 2e \longrightarrow Cr_{(s)}$ [**Ans.** 0.955V]

   [Hint : $E_3 = \frac{3E_1 - E_2}{2}$]

7. Calculate the standard emf of the cell having the standard free energy change of the cell reaction is –64.84 kJ for 2 electrons transfer. [**Ans.** $E^o = 0.336$ V]

8. Calculate the emf of the cell Zn/ZnO_2^-, $OH^-_{(aq)}$, HgO/Hg given that E^o values of OH^-, ZnO_2^- / Zn and OH^-, HgO/Hg half cells are –1.216 V and 0.098 V respectively.

   [Hint : $E^o = E^o_R - E^o_L$; $E^o = 1.314$V]

9. The equilibrium constant of cell reaction :

   $Ag_{(s)} + Fe^{3+} \rightleftharpoons Fe^{2+} + Ag^+$ is 0.335, at 25ºC. Calculate the standard emf of the cell Ag/Ag^+ ; Fe^{3+}, Fe^{2+} / Pt. Calculate Eo of half cell Fe^{3+}, Fe^{2+}/Pt if E^o of half cell Ag^+/Ag is 0.7991V. Calculate E^o of Fe^{3+}, Fe^{2+}/ Pt half cell. [**Ans.** $E^oFe^{3+}/Fe^{2+} = 0.771$V]

10. Calculate the emf of the cell having the cell reaction

    $2Ag^+ + Zn \rightleftharpoons 2Ag + Zn^{2+}$ and $E^o_{cell} = 1.56$ V at 25ºC when concentration of $Zn^{2+} = 0.1$ M and $Ag^+ = 10$ M in the solution.

    [Hint : $E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Ag^+]^2}$ [**Ans.** 1.648 V]

11. The emf values of the cell reactions $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ and $Ce^{2+} \longrightarrow Ce^{3+} + e^-$ are 0.61V and –0.85 V respectively. Construct the cell such that the free energy change of the cell is negative. Calculate the emf of the cell. [**Ans.** $E_{cell} = 0.24$ V]

12. A zinc rod is placed in 0.095 M zinc chloride solution at 25°C. emf of this half cell is –0.79V. Calculate $E^o_{Zn^{2+}/Zn}$. [**Ans.** –0.76 V]

SUMMARY :

The interconversion of chemical energy and electrical energy is an important aspect that possesses numerical applications. The differences between electrolytic and electrochemical cells are discussed. Standard hydrogen electrode construction and its electrode potential is given. The relationship between free energy change and emf of a cell is obtained. IUPAC convention for representation of a cell is discussed.

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15. ISOMERISM IN ORGANIC CHEMISTRY

15.1 ISOMERISM

Isomers are compounds having same molecular formula but differ in physical or chemical or both physical and chemical properties. This phenomenon is known as **isomerism.**

Isomerism is of two types - (i) Structural isomerism (ii) Stereoisomerism.

Structural isomerism arises out of the difference in the arrangement of atoms in a molecule, (without referring to space), type of linkage and the atoms which are linked to each other in the moelcule. Stereoisomerism arises out of the **difference** in the arrangement of atoms in the molecule, with reference to each other in space.

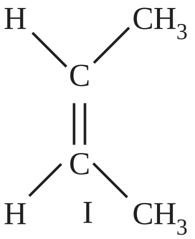
Stereoisomers (have the same structure) differ in the way the atoms are oriented in space. They have the same structure and hence do not differ much in properties.

There are **two types** of Stereoisomerism. They are (i) Geometrical isomerism and (ii) Optical isomerism.

(i) Geometrical Isomerism :

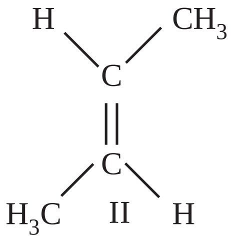
Isomerism that arises out of difference in the spatial arrangement of atoms or groups about the doubly bonded carbon atoms is called **Geometrical isomerism**. These isomers are not mirror images of each other. Rotation about C=C is not possible at normal conditions and hence the isomers are isolable.

If different atoms or groups are bonded to the 'C=C' bond in a molecule, more than one spatial arrangement is possible. For example, 2-butene exists in two isomeric forms.



I

Cis isomer



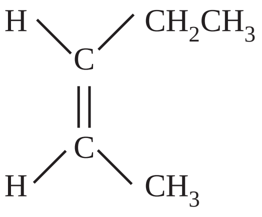
II

Trans isomer

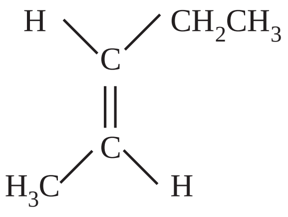
The isomer in which **similar groups** lie on the same side is called **'cis isomer' (I)**. The other in which similar groups lie in **opposite direction** is called **'Trans isomer' (II)**. This isomerism is called 'Cis-Trans' isomerism.

The two groups attached to the carbon atoms need not be same, it may be different also. e.g.,

2-pentene



Cis



Trans

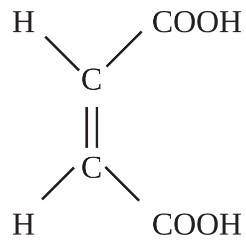
This isomerism arises out of the hindrance to rotation about the C=C bond in such molecules.

The cis-trans isomers do not differ much in chemical properties. They differ in physical properties like boiling point, melting point, crystal structure, solubility and refractive index. Highly substituted olefin is more stable than less substituted olefin. Among substituted olefins, trans olefin is more stable than cis olefin. In the cis isomer because similar groups are very near each other, Vander Waals repulsion and steric hindrance make the molecule much unstable. In the trans isomer, similar groups are diagonally opposite to each other. Hence there is no such steric interaction. Generally trans isomer is more stable than cis isomer. Hence reactivity of cis isomer may be little higher than the trans isomer. The energy of the cis isomer is greater than that of trans isomer.

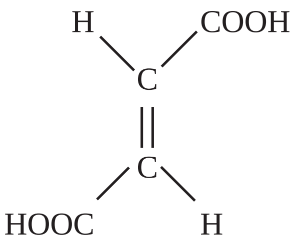
Though at room temperature, cis and trans isomers are stable and are not interconvertible, on heating to a certain temperature, trans isomer can be converted to cis isomer and vice-versa. 'Breaking of carbon-carbon π-bond and its reformation is responsible for the interconversion.'

$$\text{Trans isomer} \xrightleftharpoons{\Delta} \text{Cis isomer}$$

Consider unsaturated dicarboxylic acid - Maleic acid and Fumaric acid. These are geometrical isomers.



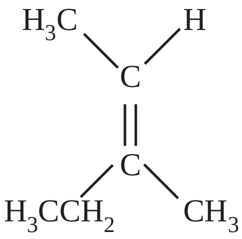
Cis
[Maleic acid]



Trans
[Fumaric acid]

‘Cis-trans’ system of nomenclature may not be suitable for many substituted olefins.

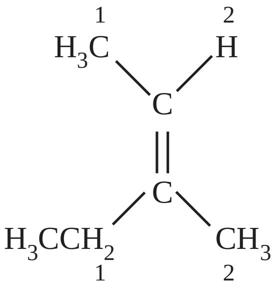
For example,



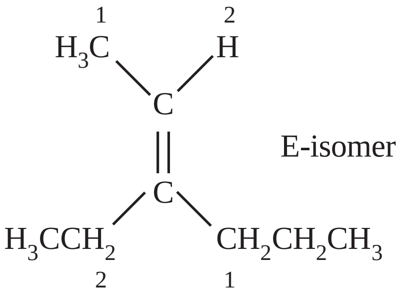
A newer system based on the priority of groups is the Cahn-Ingold-Prelog convention. This system is called the (E-Z) system, applies to alkene diastereomers of all type. If the two groups of higher priority are on the same side of the double bond, the alkene is designated ‘Z’ (from the German word Zusammen-meaning together). If the two groups of high priority are on opposite sides of the double bond, the alkene is designated ‘E’ (from the German, entgegen, meaning opposite)

The priorities follow the order of decreasing atomic number of the atom directly bonded to the carbon.

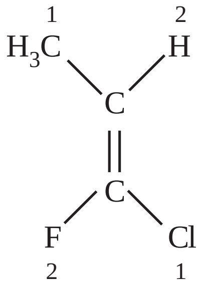
For some compounds the priority is shown by numbers as



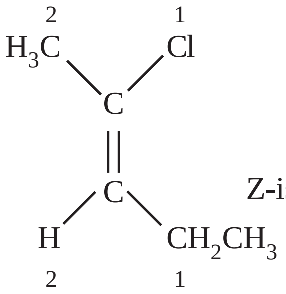
Z-isomer



E-isomer



E-isomer



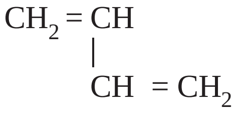
Z-isomer

Dipolemoment studies is one of the best methods of identifying cis-trans isomers. Generally cis isomers have larger dipolemoment than trans isomers. Often DPM of trans isomer is zero. e.g., Trans 2-butene and Trans 2,3-dibromo-2-butene. (Refer Chapter on disubstituted benzene)

1,3 - butadiene

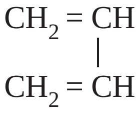
$$CH_2=CH–CH=CH_2$$

This molecule can exist in two forms.



$$\begin{array}{l} CH_2=CH \\ \qquad\;| \\ \qquad\; CH=CH_2 \end{array}$$

and

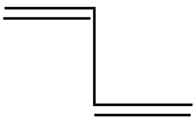


$$\begin{array}{r} CH_2=CH \\ | \\ CH_2=CH \end{array}$$

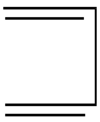
I

II

Though these two forms do not differ very much in their energy and stability, the (I) form, which is similar to ‘trans’ is more stable than (II) form which is similar to ‘cis’. These two forms do not arise out of the hindrance to rotation about C=C, instead the restricted rotation about C–C. In order to indicate that, this cis-trans isomerism is due to restricted rotation about C–C bond, they are named as,

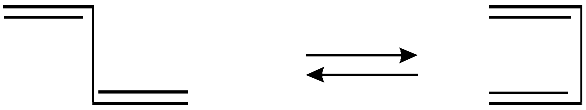


S-trans



S-cis

These are easily interconvertible and exist in equilibrium.



S-trans form is also called ‘transoid form’

S-cis form is also called ‘cisoid form’.

The energy of S-trans form is 3 Kcals less than the S-cis form.

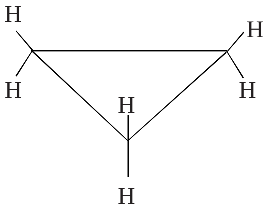
These two forms differ in chemical reactivity. Very often they give different products in reactions.

Conformation in cyclic systems :

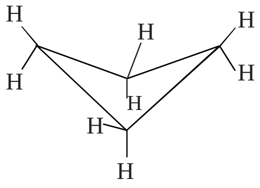
The different forms that arises out of the rotation about C–C single bond are called conformers. Free rotation about C–C single bond is not always possible. Very often the rotation is restricted depending upon the nature and the size of atoms or groups bonded to each carbon atom. The different conformers differ in energy though not appreciably.

Restriction to free rotation about C–C single bond is much pronounced in cyclic systems. In these cases, the restriction to rotation is so appreciable as to make the different forms isolable or identifiable.

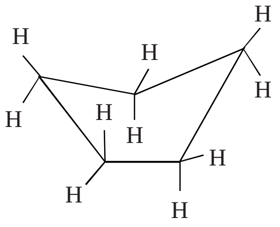
Thus cyclopropane is flat, cyclobutane can form butterfly shape while cyclopentane can form an open-envelope shape.



Cyclopropane
[Planar conformation]



Cyclo butane
[non planar conformation]

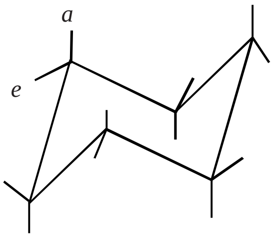


Cyclo pentane
[non planar conformation]

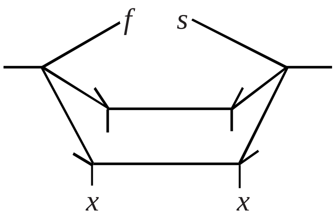
Cyclohexane :

As early as 1890, Sachse suggested that cyclohexane ring exists in two non planar forms (i.e.,) boat and chair conformations. The energy difference between these two forms was found to be only 6.5 K.cal/mole by Pitzer. The energy difference is small enough for interconversion to take place.

Both the boat form and chair form are free of angle strain called Baeyer's strain (i.e., the valence bond angle is $109^{o}28'$]



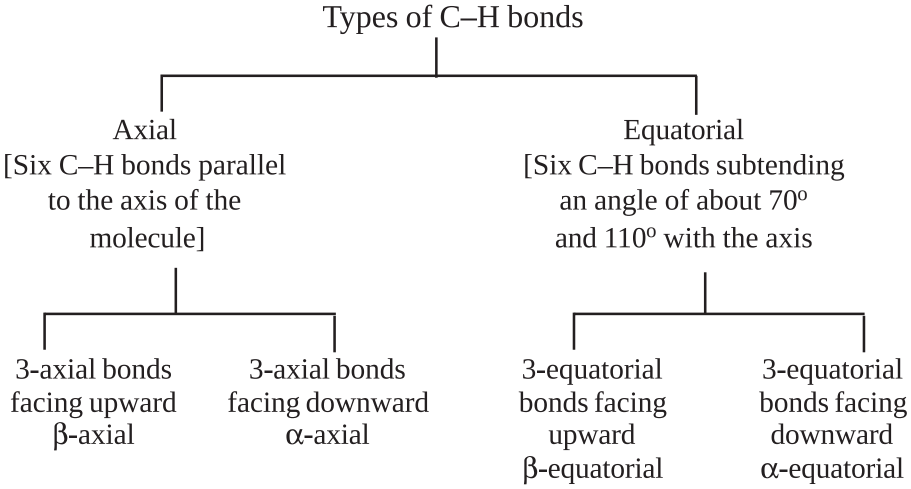
Chair conformation
a = axial, *e* = equatorial



Boat conformation
f = flagpole, *s* = bowspirit,
x-*x* = pair of eclipsing hydrogen atoms

Chair conformation :

There are two types of C–H bonds.

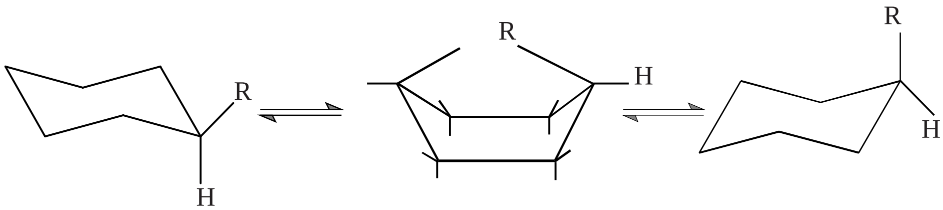


Every pair of carbon atoms (Two carbon atoms directly bonded to each other) in chair form exists in skew form.

Boat conformation

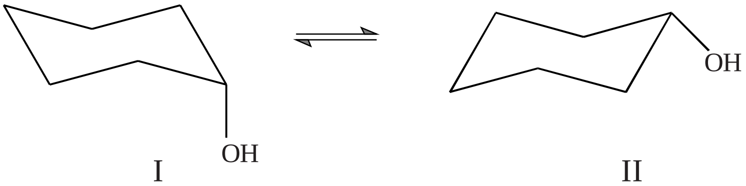
This form has two pairs of carbon atoms with eclipsing bonds. This eclipsing interaction destabilies boat form.

Though the chair form is stable, it is sufficiently flexible to turn itself upside down called ring flipping so that all bonds which are axial originally become equatorial and vice versa.



There exists an equilibrium between these two chair forms with boat form as intermediate.

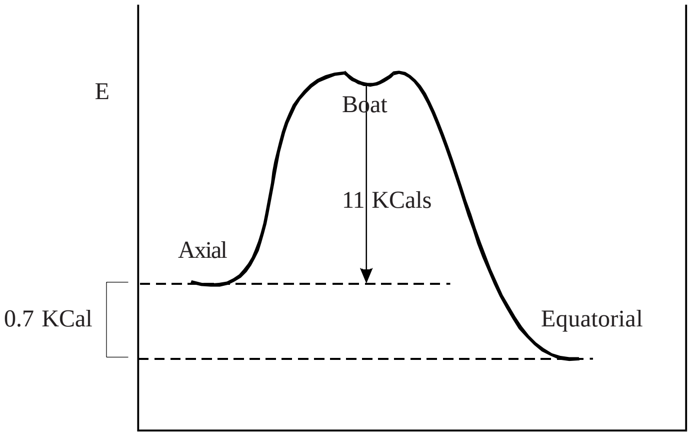
A mono substituted cyclohexane like cyclohexanol exists in the two chair forms. These two forms are interconvertible and exist in equilibrium.



I II

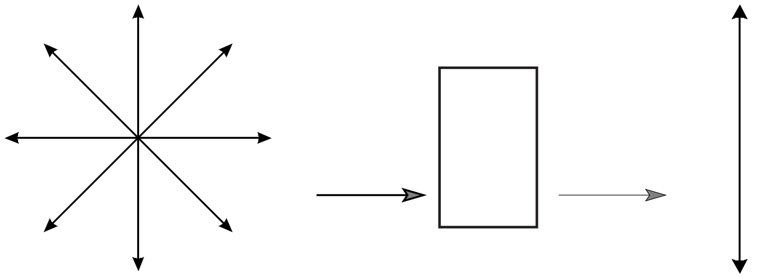
In one form (I) the –OH group is axially oriented. In the other form (II) the –OH group is equatorially oriented. The energy of the axial conformer is little higher than that of the equatorial conformer. Because the axial substituent experiences steric interaction with the axial H-atoms present at the third carbon atoms. This decreases the stability of the axial conformer. This is called 1 : 3-diaxial interaction. This interaction is absent in the equatorial conformer. Hence equatorial cyclohexanol is present to an extent of about 90% in the equilibrium mixture. The axial isomer is present only to 10%.

Energy level diagram for axial and equatorial alcohols

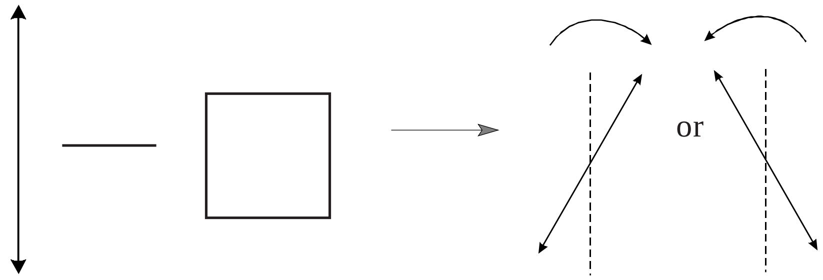


Optical activity and optical isomerism :

Light is propagated in the form of waves. Ordinary monochromatic light is supposed to consist of waves vibrating in all planes. If such a light is passed through a Nicol prism, the emergent light is found to consist of waves vibrating in only one plane. Such a light is called plane polarised light.



When the plane polarised light is passed through certain substances or solutions (such as lactic acid), the emergent light is found to be vibrating in a different plane. This is called optical rotation.



Such substances are called optically active substances. This property of such substances is called ‘Optical activity’.

If the rotation is towards the right side [clockwise] it is called dextrorotation and the substance is said to be dextrorotatory. Dextrorotation is indicated by the symbol (+) or ‘*d*’.

If the rotation is towards the left side [Anticlockwise] it is called laevorotation and the substance is said to be laevo rotatory. Laevorotation is indicated by the symbol (–) or ‘*l*’.

Conditions of optical activity :

Not all substances are optically active. For example substances like $CHCl_3$, CH_3CH_2OH, $CH_3CH_2CH{=}CH_2$, $CH_3CH_2COCH_3$ are not optically active. On the other hand substances like CHIBrCl, $CH_3CHBr–CH{=}CH_2$, $CH_3CH(OH)COCH_3$, CH_3CHDOH are found to be optically active.

When the structures of the compounds which are optically inactive and optically active, are compared, one thing is clear. All the optically active compounds, mentioned above have atleast one carbon atom that is bonded to four different atoms or groups.

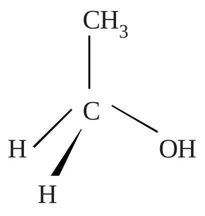
A carbon atom attached to four different atoms or groups is called ''asymmetric carbon atom''.

Pasteur suggested that optical activity arises from molecular dissymmetry which is supported by Vant-Hoff and LeBel. According to them, a carbon atom has its four valencies directed towards the four corners of a regular tetrahedron. In this situation a molecule with an 'asymmetric carbon atom' becomes asymmetric.

It so happens that an asymmetric molecule is not superimposable on its mirror image. That means an optically active molecule has more than [atleast two] one configuration. [configuration refer to three dimensional arrangement of atoms in a molecule] that is, an optically active molecule exhibits isomerism which is called optical isomerism.

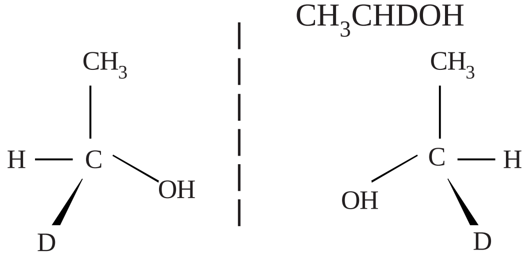
Consider ethanol and deuterated ethanol

CH_3CH_2OH



(ethanol-symmetric molecule)

CH_3CHDOH



(deuterated ethanol-asymmetric and non-superimposable)

The isomers-called optical isomers have configurations which are non super imposable.

Hence the criteria for a molecule to be asymmetric (hence optically active) is that its configuration is non superimposable on its mirror image. Such molecules are also called ‘chiral’ molecules.

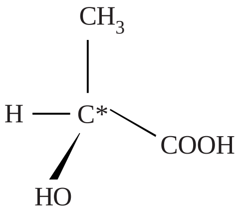
‘Chirality’ is ‘the essential and the sufficient’ condition for a molecule to be optically active.

Chirality means handedness or non superimposability. Right hand and left hand, Right leg shoe and left leg shoe are examples of objects having handedness or the property of chirality and non superimposability.

The molecules which are optically inactive are ‘achiral’.

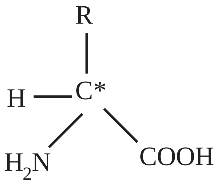
Simple optically active molecules like lactic acid, are said to have ‘‘chiral carbon’’ or ‘‘chiral center’’.

e.g.,

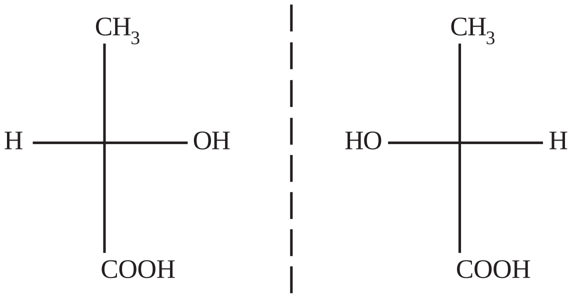


The carbon with ‘‘astreik’’ is called the chiral carbon.

All the α-amino acids (except glycine) have chiral centres (chiral carbon) and are optically active.



α-amino acid



d,l pair of lactic acid

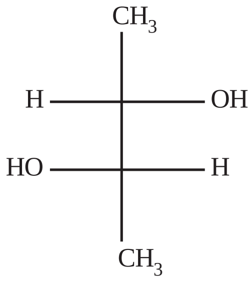
Optical isomers :

Chiral molecules can have two different configurations. Each configuration stands for one optical isomer. Thus dextrorotatory isomer has configuration which is the mirror image of the laevorotatory isomer. Such optical isomers which differ only in the sign of (or direction of) optical rotation are called ‘‘enantiomers’’.

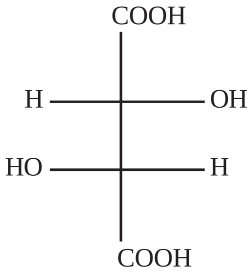
When equal amounts of d-isomer and l-isomer are mixed one gets a "racemic mixture" and this process is called racemisation. A racemic mixture becomes optically inactive. Because, in this mixture rotation towards clockwise direction by the dextro isomers is compensated by the rotation towards the anticlockwise direction by the laevo isomers. The optical inactivity of a racemic mixture is said to be due to 'external compensation'. Any how an optically inactive racemic form can be separated into two active forms. This process of separation is called "resolution of the racemic mixture".

A molecule with more than one chiral carbon

A molecule can have more than one chiral centres. Correspondingly the number of isomers is increased. In general for a molecule with *n*-different chiral centres, 2^n-isomers are possible. A molecule can have more than one identical asymmetric carbon atoms. (e.g.,) butane -2,3-diol and tartaric acid.



Diol

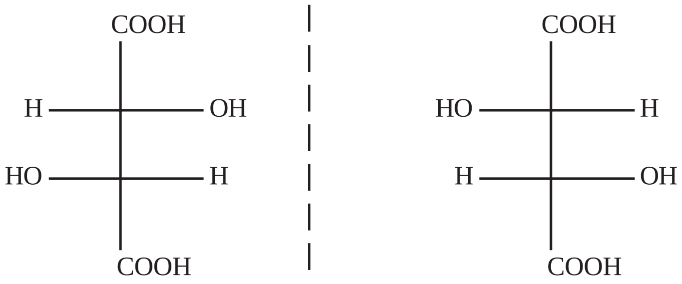


Tartaric acid

In such cases the number of optical isomers is not $2^2 = 4$, it is less than 4 (i.e.,) 3.

Isomerism in Tartaric acid :

Tartaric acid is dihydroxy dioic acid, having two identical chiral carbon atoms.

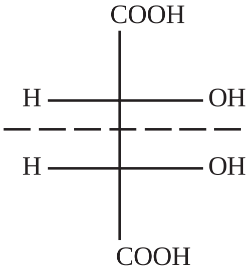


(*d*, *l* pair of tartaric acid)

The enantiomers of tartaric acid, have the same magnitude but different sign of optical rotation. They have object-mirror image relationship.

In the *d*-isomer, each of the two asymmetric carbon atoms rotate the plane of the polarised light towards right leading to overall dextro rotation. In the same way in the *l* - isomer, the overall rotation is laevo.

There is another optical isomer for tartaric acid in which one asymmetric carbon atom is dextrorotatory and the other laevorotatory-both rotating to the same extent in opposite directions. The net result is, that this isomer becomes optically inactive and is called the ‘‘Meso’’ isomer.



Though the Meso isomer has two asymmetric carbon atoms the configuration of one carbon is the mirror image of the other, the net result being the molecule as a whole becomes symmetric. This molecule is said to have a symmetric plane, which divides the molecule into two equal halves. The molecule becomes ‘‘achiral’’. It has configuration which is superimposable on its mirror image.

The optical inactivity of the ‘Meso’ isomer is due to the internal compensation. It is due to the inherent symmetry in the molecule. Mesoform cannot be separated into optically active enantiomeric pairs. This form is a single substance and not a mixture.

Racemic form	**Meso form**
1. It is a mixture that can be separated into two optically active forms.	It is a single compound and hence cannot be separated.
2. Optically inactive due to external compensation.	Optically inactive due to internal compensation.
3. Molecules of isomers present are chiral.	Molecules are achiral.

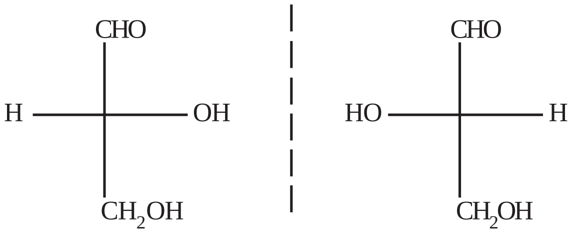
When equal amounts of *d*-tartaric acid and *l*-tartaric acid are mixed, we get racemic tartaric acid which is an optically inactive mixture. This can be separated into two optically active forms.

d- and *l*-isomers have the same magnitude but different sign of optical rotation, hence they are called enantiomers. The Meso tartaric acid differs in the magnitude of optical rotation from the *d*- or *l*- isomer. Hence Mesoform is said to be a ''diastereomer' of the active form.

Enantiomer	Diastereomer
1. Optical isomers having the same magnitude but different sign of optical rotation.	Differ in the magnitude of optical rotation.
2. They have configuration with non-super imposable object mirror image relationship.	They are never mirror images.
3. Enantiomers are identical in all properties except the sign of optical rotation.	Diastereomers differ in all physical propeties.
4. Separation of enantiomers is a tedious process.	Separation from the other pairs of enantiomers is easy.

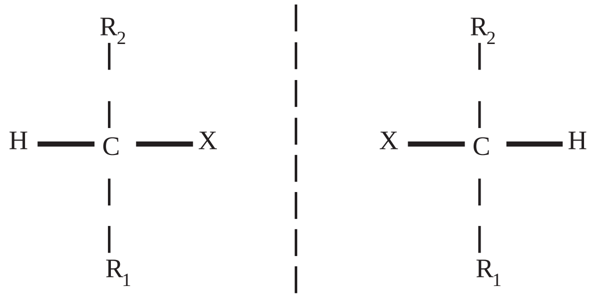
Representation of configurations of the molecule :

In order to indicate the exact spatial arrangement of atoms or groups in a molecule having asymmetric carbon atom, Fischer proposed DL-system of nomenclature. Glyceraldehyde was taken as the standard. The dextro isomer and laevo isomer of glyceraldehyde are designated as D and L as follows. These are Fischer's projection formulae.



Sign of rotation	: *d* or (+) glyceraldehyde	*l* or (–) glyceraldehyde
Designation of configuration	: D	L

In general more oxidised group is shown at the top and the reduced group at the bottom. The chiral molecule is viewed in such a way that H, X- lie above the plane of the paper and R_1, R_2-lie below the plane of the paper. The D, L-configurations are shown as :

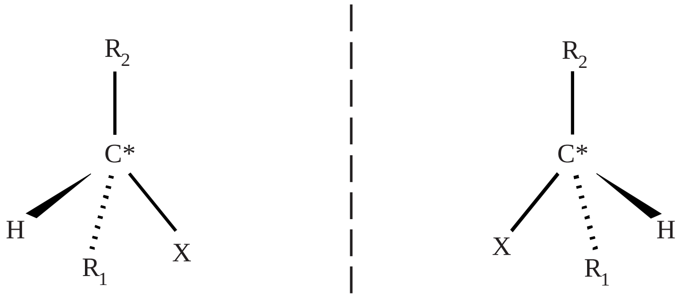


D L

R_2 = Oxidised group - COOH, CHO, CO...
R_1 = Reduced group CH_3, CH_2OH ...
X = a heteroatom or a group with hetero atom
(i.e.,) Cl, Br, I, –OH, $–NH_2$, etc.,

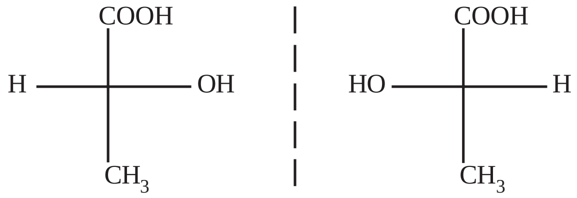
(In the projection formula, the broken lines indicate the bonds that are going below and thick lines, the bonds coming above the plane of the paper)

The above projection formulae can be understood from the following diagram.



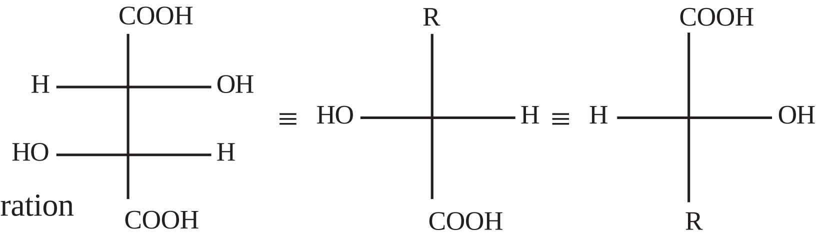
D L

Thus D and L lactic acids are



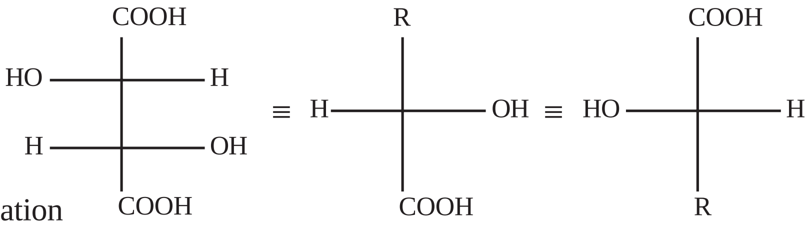
D L

and tartaric acid - (R-stands for the remaining half portion of the molecule)



D-configuration

R = –CH(OH)COOH

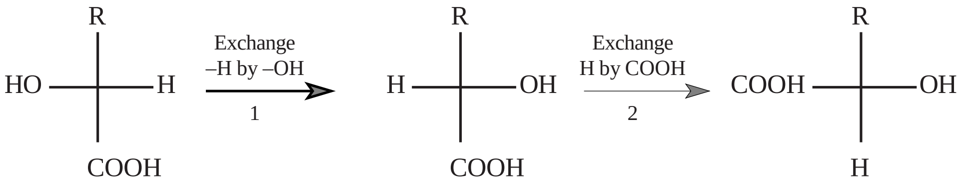


L-configuration

This system of designating configuration is of limited applicability.

In Fischer's projection formula any two exchanges of groups attached to the asymmetric carbon atom, are allowed, then the configuration is not changed.

i.e.,



I II

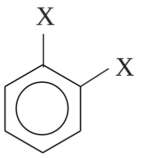
Though I and II appears to be different but both represent the same configuration. Both are identical.

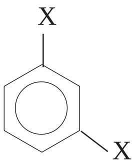
Disubstituted benzene :

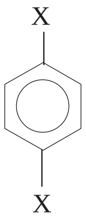
When any two hydrogen atoms of the benzene ring are replaced by any other atoms or groups disubstituted benzene is obtained.

(e.g.,) $C_6H_4Cl_2$, C_6H_4 $(OH)_2$, CH_3 C_6H_4Br, $HOC_6H_5NO_2$

The disubstituted benzenes can exist in three isomeric forms.







X = any substituent

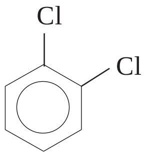
These are three distinct forms differing in many properties though they have the same formula. Hence they are said to exhibit isomerism. In these three structures the isomers differ in the relative position of the substitutents. Hence they are called position isomers.

When the substituents are in adjacent positions in the benzene ring, it is called ortho isomer.

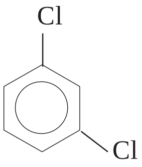
When the two substituents are exactly opposite to each other, it is a para isomer.

When the angle between two substituents is 120^o. It is a meta isomer.

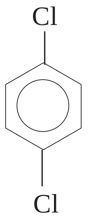
Example,



Ortho dichloro benzene



Meta dichloro benzene



Para-dichloro benzene

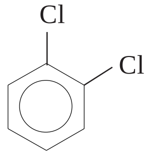
Isomers can also be named using the number of the carbon atom thus

Ortho isomer is 1,2-dichloro benzene

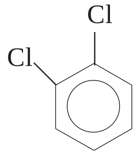
Meta isomer is 1,3-dichloro benzene

Para isomer is 1,4-dichloro benzene

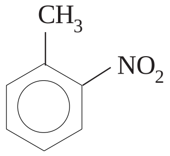
It should be remembered that there are two ortho and two meta and only one para position to the substituent already present in a molecule of benzene.



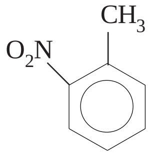
and



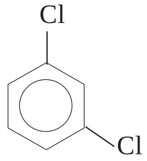
(OR)



and



These two are identical and are not isomers. Similarly the following two represent one and the same compound and are not non-superimposable mirror images.



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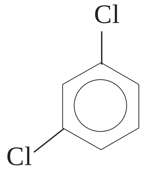
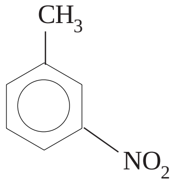


(OR)



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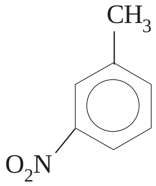
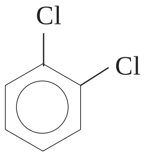
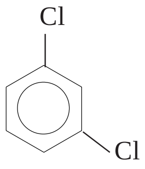
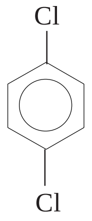


Ortho, meta and para isomers differ mainly in physical properties like melting point, refractive index, solubility. Their behaviour under an applied electric field differs widely. This behaviour is measured by a quantity called 'Dipole moment'. For disubstituted benzenes the magnitude of DPM depends on the angle between the two substituents. For example, for dichloro benzene.







angle $\theta = 60^o$ $\theta = 120^o$ $\theta = 180^o$

Their DPM, is in the order.

Ortho isomer > Meta isomer > Para isomer

for para dichloro benzene DPM = 0.

Hence dipole moment measurement is the best method of distinguishing the three isomers of disubstituted benzenes.

SELF EVALUATION

Choose the correct answer :

1. Identify chiral molecule among the following :

   (a) isopropyl alcohol (b) isobutyl alcohol

   (c) 2-pentanol (d) 1-bromo-3-butene

2. Which among the following is not having an asymmetric carbon atom ?

   (a) 2-chloro butane (b) 2-bromo-3-butene

   (c) 2-hydroxy propanal (d) isobutyric acid

3. Which among the following can be a chiral center ?

   (a) C^+ of a cabocation (b) carbon of a radical

   (c) an sp^2 carbon (d) an sp^3 carbon

4. Give the structural formulae for the simplest chiral.

   (a) alkane (b) alkene (c) alkyne (d) alcohol

   (e) aldehyde (f) ketone (g) carboxylic acid (h) amine.

GEOMETRICAL ISOMERISM

1. Which among the following exhibit geometrical isomerism ?

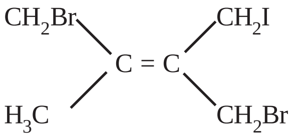
   (a) isobutyraldehyde (b) 1-butene

   (c) 1,1-dichloro ethylene (d) 1-chloro-2-bromo ethylene

2. Which among the following does not exhibit geometrical isomerism ?

   (a) $CH_3CH=CHBr$

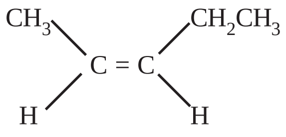
   (b)



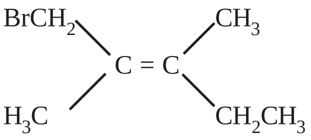
   (c) $(CH)_3C = CHC_2H_5$ (d) $CH_3CH = CHCHO$

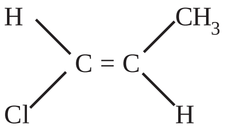
3. Give E/Z-designation for

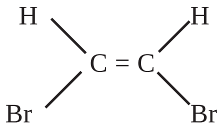
   (a)



   (b)

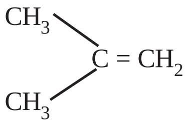


(c) 

(d) 

4. Arrange the following in the increasing order of stability.

$CH_3CH_2CH{=}CH_2$, $CH_3CH{=}CHCH_3$ (cis), $CH_3CH{=}CHCH_3$ (trans)



5. How many linear chain isomers are possible for each of the following olefins ?

Practice Questions

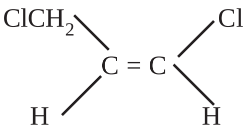
(a) C_4H_8 (b) C_5H_{10} (c) C_3H_6 (d) C_6H_{12}

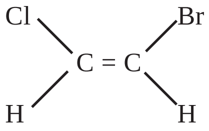
6. Draw the cis, trans isomers for the following and designate them as E or Z.

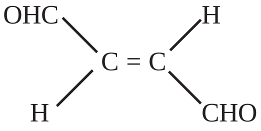
(a) $HOH_2C–CH = CHCH_2CH_3$ (b) $CH_3CH{=}CHCO_2H$

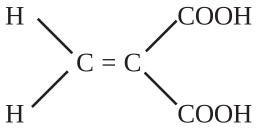
(c) $CH_3CH = CH – CHO$ (d) $CHCl = CHBr$

7. Identify each of the following alkenes as being either cis or trans.

(a) 

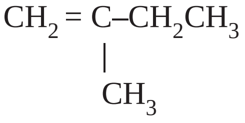
(b) 

(c) 

(d) 

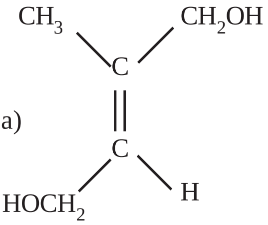
8. Which of the following can exist as geometric isomers ?

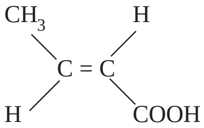
(a) $ClCH_2C \equiv CCH_3$ (b) $ClCH_2–CH = CH–CH_2Cl$

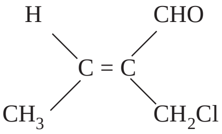
(c) $CH_2 = CHCHO$ (d) 

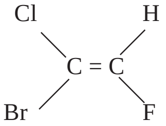
$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}–CH_2CH_3$$

9. Label the following as, E, Z isomers.

(a) 

(b) 

(c) 

(d) 

10. Give the structure of Z and E forms of cinnamic acid.

CONFORMATION

1. Which among the following can have different conformations ?

   (a) CH_4 (b) $CHCl_3$ (c) CH_3COOH (d) CH_3CH_2OH

2. Arrange the following conformation of n-butane with increasing order of energy, staggared (anti), partially eclipsed, eclipsed and skew conformations.
3. The eclipsed form of which of the following has the highest energy.

   Ethane, propane, n-butane, ethylene dibromide.

4. What is the relative composition of the equilibrium mixture of all the conformers of n-butane ?
5. Draw the different conformation of cyclohexane clearly indicating the various C–H bonds.
6. Explain the energy level diagram for axial-equitorial cyclo hexanol conformational changes.
7. Describe the conformations of cyclohexanol. Comment on their stability.

Short answer questions.

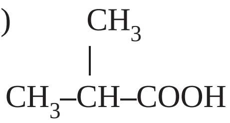
1. Explain the following with examples.

   (a) cis-trans isomerism (b) optical isomerism.

2. Distinguish enantiomers and diasteromers ?
3. What is a racemic mixture ? Explain with suitable example.
4. Mesotartaric acid is an optically inactive compound with chiral carbon atoms. Justify.
5. Distinguish racemic form from Mesoform.
6. Describe the D, L-system of designation of configurations.

OPTICAL ACTIVITY - KEY

1. (b) $CH_3CH_2CH_2\text{–}CH(OH)CH_3$
2. (d)

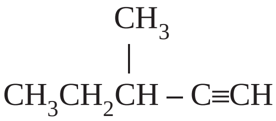


$CH_3\text{–}CH(CH_3)\text{–}COOH$

3. (d) *sp*^{3} carbon
4. (a) $CH_3CH_2\text{–}CH\ (CH_3)CH_2\ CH_2\ CH_3$

   (b) $CH_3CH_2\text{–}CH\ (CH_3) – CH{=}CH_2$

   (c)



$CH_3CH_2CH(CH_3) – C{\equiv}CH$

   (d) $CH_3CH_2\text{–}\ CH\ (OH)\ CH_3$

   (e) $CH_3CH_2\text{–}CH\ (CH_3)CHO$

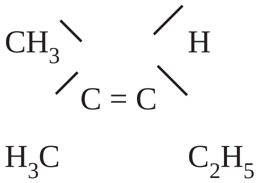
   (f) $CH_3COCH(CH_3)CH_2CH_3$

   (g) $CH_3CH_2CH(CH_3)COOH$

   (h) $CH_3CH_2CH\ (CH_3)NH_2$

Geometrical isomerism

1. (d) CHCl=CHBr
2. (c)



3. (a) Z (b) E (c) E (d) Z

4. $CH_3CH_2CH=CH_2 < (CH_3) CH=CH_2CH_3$ (cis)
$< (CH_3)_2 C =CH_2 < CH_3CH=CHCH_3$ (trans)

5. (a) $CH_3CH_2CH=CH_2$
$CH_3CH=CHCH_3$ (cis, trans)

(b) $CH_3CH_2CH_2CH=CH_2$, $CH_3CH_2CH=CH\ CH_3$ (cis, trans)

(c) $CH_3CH=CH_2$ one

(d) $CH_3CH_2CH_2CH_2CH=CH_2$(1), $CH_3CH_2CH_2CH=CHCH_3$ (cis, trans)
$CH_3CH_2CH=CHCH_2CH_3$ (cis, trans)

CONFORMATIONS

1. (d)
2. Staggard < skew < partially eclipsed < eclipsed.
3. Ethylene dibromide (Br has larger size than CH_3- group).
4. eclipsed < partially eclipsed < skew < staggard.
5. refer energy level diagram of equitorial - axial cyclohexanol

SUMMARY :

ISOMERISM IN ORGANIC CHEMISTRY

Isomerism - Stereoisomerism - Geometrical isomerism and optical isomerism

Geometrical isomerism - difference in the relative orientation of groups attached to C = C Condition.

Stereoisomers which are not mirror images - Cis and trans isomers - E, Z nomenclature - examples.

Conformation - rotation about C – C bond - Conformation of cyclopropane, cyclobutane and cyclopentane.

Non-coplanar arrangement of carbon atoms in cyclo-hexane - chair and boat conformation - relative stability

Cyclohexanol - conformation - axial and equitorial alcohol - energy level diagram.

Optical isomerism - the phenomenon of optical activity - cause of optical activity - asymmetric carbon atom

Chirality - Chiral centre - Chiral molecules - isomers with nonsuperimposable object - mirror image relationship - dextro rotatory and laevorotatory isomers - enantiomers -

Racemic mixture - mixture of enantiomers - optically inactive.

Optical isomers with more than one asymmetric carbon atom - Tartaric acid - enantiomers and diastereomer - mesoform - optically inactive.

Designation of configuration - D, L - notation.

Position isomerism - disubstituted benzene - ortho, meta and para isomers - Identification - Dipole moment.

REFERENCES :

1. Problems in sterochemistry and conformations by Samuel Delvin.
2. Stereochemistry of organic compounds by Eliel.
3. Organic chemistry by Morrison Boyd.

16. HYDROXY DERIVATIVES

LEARNING OBJECTIVES

- *Alcohols - structure - isomerism.*
- *Nomenclature - Common system, Carbinol system, IUPAC system of naming alcohols.*
- *Classification - monohydric, dihydric and trihydric alcohols - Recognising primary, secondary and tertiary alcohols.*
- *Learning general methods of preparation.*
- *Uses of Grignard reagent in the preparation of alcohols.*
- *Physical and Chemical properties - related to structure - uses.*
- *Distinction between primary, secondary and tertiary alcohols.*
- *To learn the methods of preparation, physical and chemical properties and uses of dihydric and trihydric alcohols - ethylene glycol and glycerol.*
- *Oxidation of glycol and glycerol - different methods.*
- *Learning the methods of preparation, properties and uses of aromatic alcohol - benzyl alcohol.*
- *Phenols - classification - preparation, properties*
- *Resonance in phenol - acidic property, difference from alcohol - uses.*

16.1 HYDROXY COMPOUNDS

These are compounds having hydroxyl group directly linked to a carbon atom. These comprise a variety of organic compounds starting from simple alcohols and phenols to complex naturally occuring substances like starch and cellulose.

Alcohol is one of the most important class of compounds. Nearly every other kind of aliphatic compounds like - alkenes, ethers, aldehydes, ketones, acids, esters and a host of other compounds can be made from alcohol. They are not only used as raw materials but frequently as solvents in which reactions are carried out and from which products are crystallised.

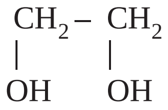
This chapter on alcohol deals with the study of (a) structure and classification, (b) nomenclature, (c) isomerism, (d) general methods of preparation, (e) properties - physical and chemical - relating to structure and (f) uses of alcohols.

16.2 CLASSIFICATIONS AND STRUCTURE

Alcohols are compounds having hydroxy group directly bonded to a saturated carbon atom, having the general formula R–OH.

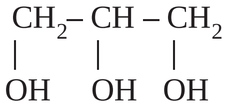
'R' can be	(i) aliphatic saturated	-	ethyl alcohol
	(ii) unsaturated	-	allyl alcohol
	(iii) aralkyl	-	benzyl alcohol

A compound can have more than one hydroxy group such as ethylene glycol, a dihydric alcohol and



$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}$$

Glycerol a trihydric alcohol.



$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}$$

Alcohols can be further classified as primary, secondary and tertiary according to the kind of carbon to which the –OH group is linked.

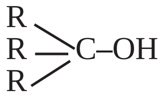
$R - CH_2OH$

Primary

1°

Secondary

2°



Tertiary

3°

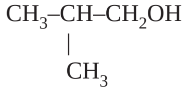
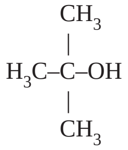
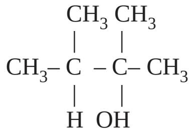
They differ in the rate and mechanism of reaction, often in reactions which directly involve the hydrogen atom attached to the carbon bearing the –OH group an entirely different course for each class of alcohol take place.

16.2.1 NOMENCLATURE

Alcohols are named by three systems of nomenclature.

1. For simple alcohols common names are often used. A common name consists of the name of the alkyl group followed by the word alcohol.
2. The carbinol system of nomenclature considers alcohols as being derived from methanol (called carbinol) by the replacement of one or more hydrogen by alkyl group.
3. In the IUPAC system a set of rules is followed.
   (a) the longest carbon chain that contains the –OH group is taken as the parent structure.
   (b) The name is arrived at by replacing the terminal '*e*' of the corresponding alkane by *-ol.*
   (c) Indicate the number and position of the –OH group in the parent chain using the lowest possible number.

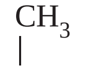
M.F	**Common name**	**Carbinol name**	**IUPAC name**
CH_3CH_2OH	ethyl alcohol	methyl carbinol	ethanol
$CH_3CH_2CH_2OH$	n-propyl alcohol	ethyl carbinol	1-propanol
$CH_3-CHOHCH_3$	isopropyl alcohol	dimethyl carbinol	2-propanol
$CH_3CH_2-\underset{\underset{CH_3}{\vert}}{CH}-OH$	secondary butyl alcohol	ethyl methyl carbinol	2-butanol

 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2OH$	Isobutyl alcohol	isopropyl carbinol	2-methyl-1-propanol
 $H_3C-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-OH$	tert-butyl alcohol	trimethyl carbinol	2-methyl-2-propanol
$C_6H_5CH_2OH$	Benzyl alcohol	phenyl carbinol	phenyl methanol
$CH_3CH_2CHOHCH_2CH_2CH_3$	---	ethyl, propyl carbinol	3-hexanol
 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{H}{\underset{\vert}{C}}}}-\overset{CH_3}{\overset{\vert}{\underset{OH}{\underset{\vert}{C}}}}-CH_3$	----	dimethyl isopropyl carbinol	2,3- dimethy1-2 butanol

Isomerism : Alcohols exhibit three kinds of isomerism.

1. Chain isomerism : arising out of the difference in the carbon chain structure of the parent hydrocarbon.

$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}OH$
1-butanol
(linear chain)


$CH_3-\overset{CH_3}{\overset{\vert}{CH}}-CH_2OH$
2-methyl-1-propanol
(branched chain)

2. Position isomerism : arising out of the difference in the position of –OH group, the hydrocarbon chain being the same.

$CH_3CH_2-CHOH-CH_2CH_3$
3-pentanol

$CH_3CH_2CH_2CHOHCH_3$
2-pentanol

$CH_3CH_2CH_2CH_2CH_2OH$
1-pentanol

3. Functional isomerism :

Alcohols are isomeric with ethers, having the same formula with different functional groups.

$CH_3CH_2CH_2OH$
n-propyl alcohol

$CH_3OCH_2CH_3$
ethyl methyl ether

16.3 GENERAL METHODS OF PREPARATION

Simple alcohols are obtained from natural sources. Thus methyl alcohol is obtained from the liquid formed by the destructive distillation of wood. Hence it is called wood spirit.

Ethyl alcohol is manufactured by the fermentation of sugar present in grains and fruits and hence called ‘grain alcohol’. Other alcohols can be prepared by using any one of the following methods.

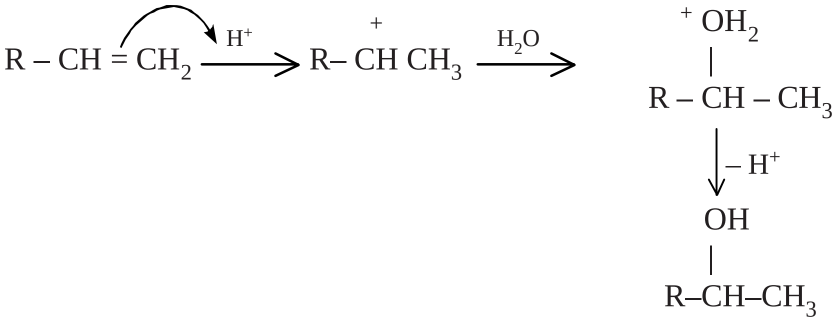
In the light of mechanism involved, alcohol can be prepared by (1) addition reaction, (2) substitution reaction.

(1) Addition reactions

(a) Markownikoff’s addition of water to olefins in presence of dilute sulphuric acid.

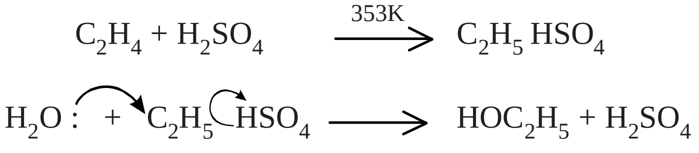
$$\underset{\text{propylene}}{CH_3CH = CH_2} + H_2O \xrightarrow{H_2SO_4} CH_3 - CHOH - CH_3$$

Hydration normally proceeds by protonation of olefins to form carbocation, followed by nucleophilic attack by water.



$$R - CH = CH_2 \xrightarrow{H^+} R - \overset{+}{C}H\ CH_3 \xrightarrow{H_2O} R - \underset{}{\overset{\overset{+}{O}H_2}{\overset{|}{C}H}} - CH_3 \xrightarrow{-H^+} R - \overset{OH}{\overset{|}{C}H} - CH_3$$

Simple alcohol (C_2H_5OH) can be prepared by absorbing olefin in con. H_2SO_4 with the formation of ethyl hydrogen sulphate, which undergoes hydrolysis to give alcohol.

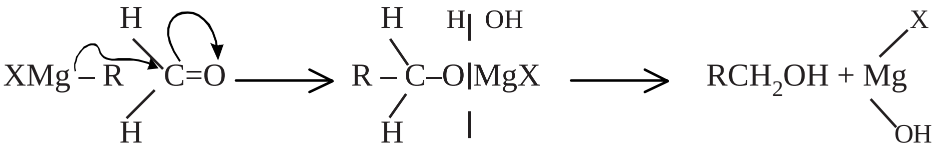


$$C_2H_4 + H_2SO_4 \xrightarrow{353K} C_2H_5\ HSO_4$$

$$H_2O: + C_2H_5 - HSO_4 \longrightarrow HOC_2H_5 + H_2SO_4$$

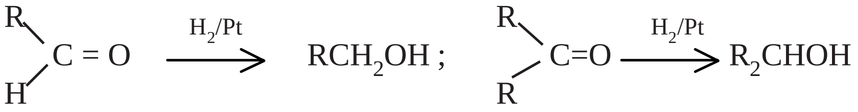
(b) Grignard addition : Grignard reagent adds to carbonyl compounds forming adducts which on hydrolysis form alcohols.

Primary alcohols from formaldehyde.

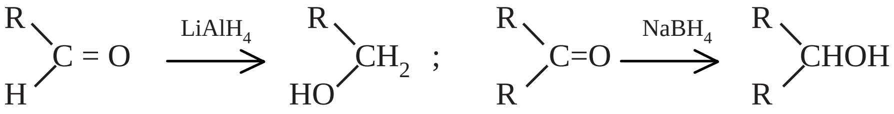


It is a nucleophilic addition where the nucleophile is the carbanion (R^-) generated by the Grignard reagent (RMgX).

(c) By catalytic hydrogenation of aldehydes and ketones



(d) By the reduction of aldehydes and ketones using hydrides.



(2) Nucleophilic substitution

(a) Alkyl halides undergo the nucleophilic substitution reaction. Thus alkyl halides are converted to alcohols by aqueous alkaline solution or silver oxide suspended in water. The nucleophile is OH^- ion and the leaving group is the halide ion.

$$RX + NaOH \xrightarrow{H_2O} R\text{–}OH + NaX$$

$$RX + AgOH \longrightarrow R\text{–}OH + AgX$$

(b) Aliphatic primary amines react with Nitrous acid forming alcohols. Diazonium ion is formed as an intermediate.

$$RNH_2 + HONO \xrightarrow{-H_2O} \underset{\text{unstable}}{[R\text{–}N{=}N^+]} \xrightarrow{H_2O} N_2 + R\text{–}OH$$

The nucleophile is water and the leaving group is Nitrogen molecule.

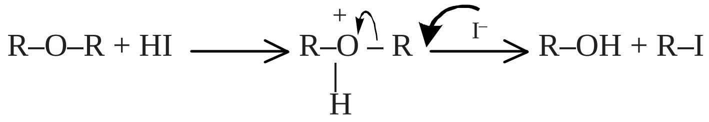
(c) Hydrolysis of esters by either acid or alkali.

$$R'COOR + H_2O \xrightarrow{H^+} R'COOH + ROH$$

$$R'COOR + NaOH \xrightarrow{OH^-} R'COONa + R{-}OH$$

The above reactions proceed with nucleophilic addition to carbonyl carbon atom by water or OH^- ion followed by elimination of ROH.

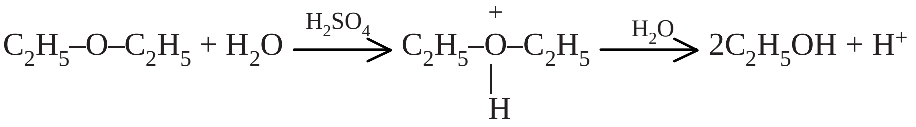
(d) Ethers can be cleaved to alcohols and alkyl iodide by treating with HI.



$$R{-}O{-}R + HI \longrightarrow R{-}\overset{+}{\underset{\substack{|\\ H}}{O}}{-}R \xrightarrow{I^-} R{-}OH + R{-}I$$

First step involves protonation which is followed by nucleophilic displacement by Iodide ion.

Ethers can also be hydrolysed by treating with dilute H_2SO_4 under pressure.



$$C_2H_5{-}O{-}C_2H_5 + H_2O \xrightarrow{H_2SO_4} C_2H_5{-}\overset{+}{\underset{\substack{|\\ H}}{O}}{-}C_2H_5 \xrightarrow{H_2O} 2C_2H_5OH + H^+$$

Protonation of ether oxygen, followed by nucleophilic displacement of ethyl alcohol by water.

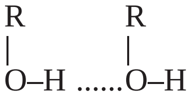
16.3.1 Physical Properties

(a) Alcohols are neutral substances whereas inorganic hydroxides are basic in nature. Physical properties of an alcohol are best understood if we recognise that structurally an alcohol is a composite of an alkane and water.

$$R{-}H \qquad H{-}OH \qquad R{-}OH$$

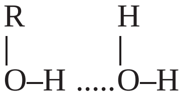
Hence alcohol contains alkane like alkyl group and water like hydroxyl group. The OH^- group gives the alcohol its characteristic properties and the alkyl group modifies it.

The hydroxy group contains highly electro negative element oxygen bonded to hydrogen. Hence this group is polar. This is capable of forming hydrogen bond as shown.



$$\overset{R}{\overset{|}{O}}\text{–H} \;\ldots\ldots \overset{R}{\overset{|}{O}}\text{–H}$$

,



$$\overset{R}{\overset{|}{O}}\text{–H} \;\ldots\ldots \overset{H}{\overset{|}{O}}\text{–H}$$

Many of the physical properties are affected by hydrogen bonding.

1. The boiling point of alcohols are far higher than the hydrocarbons having the same molecular weight and structure.

Compound	**Mol.wt.**	**Boiling point. K**
CH_3OH	32	333
CH_3CH_3	30	184.4
C_2H_5OH	46	351.5
C_3H_8	44	228.5

This is because alcohols are associated liquids. Their abnormal boiling points are due to the greater energy needed to break the hydrogen bonds that hold the molecules together.

Hence lower members are colourless mobile liquids. Higher members are oils, liquids or waxy solids.

(b) Solubility

Alcohols are soluble in water and other hydroxy compounds in contrast to hydrocarbons. This is also explained on the basis of intermolecular hydrogen bonding. The energy required to break intermolecular forces between alcohol molecules is provided by the formation of hydrogen bond between a water molecule and an alcohol molecule. Lower members are completely miscible with water and the solubility decreases with increase in molecular weight. This is because of the increase in size of the hydrophobic alkyl group in the alcohol.

Chemical Properties

Alcohols can be considered to be derived from alkane as well as water.

$$CH_3H \longrightarrow CH_3OH \longleftarrow HOH$$

This is easily seen as the alcohols have properties in between methane and water.

Properties	Methane	Methanol	Water
m.p	89 K	176.8 K	273 K
b.p	159 K	338 K	373 K
Solubility in water	insoluble in water	soluble in water and slightly soluble in hydro carbon.	insoluble in hydro carbon

Similar to water forming hydrate with salts, lower alcohols also form addition compounds with salts (e.g.,) $CaCl_2 \cdot 4C_2H_5OH$, $MgCl_2 . 6CH_3OH$

In chemical reactions also alcohols bear striking resemblance to water and alkane.

Properties due to the acidic nature of hydrogen of the –OH group.

1. Alcohols are weaker acid than water because of +I effect of alkyl groups. Hence alcohols react only with electro positive metals evolving hydrogen.

$$R\text{–}OH + Na \longrightarrow \underset{\text{(Sodium alkoxide)}}{RONa} + \tfrac{1}{2} H_2$$

$$2C_2H_5OH + 2Na \longrightarrow \underset{\text{(Sodium ethoxide)}}{2C_2H_5ONa} + H_2$$

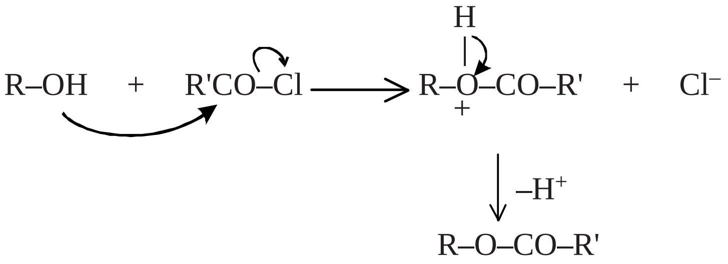
The acid strength decreases in the order $1^o > 2^o > 3^o$ because of the electron releasing effect of the alkyl groups.

2. Strongly basic substances like organometallic compounds are decomposed by alcohol.

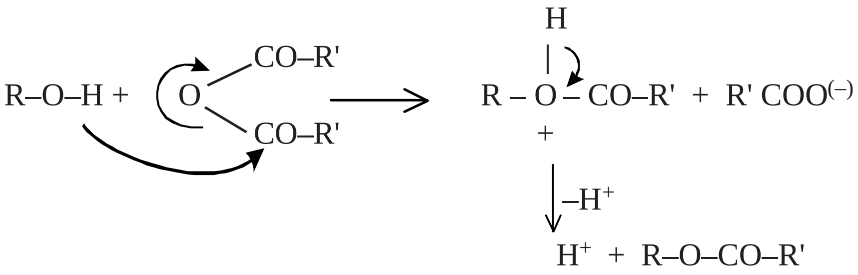
$$R\text{–}OH + CH_3MgBr \longrightarrow RO\text{–}Mg\text{–}Br + CH_4$$

Hence alcohols cannot be used as a solvent for Grignard's reagents.

3. Alcohols react with acid chlorides and acid anhydrides to form esters. This involves nucleophilic attack by alcohol on the carbonyl carbon. The leaving groups are Cl^- or CH_3COO^-



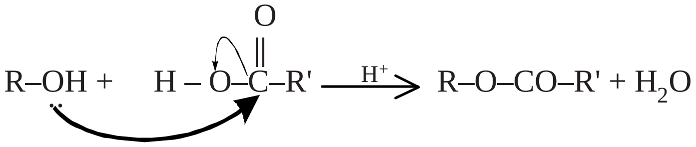
$$R{-}OH + R'CO{-}Cl \longrightarrow R{-}\overset{H}{\underset{+}{O}}{-}CO{-}R' + Cl^- \xrightarrow{-H^+} R{-}O{-}CO{-}R'$$



$$R{-}O{-}H + O\begin{matrix}CO{-}R'\\CO{-}R'\end{matrix} \longrightarrow R - \overset{H}{\underset{+}{O}} - CO{-}R' + R'\,COO^{(-)} \xrightarrow{-H^+} H^+ + R{-}O{-}CO{-}R'$$

Reactions in which the –OH group is involved.

1. Alcohols react with carboxylic acids in presence of con. sulphuric acid. Alcohol molecule brings forth a nucleophilic attack on the carbonyl carbon to form ester.



$$R{-}OH + H - O{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow{H^+} R{-}O{-}CO{-}R' + H_2O$$

$$C_2H_5OH + CH_3COOH \xrightarrow{H^+} \underset{\text{(ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

2. Alcohols form alkyl chlorides. When treated with anhydrous zinc chloride and hydrogen chloride.

$$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

This reaction involves protonation of the alcohol followed by nucleophilic attack by chloride ion. Protonation weakens the C–O bond considerably.

The removal of water from the protonated species is facilitated by anhydrous zinc chloride. Reactivitiy in this reaction with respect to alcohols is $3^o > 2^o > 1^o$. This reaction is used in Lucas Test.

$$(CH_3)_3\ COH \xrightarrow[\text{anhyd. }ZnCl_2]{\text{con.HCl}} (CH_3)_3\ C–Cl + H_2O$$

3^o alcohol

(Turbidity appears immediately)
at room temperature

$$(CH_3)_2\ CHOH \xrightarrow[\text{anhyd. }ZnCl_2]{\text{con.HCl}} (CH_3)_2CHCl + H_2O$$

2^o alcohol

(Turbidity appears after 5-10 minutes)
at room temperature

$$CH_3CH_2OH \xrightarrow[\text{anhydrous }ZnCl_2]{\text{Conc. HCl}} CH_3CH_2Cl + H_2O$$

1^o alcohol

(No turbidity appears easily)
but only on heating

3. Similarly alcohols are converted to alkyl chlorides by thionyl chloride in presence of pyridine.

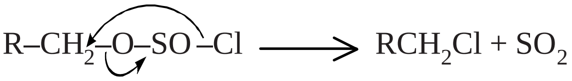
$$RCH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} RCH_2Cl + SO_2 + HCl$$

HCl is removed by pyridine and sulphur dioxide, being a gas escapes. Hence there is no separation problem in this method.

This reaction involves the formation of alkyl chloro sulphite as intermediate.

$$RCH_2OH + ClSOCl \longrightarrow RCH_2–O–SO–Cl$$

Intramolecular nucleophilic attack by the chlorine in the intermediate, on the carbinol carbon atom, results in the removal of sulphur dioxide forming alkyl chloride with retention of configuration.



This reaction belongs to S_Ni (Nucleophilic substitution internal)

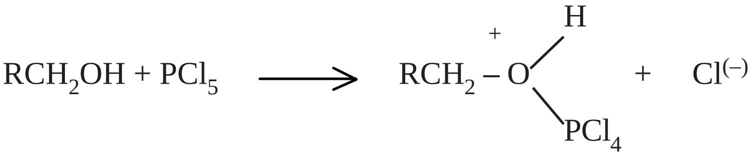
4. Alcohols are converted to their halides by the action of phosphorous halides.

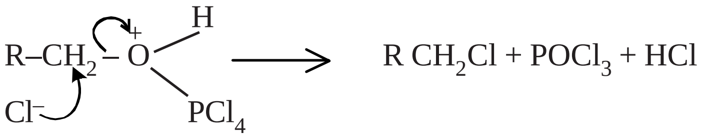
$$R{-}OH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

Similarly alkyl bromide by phosphorous and bromine, alkyl iodide by phosphorous and iodine can be made.

In all these cases an intermediate is formed, which undergoes nucleophilic displacement reaction with halide ion.

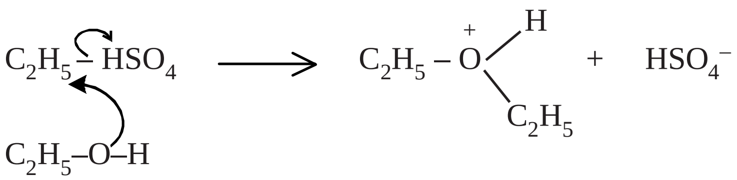


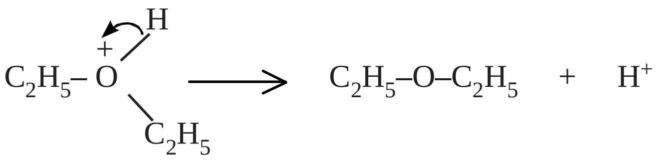


5. Dehydration

(a) Alcohols undergo intermolecular dehydration by treating with con. H_2SO_4 acid to give ethers. In the first step alkyl hydrogen sulphate is formed which with excess alcohols undergoes nucleophilic displacement reaction.

$$C_2H_5OH + H_2SO_4 \xrightarrow{410K} C_2H_5 . HSO_4 + H_2O$$





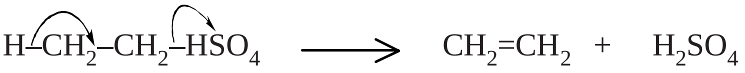
$$C_2H_5-\overset{+}{O}(H)(C_2H_5) \longrightarrow C_2H_5-O-C_2H_5 + H^+$$

(b) Intramolecular dehydration takes place leading to the formation of olefins. This reaction involves β-elimination. It is E_1 reaction and the intermediate is carbonium ion.

$$(CH_3)_3\,COH \xrightarrow{H^+} (CH_3)_3\,\overset{+}{C} + H_2O$$

$$(CH_3)_3\,C^+ \longrightarrow (CH_3)_2\,C = CH_2 + H^+$$

It follows E_2 mechanism if the ethyl hydrogen sulphate is involved as shown.



$$H-CH_2-CH_2-HSO_4 \longrightarrow CH_2=CH_2 + H_2SO_4$$

Thus ethyl alcohol gives ethylene on treating with excess con. H_2SO_4 acid at 440 K.

(c) Dehydration can also be carried out by passing the alcohol vapour over alumina at 620 K.

$$CH_3CH_2OH \xrightarrow[620\ K]{Al_2O_3} CH_2=CH_2$$

(d) Alcohols react with ammonia in presence of heated Alumina or thoria catalyst at 633 K to form mixture of amines.

$$R-OH + NH_3 \xrightarrow[633\ K]{Al_2O_3} RNH_2 \xrightarrow{ROH} R_2NH \xrightarrow{ROH} R_3N$$

Heated alumina removes the water formed.

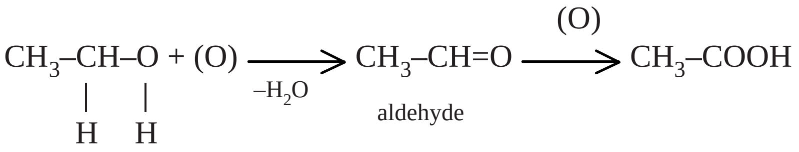
16.3.2 Methods of distinction between three classes of alcohols (1^o, 2^o and 3^o)

Reaction involving hydrogen α- to the –OH group.

Since primary, secondary and tertiary alcohols differ in the number of α-hydrogen atoms, these reactions can be used to distinguish them.

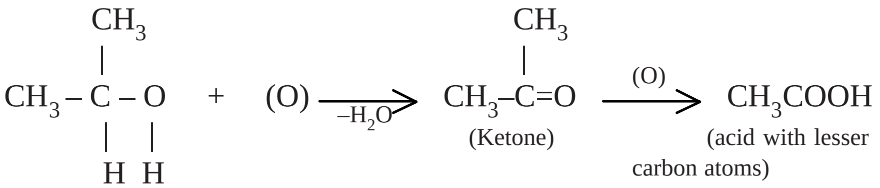
1. Oxidation

Oxidation of alcohols with acidified potassium dichromate gives different oxidation products.



$$CH_3-\underset{H}{\underset{|}{C}}H-\underset{H}{\underset{|}{O}} + (O) \xrightarrow[-H_2O]{} \underset{\text{aldehyde}}{CH_3-CH=O} \xrightarrow{(O)} CH_3-COOH$$

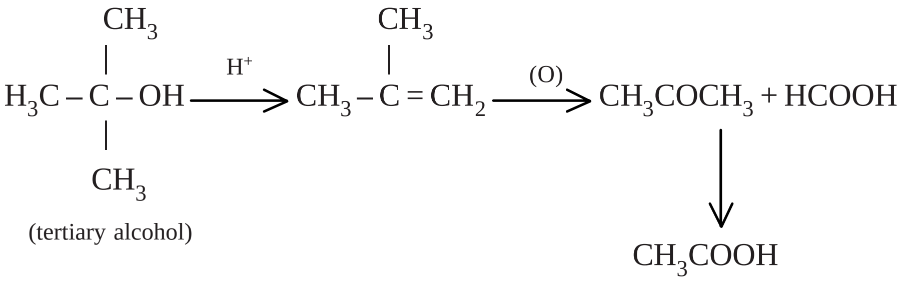
(primary alcohol)



$$CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{O}} + (O) \xrightarrow[-H_2O]{} \underset{\text{(Ketone)}}{CH_3-\overset{CH_3}{\overset{|}{C}}=O} \xrightarrow{(O)} CH_3COOH$$

(acid with lesser carbon atoms)

(secondary alcohol)



$$H_3C-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow{H^+} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{(O)} CH_3COCH_3 + HCOOH$$

$$CH_3COCH_3 \downarrow CH_3COOH$$

(tertiary alcohol)

As the number of α-hydrogen decreases, reactivity with respect to oxidation also decreases.

Hence the presence of α-hydrogen is essential for normal oxidation reactions of alcohols.

Acidified potassium permanganate oxidises the alcohols directly to the carboxylic acid.

$$CH_3CH_2OH \xrightarrow{(O)} CH_3CHO \xrightarrow{(O)} CH_3COOH$$

The breath analysis test for the detection of ethanol involves the oxidation of alcohol in the breath of a person who has consumed alcohol, by acidic potassium dichromate and observing the change in the colour of the chromium ion (Cr^{VI}) from yellow orange to $Cr^{(III)}$ which is blue green colour.

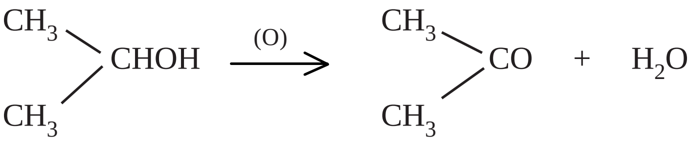
2. Reaction with chlorine water

When alcohols are treated with chlorine water, or sodium hypochlorite or bleaching powder solution, they are oxidised.

Primary alcohols are oxidised to aldehydes

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{(O)} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

Secondary alcohols are oxidised to ketones.



$$(CH_3)_2CHOH \xrightarrow{(O)} (CH_3)_2CO + H_2O$$

Isopropyl alcohol

Acetone

Tertiary alcohols do not undergo this reaction because it does not contain α-hydrogen which is involved.

The carbonyl compounds formed undergo further chlorination forming chlorinated aldehydes and ketones.

$$CH_3CHO \xrightarrow{Cl_2} CCl_3\,CHO \text{ (chloral)}$$

$$CH_3COCH_3 \xrightarrow{Cl_2} \underset{\text{Trichloro acetone}}{CCl_3\,COCH_3}$$

When alcohols containing CH_3CHOH- group is treated with iodine and potassium hydroxide, yellow crystals of iodoform is formed. The tri-iodo carbonyl compound formed is decomposed by the alkali to give iodoform and potassium salt of an acid.

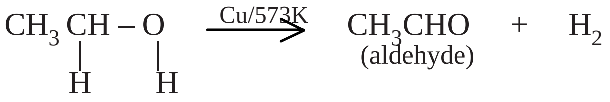
$$C_2H_5OH \xrightarrow{I_2/KOH} CH_3CHO \xrightarrow{I_2} CI_3CHO \xrightarrow{KOH} CHI_3 + HCOOK$$

$$CH_3CHOHCH_3 \xrightarrow{I_2/KOH} CH_3COCH_3 \xrightarrow{I_2} CI_3COCH_3 \xrightarrow{KOH} CHI_3 + CH_3COOK$$

The formation of haloform in general by this procedure is called haloform reaction. Since methanol does not contain CH_3CHOH group, it does not undergo haloform reaction.

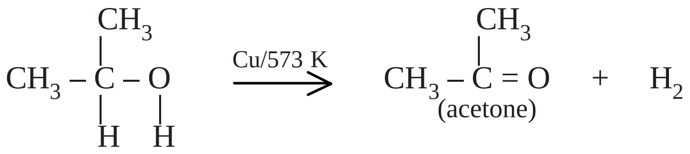
2. Catalytic dehydrogenation :

Dehydrogenation of alcohols by passing the vapours over heated copper at 573 K.



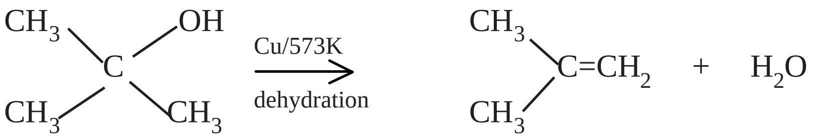
$$CH_3\underset{\underset{H}{|}}{CH} - \underset{\underset{H}{|}}{O} \xrightarrow{Cu/573K} \underset{\text{(aldehyde)}}{CH_3CHO} + H_2$$

Primary alcohol



$$CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}} - \underset{\underset{H}{|}}{O} \xrightarrow{Cu/573\ K} \underset{\text{(acetone)}}{CH_3 - \overset{\overset{CH_3}{|}}{C} = O} + H_2$$

Secondary alcohol



Tertiary alcohol Isobutylene

Absence of α-hydrogen in tertiary alcohol under the above condition leads to only dehydration to olefin.

3. Victor Meyers Test

This test consists of the following steps.

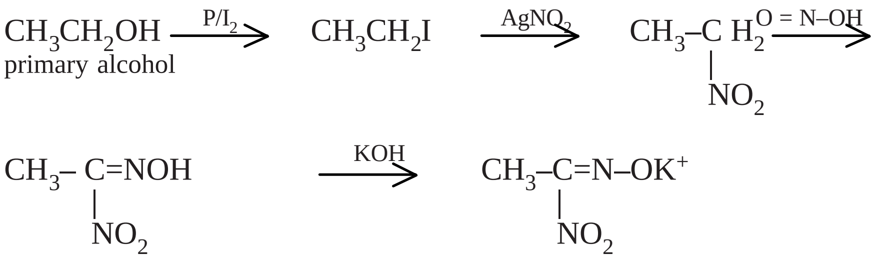
(a) Alcohol is converted into alkyl iodide by treatment with P/I_2

(b) The alkyl iodide is then converted into nitro alkane by silver nitrite ($AgNO_2$).

(c) The nitro alkane is treated with Nitrous acid (HNO_2) and then with aqueous KOH.

The alcohols are identified from the colour of the product.

(a) Primary alcohol:



$$CH_3CH_2OH \xrightarrow{P/I_2} CH_3CH_2I \xrightarrow{AgNO_2} \underset{\displaystyle NO_2}{CH_3-\underset{|}{C}H_2} \xrightarrow{O = N-OH}$$

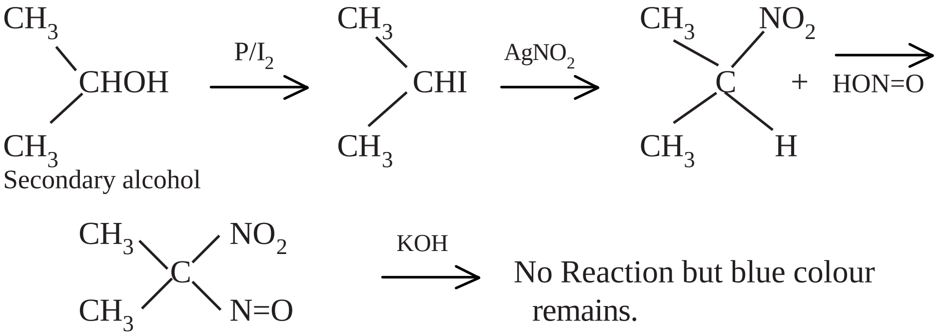
$$\underset{\displaystyle NO_2}{CH_3-\underset{|}{C}=NOH} \xrightarrow{KOH} \underset{\displaystyle NO_2}{CH_3-\underset{|}{C}=N-OK^+}$$

primary alcohol

(Nitroxime or nitrolic acid)

Potassium salt of nitrolic acid (red colour)

(b) Secondary alcohol :

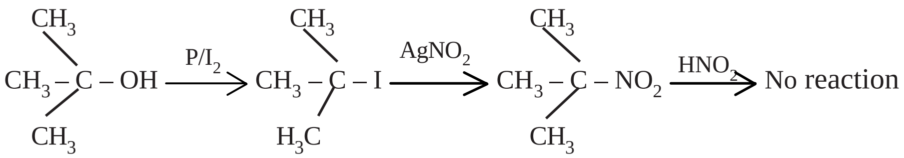


Secondary alcohol

(Pseudo nitrol) blue colour

No Reaction but blue colour remains.

(c) Tertiary alcohol :



Nitro compound colourless

Absence of α-H in tertiary alcohol makes it inactive to nitrous acid.

USES OF ALCOHOLS

(a) Methyl alcohol is used as an industrial solvent (b) as an antifreeze in automobile radiators, (c) for the manufacture of formaldehyde.

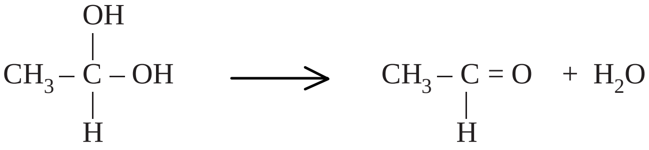
Methanol is poisonous in nature and when taken orally can cause blindness and even death. Ethanol which contains 5% methanol is known as methylated or denatured spirit. It is used as a fuel in spirit lamp and as a solvent for wood polish, methanol is used as a motor fuel along with petrol.

Ethyl alcohol one of the most extensively used organic compound (a) in alcoholic beverage, (b) industrial solvent, (c) in pharmaceutical preparation, (d) as a preservative for biological specimens, (e) in the preparation of large number of other organic compounds like ether, iodoform, acetaldehyde etc., and (f) as a good solvent for recrystallisation and extraction of plant materials etc.

16.4 DIHYDRIC ALCOHOLS

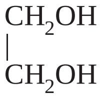
Compounds having two hydroxyl groups are known as dihydric alcohols or diols. If two hydroxyl groups are linked to the same carbon atom, it is called **'gem diols'. These are unstable.** The relative position of the two hydroxyl groups can be 1, 2 or 1, 3 or 1, 4 and so on.

Example,



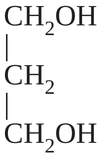
$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-OH \longrightarrow CH_3-\underset{\underset{H}{|}}{C}=O \;+\; H_2O$$

'Gemdiol'



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

1,2 ethane diol



$$\begin{array}{l} CH_2OH \\ | \\ CH_2 \\ | \\ CH_2OH \end{array}$$

1,3 propane diol

Nomenclature of 1,2-diols

1. In the common system, the name is arrived at by adding the word 'glycol' to the name of the olefin from which it is derived.

$HOCH_2-CH_2OH$ ethylene glycol

$CH_3CH(OH)CH_2OH$ propylene glycol

2. In the IUPAC system, the suffix 'diol' is added to the name of parent alkane.

$HOCH_2-CH_2OH$ ethane-1,2-diol

$CH_3CH(OH)CH_2OH$ propane-1,2-diol

ISOMERISM

Position Isomerism

Diols having the same molecular formula differ in the position of the hydroxyl groups.

$CH_3CH(OH)CH_2OH$	propane-1,2-diol
$CH_2(OH)CH_2CH_2OH$	propane 1,3-diol

Functional Isomerism

Diols are **isomeric** with ethers or hydroxy ethers.

$CH_3CH(OH)CH_2OH$ is isomeric with

$CH_3OCH_2OCH_3$ and $CH_3OCH_2CH_2OH$

Dimethoxy methane   2-methoxy-ethanol

16.4.1 GENERAL METHODS OF PREPARATION OF GLYCOLS

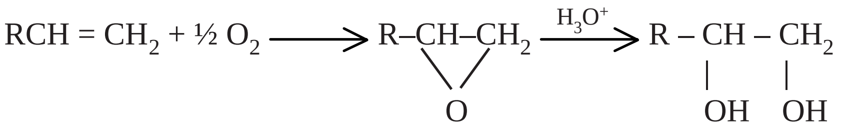
1. By addition reactions

(a) **Dihydroxylation**

By the action of cold dilute alkaline potassium permanganate solution which is known as Baeyer's reagent on olefins, diols are formed.

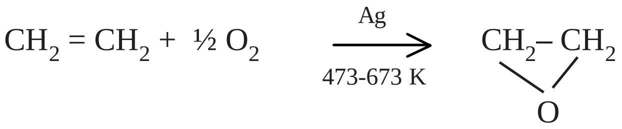
$$RCH=CH_2 + H_2O + (O) \longrightarrow RCHOH-CH_2OH$$

(b) Addition of oxygen to form olefin oxide from olefin followed by acid hydrolysis to give glycol.

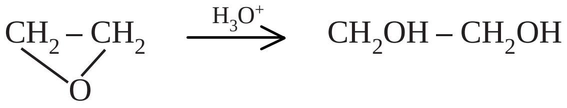


$$RCH=CH_2 + \tfrac{1}{2}O_2 \longrightarrow R-\underbrace{CH-CH_2}_{O} \xrightarrow{H_3O^+} R-\underset{OH}{CH}-\underset{OH}{CH_2}$$

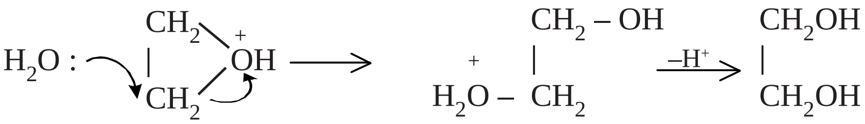
Thus ethylene forms ethylene epoxide.



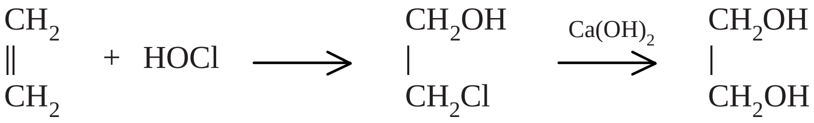
This is hydrolysed to ethylene glycol by dil. HCl or sulphuric acid at 333 K.



This reaction proceeds via the nucleophilic attack by water on the **protonated epoxide.**



(c) Olefins are converted to chlorohydrins and are then hydrolysed with **milk of lime.** Ethylene glycol itself is prepared as follows :



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + HOCl \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2Cl \end{matrix} \xrightarrow{Ca(OH)_2} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

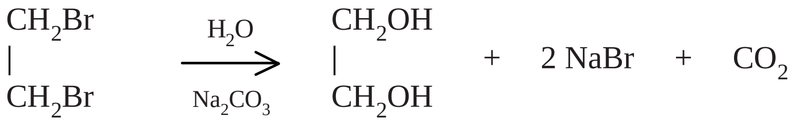
In the above, first step involves **addition across** the double bond and the **second step** a S_N2 attack by the **OH– ion.**

The latter two methods are of **commercial** importance.

2. By substitution reactions :

1,2-dihaloalkanes are hydrolysed with **aqueous sodium carbonate.**

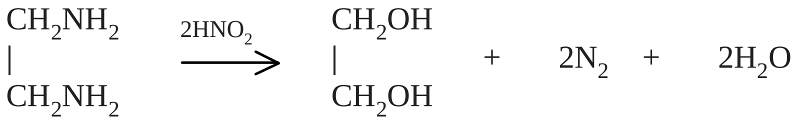
(a) Ethylene dibromide is heated with moist silver oxide or aqueous sodium carbonate solution to form ethylene glycol.



$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \xrightarrow[Na_2CO_3]{H_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2\,NaBr + CO_2$$

This reaction involves **S_N2 attack by OH^- and the leaving group is Br^-.**

(b) Action of nitrous acid on ethylene diamine leads to ethylene glycol.

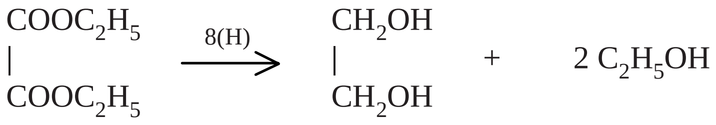


$$\begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array} \xrightarrow{2HNO_2} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2N_2 + 2H_2O$$

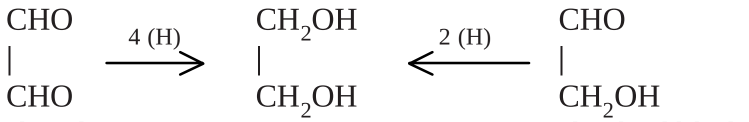
An unstable diazonium ion is formed in the first step, which undergoes **nucleophilic attack** by OH^- to form glycol.

3. By Reduction reactions

This procedure is similar to the preparation of alcohol by **'Bouveault-Blanc Reduction'** where aldehyde or ketone or ester can be reduced to alcohol by **sodium and ethanol.** Thus ethylene glycol is prepared from diethyl oxalate.



$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \xrightarrow{8(H)} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2\,C_2H_5OH$$



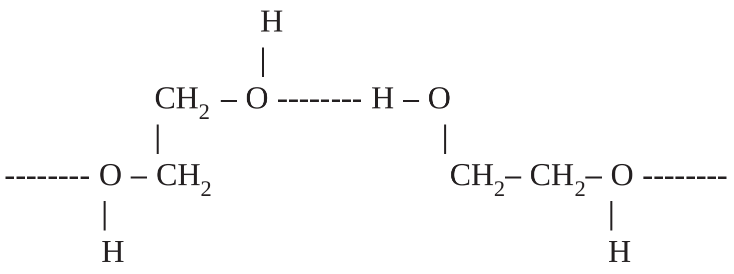
$$\begin{array}{l} CHO \\ | \\ CHO \end{array} \xrightarrow{4\,(H)} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xleftarrow{2\,(H)} \begin{array}{l} CHO \\ | \\ CH_2OH \end{array}$$

glyoxal

glycolic aldehyde

16.4.2 PROPERTIES

Because of the presence of two hydroxyl groups the **intermolecular hydrogen bonding is made much stronger.** Hydrogen bond can be formed between both OH groups resulting in a polymeric structure.



$$\begin{array}{lllll} & & \text{H} & & \\ & & | & & \\ & \text{CH}_2-\text{O} & \text{--------} & \text{H}-\text{O} & \\ & | & & | & \\ \text{--------}\ \text{O}-\text{CH}_2 & & & \text{CH}_2-\text{CH}_2-\text{O} & \text{--------} \\ | & & & | & \\ \text{H} & & & \text{H} & \end{array}$$

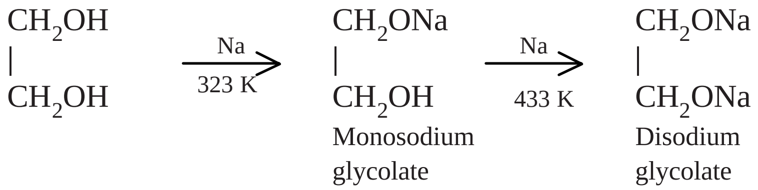
This leads to high viscosity and boiling point (470 K). This is miscible with water and alcohol in all proportions but immiscible with ether. Water or alcohol forms stronger H-bonding with glycol, breaking the polymeric structure. This explains the **'hygroscopic'** nature of glycol. It is a colourless liquid with sweet taste, but toxic in effect.

CHEMICAL PROPERTIES

The molecule of ethylene glycol contains two primary alcoholic groups. It exhibits the general chemical characteristics of primary alcohols twice over. However in most of the reactions both these groups are not equally reactive. One hydroxyl group reacts completely before the other one participates in the reaction. In general this resembles a primary alcohol in all chemical reactions.

1. Replacement of acidic hydrogen

The hydrogen atom of the –OH group is replaced by electropositive metals like sodium step by step, with evolution of hydrogen.



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} \xrightarrow[323\ K]{Na} \begin{array}{l}CH_2ONa\\|\\CH_2OH\end{array} \xrightarrow[433\ K]{Na} \begin{array}{l}CH_2ONa\\|\\CH_2ONa\end{array}$$

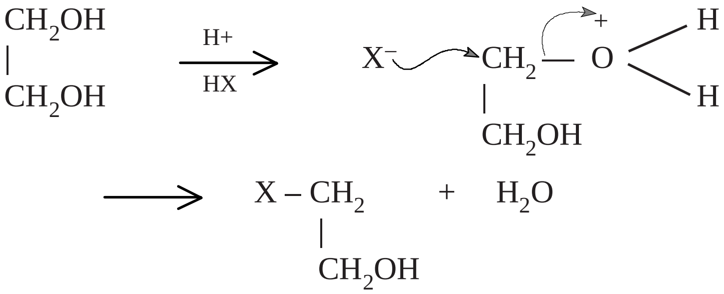
Monosodium glycolate

Disodium glycolate

2. Reactions in which –OH group is replaced

(a) Reaction with organic and inorganic acids to form esters.

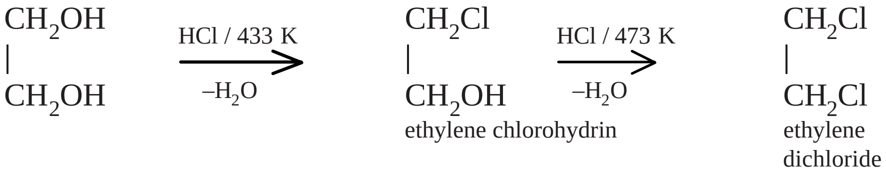
(i) In all these reactions, protonation of the –OH is followed by nucleophilic attack by the anion of the acid.



$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[HX]{H+}X^-\ \begin{array}{l}CH_2-\overset{+}{O}\begin{array}{l}H\\H\end{array}\\|\\CH_2OH\end{array}$$

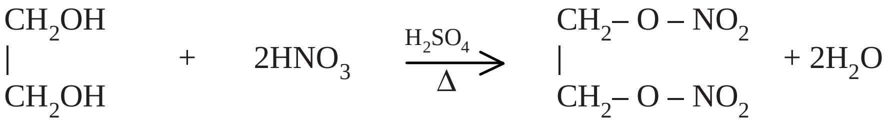
$$\longrightarrow\begin{array}{l}X-CH_2\\ \quad|\\ \quad CH_2OH\end{array}+H_2O$$

Ethylene glycol reacts with hydrogen chloride gas as follows :



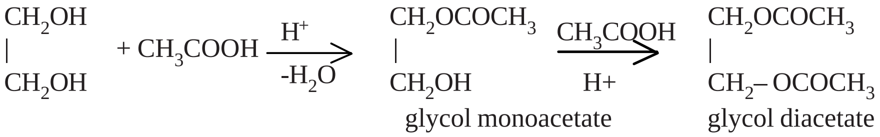
$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[-H_2O]{HCl\ /\ 433\ K}\begin{array}{l}CH_2Cl\\|\\CH_2OH\\\text{ethylene chlorohydrin}\end{array}\xrightarrow[-H_2O]{HCl\ /\ 473\ K}\begin{array}{l}CH_2Cl\\|\\CH_2Cl\\\text{ethylene}\\\text{dichloride}\end{array}$$

(ii) On heating with nitric acid in presence of catalytic amount of con. sulphuric acid, ethylene glycol forms ethylene dinitrate, an explosive liquid.



$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}+2HNO_3\xrightarrow[\Delta]{H_2SO_4}\begin{array}{l}CH_2-O-NO_2\\|\\CH_2-O-NO_2\end{array}+2H_2O$$

(iii) Ethylene glycol reacts with organic acids like acetic acid in presence of mineral acid, forming glycol mono and diacetate.

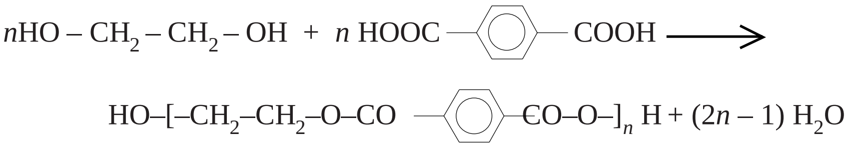


$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+CH_3COOH\xrightarrow[-H_2O]{H^+}\begin{array}{l}CH_2OCOCH_3\\|\\CH_2OH\\\text{glycol monoacetate}\end{array}\xrightarrow[H+]{CH_3COOH}\begin{array}{l}CH_2OCOCH_3\\|\\CH_2-OCOCH_3\\\text{glycol diacetate}\end{array}$$

Acetyl chloride, acetic anhydride also form the same products with ethylene glycol.

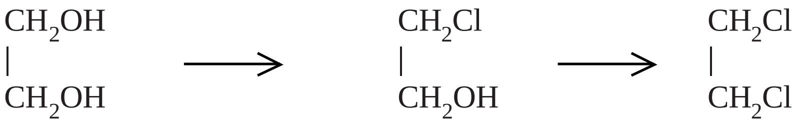
(iv) Reaction of ethylene glycol with dicarboxylic acid.

Both glycol and dicarboxylic acid being molecules with two functional groups, react forming condensation polymers. Thus with Terephthalic acid, ethylene glycol forms the polymer ‘Terylene’ (**also known as dacron or terene**), which is extensively used as a synthetic fibre.



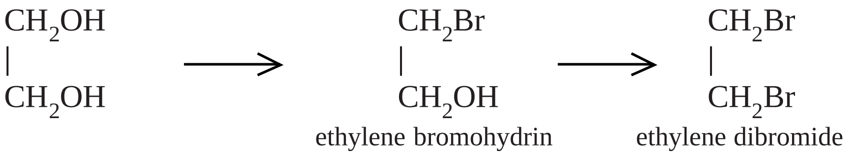
(v) With phosphorous halides

Ethylene glycol forms ethylene chlorohydrin and ethylene dichloride with either PCl_5 or PCl_3.



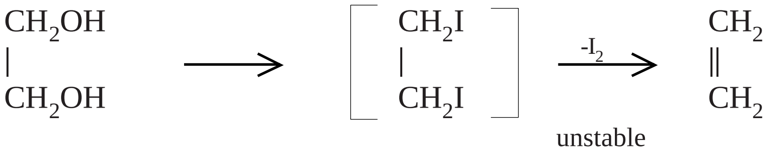
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Similarly PBr_3 forms mono and dibromide.



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \longrightarrow \underset{\text{ethylene bromohydrin}}{\begin{array}{c} CH_2Br \\ | \\ CH_2OH \end{array}} \longrightarrow \underset{\text{ethylene dibromide}}{\begin{array}{c} CH_2Br \\ | \\ CH_2Br \end{array}}$$

With PI_3, it forms ethylene diiodide, which being **unstable decomposes to form ethylene.**

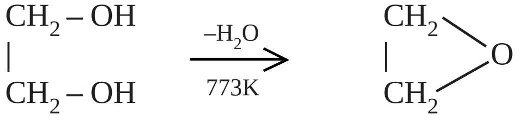


$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} \longrightarrow \left[\begin{array}{c} CH_2I \\ | \\ CH_2I \end{array}\right] \xrightarrow[\text{unstable}]{-I_2} \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$$

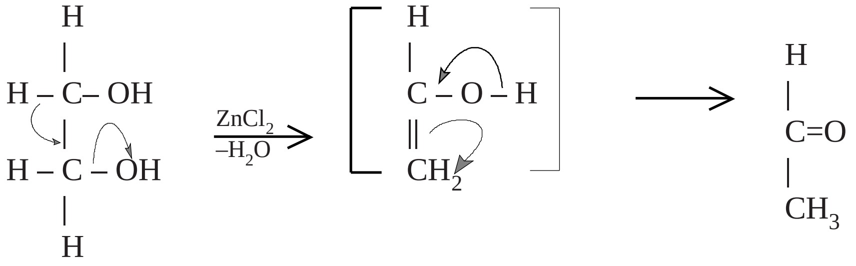
3. DEHYDRATION

Ethylene glycol undergoes dehydration under different conditions to form different products.

(i) When heated alone up to 773 K it forms ethylene oxide or ethylene epoxide. This is an intra molecular reaction in which a water molecule is eliminated from the two –OH groups.



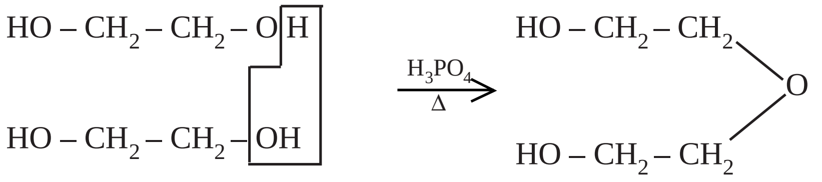
(ii) When heated with anhydrous zinc chloride, ultimately acetaldehyde is formed. This involves β-elimination.



In the second step hydrogen migrates from –OH group to CH_2 carbon.

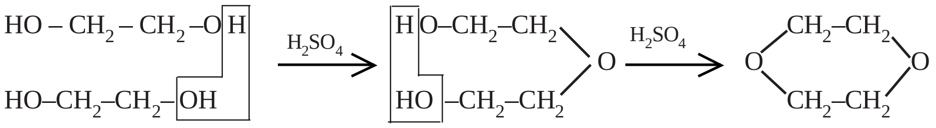
(iii) Intermolecular dehydration

When heated with conc. phosphoric acid, ethylene glycol eliminates a molecule of water forming diethylene glycol.



This involves the nucleophilic attack by the –OH group of one molecule, to displace the protonated –OH group of another molecule.

(iv) Concentrated sulphuric acid being more powerful acid and dehydrating agent removes two molecules of water forming **dioxan.**



4. OXIDATION REACTION

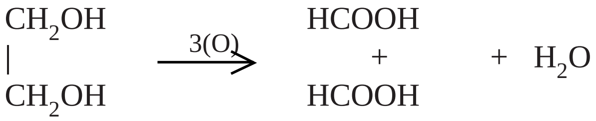
Ethylene glycol contains two primary alcohol groups, hence number of oxidation products are possible. That depends on

(i) The nature of the oxidising agent.

(ii) The quantity of the oxidising agent used.

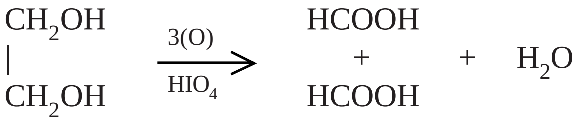
(iii) Whether one or both the primary alcoholic groups are oxidised.

(a) Acidified potassium dichromate or potassium permanganate is very powerful oxidising agent. Hence they are capable of cleaving the C–C bond forming formic acid.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \xrightarrow{3(O)} \begin{array}{c}HCOOH\\ +\\ HCOOH\end{array} + H_2O$$

(b) Periodic acid is a specific reagent to bring about such a C–C bond cleavage by oxidation.

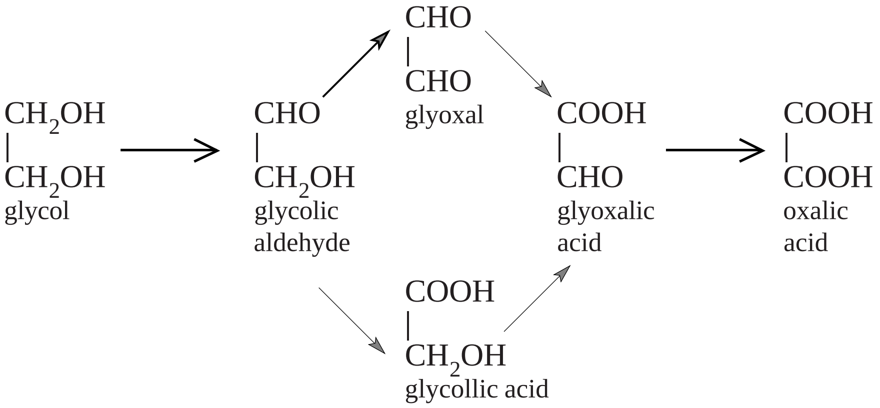


$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \xrightarrow[HIO_4]{3(O)} \begin{array}{c}HCOOH\\ +\\ HCOOH\end{array} + H_2O$$

This undergoes cleavage at carbon-carbon single bond forming two molecules of aldehyde. This further gets oxidised to acids.

Both these reactions involve the formation of cyclic diester with the reagent, as intermediate.

(c) Dilute nitric acid or alkaline $KMnO_4$ oxidises ethylene glycol to the following oxidation products. The first step involves the formation of aldehyde by the oxidation of one $–CH_2OH$ group. The second step may involve (i) oxidation of the other $–CH_2OH$ group to aldehyde or (ii) the further oxidation of –CHO group to –COOH group. Ultimately oxalic acid is formed.



16.4.3 Uses :

(i) As an antifreeze in automobile radiators.

(ii) As a coolant in aeroplane engines.

(iii) As an explosive.

(iv) In the preparation of synthetic fibre, terylene.

(v) As a solvent and preservative.

(vi) In the preparation of numerous compounds like dioxan.

16.5 TRIHYDRIC ALCOHOLS

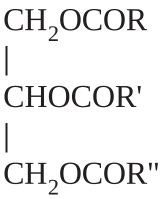
The compounds containing three hydroxyl groups are known as **Trihydric alcohols.** These three hydroxyl groups are attached to three different carbon atoms for stability of the compound. The most important compound of the series is glycerol.

$$\overset{3}{C}H_2OH - \overset{2}{C}HOH - \overset{1}{C}H_2OH$$

This is also known as propane-1,2,3-triol in IUPAC system. This was first discovered by Scheele in 1779 who obtained it by the hydrolysis of olive oil.

It occurs in the combined state as glyceryl ester of higher fatty acids in almost all vegetable and animal oils and fats. The higher fatty acids present in glyceryl esters (oils or fats) are usually palmitic acid ($C_{15}H_{31}COOH$), olecic acid ($C_{17}H_{33}COOH$) and stearic acid ($C_{17}H_{35}COOH$).

The general formula of triester of glycerol is



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR' \\ | \\ CH_2OCOR'' \end{array}$$

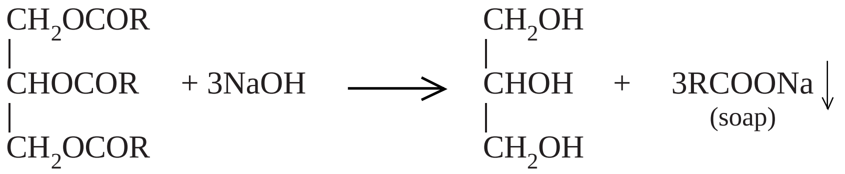
R, R' and R" can be same or different.

The triester is called triglyceride. If R=R'=R" it is called simple triglyceride, if different it is called mixed triglyceride.

Saponification Reaction

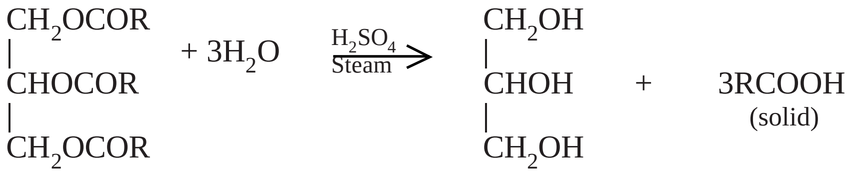
Glycerol is prepared in a large scale by the hydrolysis of oils or fats either by using alkali (in soap industry) or by super heated steam (in candle industry). Hydrolysing with alkali, forms sodium or potassium salt of higher fatty acids as solids. These are called soaps.

In general hydrolysis of esters using alkali is called **'Saponification' reaction.**



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{(soap)}}{3RCOONa\downarrow}$$

Glycerol is formed as byproduct in the soap industry. When the oil is hydrolysed using steam, higher fatty acids are formed as solids. These are used in candle industry.

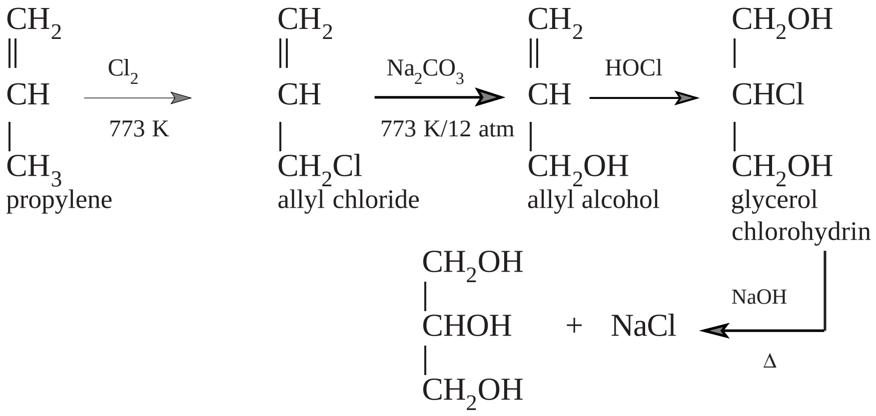


$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3H_2O \xrightarrow[\text{Steam}]{H_2SO_4} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{(solid)}}{3RCOOH}$$

Glycerol is the other product formed in this.

3. Synthesis of Glycerol

Starting from propylene (obtained in the cracking of petroleum) glycerol is synthesised as given below :



$$\underset{\text{propylene}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_3 \end{array}} \xrightarrow[773\text{ K}]{Cl_2} \underset{\text{allyl chloride}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2Cl \end{array}} \xrightarrow[773\text{ K}/12\text{ atm}]{Na_2CO_3} \underset{\text{allyl alcohol}}{\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}} \xrightarrow{HOCl} \underset{\text{glycerol chlorohydrin}}{\begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}}$$

$$\text{glycerol chlorohydrin} \xrightarrow[\Delta]{NaOH} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + NaCl$$

I step involves the (chlorination) substitution of the methyl hydrogen forming allyl chloride.

II step involves hydrolysis - Nucleophilic substitution reaction.

III step addition of hypochlorous acid to olefinic part of allyl alcohol.

IV step hydrolysis with Nucleophilic displacement of chlorine by hydroxyl group.

16.5.1 Physical Properties :

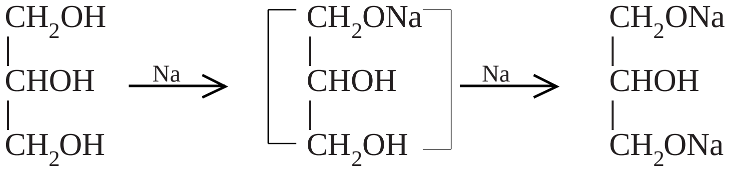
It is a colourless and odourless liquid. It is a highly viscous and hygroscopic liquid with high boiling point (536 K). The latter properties can be explained on the basis of **intermolecular** hydrogen bond leading to complex polymeric structure. It is miscible with water and alcohol in all proportions but insoluble in organic solvents.

Chemical Properties

Glycerol molecule contains **two primary alcoholic groups** and **one secondary alcoholic group.** However both alcoholic groups are not equally reactive though in many of the reactions it resembles alcohol and glycol.

1. Reaction with electropositive metals like sodium :

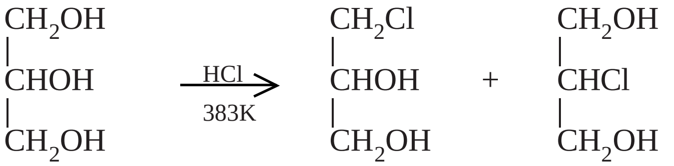
Monosodium glycerolate is readily obtained and the disodium glycerolate at higher temperature. The secondary alcoholic group does not react.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{Na} \left[\begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array}\right] \xrightarrow{Na} \begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \end{array}$$

2. Reaction with hydrogen halides :

Glycerol reacts with hydrogen chloride at 383 K to give both α and β-mono chloro derivative.

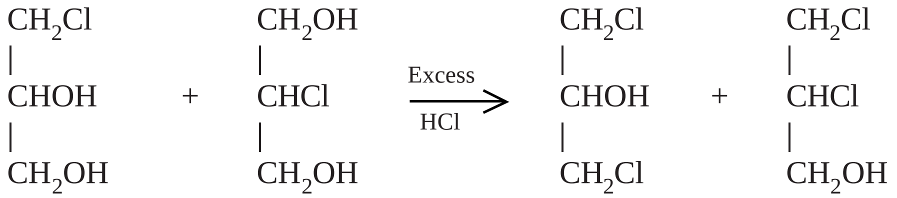


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[383K]{HCl} \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}$$

glycerol α-chlorohydrin

glycerol β-chlorohydrin

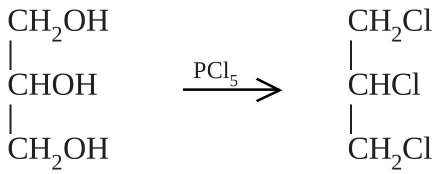
With excess of hydrogen chloride, α, α' - and α, β dichlorohydrins are obtained.



$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array} \xrightarrow[HCl]{Excess} \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} + \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array}$$

α-α' dichlorohydrin α,β- dichloro hydrin

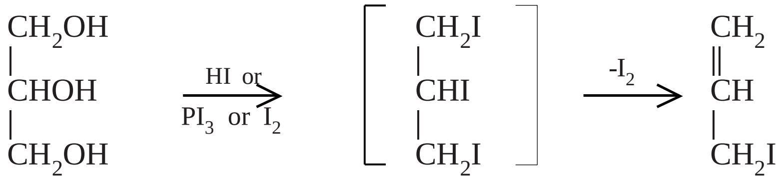
3. Phosphorous pentachloride forms glyceryl trichloride :



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{PCl_5} \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}$$

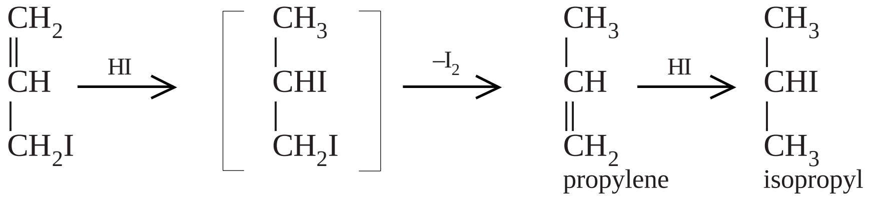
Hydrogen bromide and phosphorous tribromide react in the same way.

With hydrogen iodide or phosphorous triiodide, allyl iodide is formed. An unstable triiodide is formed as an intermediate which loses iodine to give allyl iodide.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[PI_3 \text{ or } I_2]{HI \text{ or}} \left[\begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{array} \right] \xrightarrow{-I_2} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array}$$

With excess of the reagent allyl iodide further reacts giving ultimately isopropyl iodide.



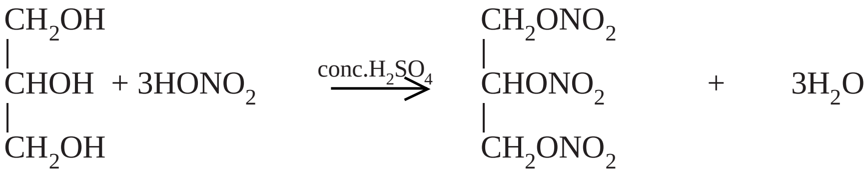
$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array} \xrightarrow{HI} \left[\begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_2I \end{array} \right] \xrightarrow{-I_2} \begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} \xrightarrow{HI} \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array}$$

propylene isopropyl iodide

I Step II Step III Step

The first and the third step involves Markownikoff's addition of HI to the carbon-carbon double bond. The second step involves β-elimination of iodine.

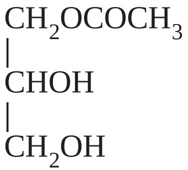
5. With a **well cooled mixture of concentrated sulphuric acid** and fuming nitric acid, nitroglycerine is formed.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HONO_2 \xrightarrow{conc.H_2SO_4} \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + 3H_2O$$

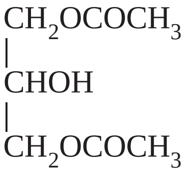
Nitroglycerine
or
Glyceryl trinitrate

Similarly with acetic acid, acetic anhydride (or) acetyl chloride mono, di and tri acetates are formed depending upon the amount of reagent used.



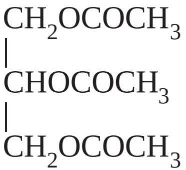
$$\begin{array}{l} CH_2OCOCH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol
Monoacetate



$$\begin{array}{l} CH_2OCOCH_3 \\ | \\ CHOH \\ | \\ CH_2OCOCH_3 \end{array}$$

Glycerol
Diacetate

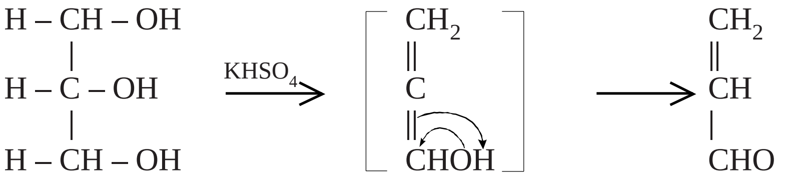


$$\begin{array}{l} CH_2OCOCH_3 \\ | \\ CHOCOCH_3 \\ | \\ CH_2OCOCH_3 \end{array}$$

Glycerol
Triacetate

6. Dehydration :

When glycerol is heated with potassium bisulphate or **conc. sulphuric acid or phosphorous pentoxide** dehydration takes place. Two β-elimination reaction takes place to give acrolein or acrylic aldehyde.



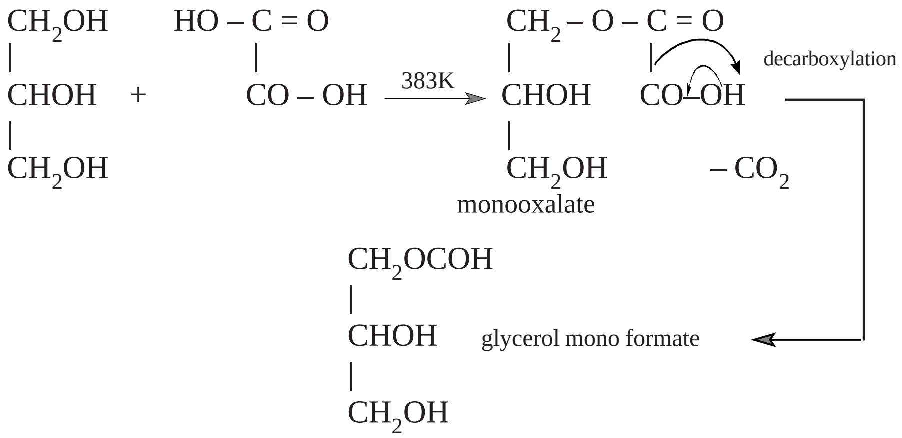
$$\begin{array}{l} H-CH-OH \\ \quad\;\; | \\ H-C-OH \\ \quad\;\; | \\ H-CH-OH \end{array} \xrightarrow{KHSO_4} \left[\begin{array}{l} CH_2 \\ \| \\ C \\ \| \\ CHOH \end{array}\right] \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array}$$

unstable

acrolein

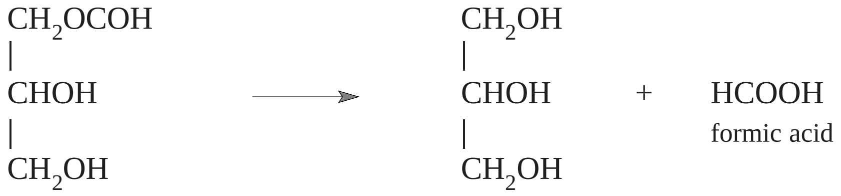
7. Action with oxalic acid :

Depending upon the temperature, glycerol is converted to allyl alcohol or formic acid. At 383 K glycerol mono formate is formed.



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \begin{array}{l}HO-C=O\\ \quad\;|\\ CO-OH\end{array} \xrightarrow{383K} \underset{\text{monooxalate}}{\begin{array}{ll}CH_2-O-C=O & \\ | \qquad\quad | & \\ CHOH \quad CO-OH & \\ | & \\ CH_2OH & \end{array}} \xrightarrow[-CO_2]{\text{decarboxylation}} \underset{\text{glycerol mono formate}}{\begin{array}{l}CH_2OCOH\\|\\CHOH\\|\\CH_2OH\end{array}}$$

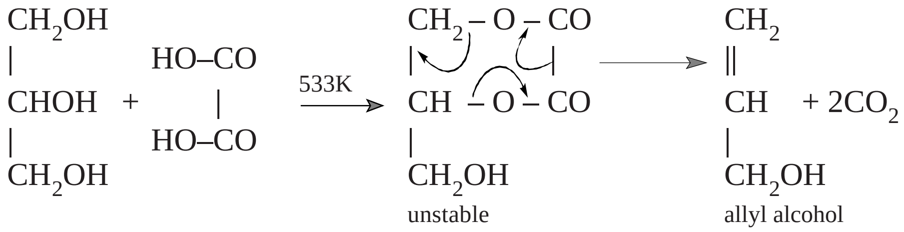
This on hydrolysis gives formic acid.



$$\begin{array}{l}CH_2OCOH\\|\\CHOH\\|\\CH_2OH\end{array} \longrightarrow \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \underset{\text{formic acid}}{HCOOH}$$

In this reaction glycerol acts as a catalyst.

(b) At 533 K, glyceryl dioxalate is formed which eliminates two molecules of carbondioxide forming **allyl alcohol.**



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \begin{array}{l}HO-CO\\ \quad\;|\\ HO-CO\end{array} \xrightarrow{533K} \underset{\text{unstable}}{\begin{array}{l}CH_2-O-CO\\| \qquad\qquad |\\CH\;-O-CO\\|\\CH_2OH\end{array}} \longrightarrow \underset{\text{allyl alcohol}}{\begin{array}{l}CH_2\\||\\CH\\|\\CH_2OH\end{array}} + 2CO_2$$

The elimination of two molecules of carbondioxide takes place by the cyclic reorganisation of bonds in the diester.

8. Oxidation :

Theoretically glycerol can give rise to a large variety of oxidation products. The actual product obtained depends upon the nature of the oxidising agent and their concentration.

(a) With dil. Nitric acid glyceric acid is formed.

(b) With con. Nitric acid glyceric acid and tartronic acids are formed.

(c) Bismuth nitrate converts glycerol to **Mesoxalic** acid.

(d) Milder oxidising agents like bromine water or Fenton's reagent [$FeSO_4 + H_2O_2$] or sodium hypobromite-oxidises glycerol to **'glycerose'** - a mixture of glyceraldehyde and **dihydroxy acetone.**

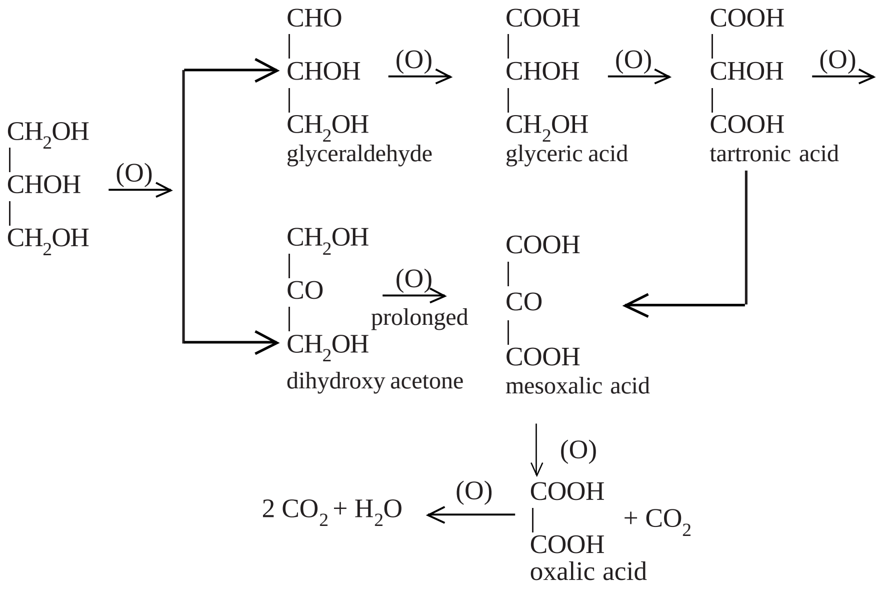
(e) Strong oxidising agents like warm acidified permanganate convert glycerol to oxalic acid and carbondioxide.

Note :

$$\underset{\text{primary alcohol}}{-CH_2OH} \xrightarrow{[O]} \underset{\text{aldehyde}}{-CHO} \xrightarrow{[O]} \underset{\text{acid}}{-COOH}$$

$$\underset{\text{Secondary alcohol}}{-CHOH-} \xrightarrow{[O]} \underset{\text{Ketone}}{>C=O} \xrightarrow{[O]} -COOH + \underset{\text{etc.}}{CO_2}$$

Oxidation reaction of glycerol



16.5.1 Uses :

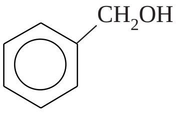
1. In the manufacture of explosives like TNG.
2. as an antifreeze in automobile radiators.
3. as a sweetening agent in beverages.
4. in moisturising creams and other cosmetics.
5. in copying inks and stamp pad inks.

16.6 AROMATIC ALCOHOL

Benzyl alcohol :

Aromatic compounds containing hydroxyl group in the side chain are called aromatic alcohols. A typical example is Benzyl alcohol –$C_6H_5CH_2OH$. It is also called **'phenyl carbinol'** or in the IUPAC system phenyl methanol.

The structure is



It can be considered as an arylated aliphatic alcohol. Benzyl alcohol occurs in nature either in free form or in the form of esters in jasmine oil. It is **isomeric with cresols and anisole.**

16.6.1 Methods of preparation :

1. By the hydrolysis of benzyl chloride

Obtained by the chlorination of Toluene followed by hydrolysis with aqueous NaOH.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + NaCl$$

The formation of benzyl alcohol from benzyl chloride **involves nucleophilic substitution.**

This method is used in the large scale preparation of benzyl alcohol.

2. Reduction of benzaldehyde

Benzaldehyde is reduced to benzyl alcohol on treatment with sodium amalgam and water or zinc and hydrochloric acid or Lithium aluminium hydride.

$$C_6H_5CHO + 2\,[H] \longrightarrow C_6H_5CH_2OH$$

3. By Cannizzaro Reaction :

Simple Cannizzaro reaction of benzaldehyde or a crossed Cannizzaro reaction of a mixture of benzaldehyde and formaldehyde is effected by treating them with 50% caustic soda solution.

$$\text{(i)}\quad \begin{array}{l} C_6H_5CHO \\ \qquad\qquad + H_2O \\ C_6H_5CHO \\ \text{(simple)} \end{array} \xrightarrow{OH^-} \begin{array}{ll} C_6H_5CH_2OH & \text{Benzyl alcohol} \\ \quad + & \\ C_6H_5COOH & \text{Benzoic acid} \end{array}$$

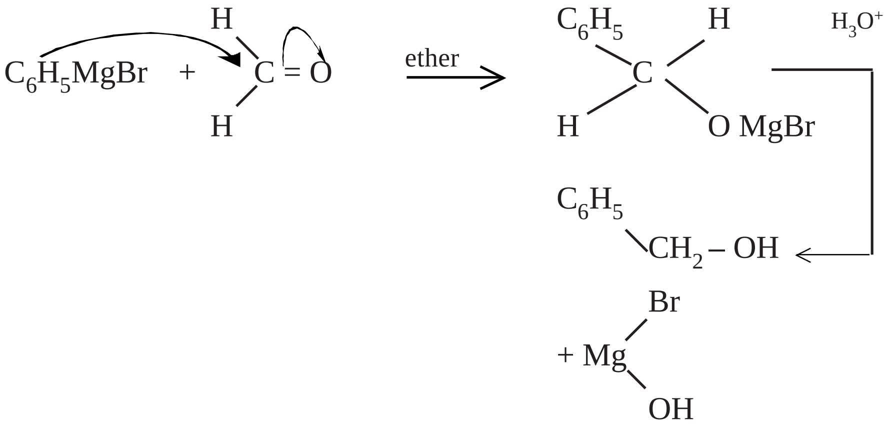
$$\text{(ii)}\quad \begin{array}{l} C_6H_5CHO \\ \qquad\qquad + \; H_2O \\ HCHO \\ \text{(crossed)} \end{array} \xrightarrow{OH^-} \begin{array}{ll} C_6H_5CH_2OH & \text{Benzyl alcohol} \\ \quad + & \\ HCOOH & \text{Formic acid} \end{array}$$

This reaction involves oxidation of one aldehyde molecule to acid, while the other aldehyde molecule is reduced to alcohol.

In the crossed Cannizzaro reaction of benzaldehyde with formaldehyde, it is the formaldehyde that is converted to the acid and benzaldehyde to alcohol. Because formaldehyde can be more easily oxidised than benzaldehyde.

4. Grignard's synthesis

Since benzyl alcohol is a primary alcohol, it is prepared by the action of phenyl magnesium bromide on formaldehyde.



16.6.2 Properties :

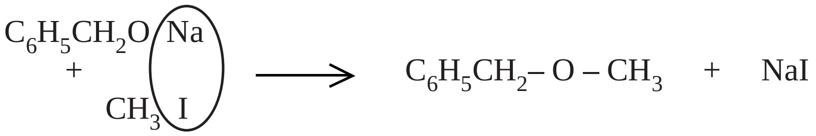
It is a colourless pleasant smelling liquid with b.p. 478 K. It is sparingly soluble in water, because of the presence of hydrophobic phenyl group (larger in size when compared to methyl or ethyl group). But it is soluble in organic solvents like benzene and alcohol.

Chemically it resembles aliphatic primary alcohol.

1. It is not so acidic as to dissolve in sodium hydroxide but reacts with sodium metal forming sodium benzylate or sodium benzoxide.

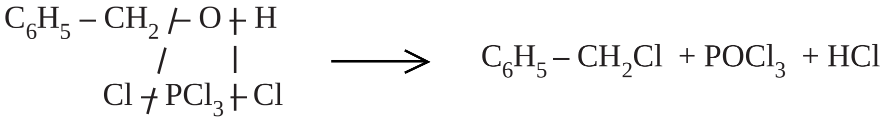
$$2C_6H_5CH_2OH + 2Na \longrightarrow 2C_6H_5CH_2ONa + H_2$$

Sodium benzoxide brings about nucleophilic substitution at methyl carbon atom of the methyl iodide forming ethers.

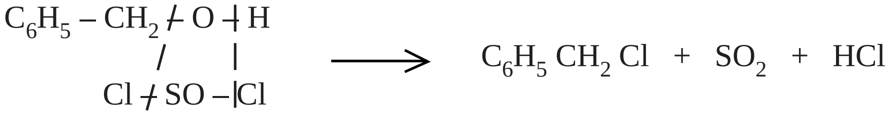


$$C_6H_5CH_2ONa + CH_3I \longrightarrow C_6H_5CH_2-O-CH_3 + NaI$$

2. Reagents like PCl_5, $SOCl_2$ and HCl readily forms benzyl chloride with benzyl alcohol.

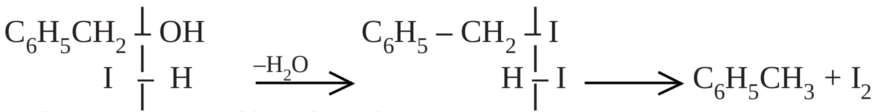


$$C_6H_5-CH_2-O-H + Cl-PCl_3-Cl \longrightarrow C_6H_5-CH_2Cl + POCl_3 + HCl$$



$$C_6H_5-CH_2-O-H + Cl-SO-Cl \longrightarrow C_6H_5\ CH_2\ Cl + SO_2 + HCl$$

4. On heating with phosphorous and hydriodic acid, it is reduced to Toluene. Benzyl iodide is the intermediate in this reaction.



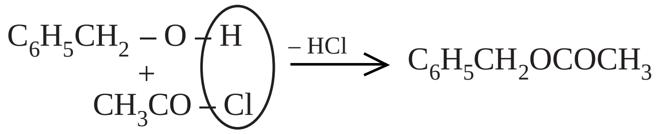
$$C_6H_5CH_2-OH + I-H \xrightarrow{-H_2O} C_6H_5-CH_2-I + H-I \longrightarrow C_6H_5CH_3 + I_2$$

Iodine is removed by **phosphorous.**

Hydrogen in presence of Palladium is the other reagent that can reduce benzyl alcohol to Toluene.

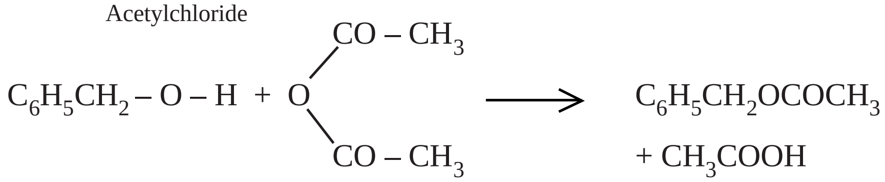
5. Benzyl alcohol forms esters with carboxylic acids in presence of conc. sulphuric acid, and also with acid chlorides and acid anhydrides.

$$C_6H_5CH_2\boxed{OH + H}OCOCH_3 \xrightarrow[-H_2O]{H+} \underset{\text{benzyl acetate}}{C_6H_5CH_2OCOCH_3}$$



$$\begin{matrix} C_6H_5CH_2 - O - H \\ + \\ CH_3CO - Cl \end{matrix} \xrightarrow{-HCl} C_6H_5CH_2OCOCH_3$$

Acetylchloride



$$C_6H_5CH_2 - O - H + O\begin{matrix} CO - CH_3 \\ \\ CO - CH_3 \end{matrix} \longrightarrow \begin{matrix} C_6H_5CH_2OCOCH_3 \\ + CH_3COOH \end{matrix}$$

Acetic anhydride

6. Oxidation :

(i) With mild oxidising agents like copper nitrate or lead nitrate, benzyl alcohol is converted to benzaldehyde.

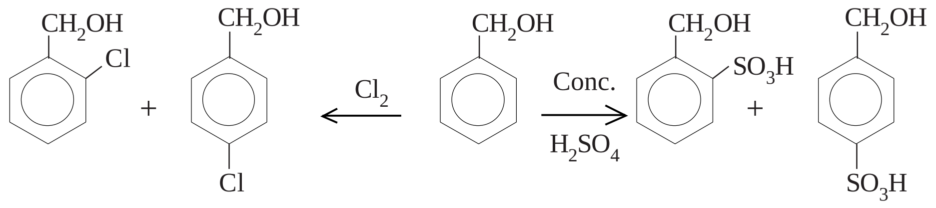
$$C_6H_5CH_2OH \xrightarrow[\text{or } Cu(NO_3)_2]{Pb(NO_3)_2} C_6H_5CHO + H_2O$$

Decomposition of the metallic nitrate provide the source for the above oxidation.

(ii) In the oxidation with acidified potassium dichromate or alkaline potassium permanganate, benzaldehyde is first formed which undergoes further oxidation to benzoic acid.

$$C_6H_5CH_2OH \xrightarrow[Na_2CO_3/KMnO_4]{Na_2Cr_2O_7/H^+ \text{ or}} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

7. In addition to the above reactions, it undergoes reactions characteristic of the benzene ring-namely electrophilic substitution reactions like halogenation, nitration, sulphonation etc. In all these cases substitution takes place in the benzene ring. Like CH_3– and CH_2Cl– groups, CH_2OH– is also **ortho, para directing** group. Hence ortho or para substituted products are formed.



o- and p- chloro
substituted compounds

o- and p-
sulphonic acid derivatives

16.6.3 Uses

(i) Used as a local anaesthetic in intravenus subcutaneous injections.

(ii) as an antiseptic in ointments.

(iii) as esters in perfumery. (Benzyl acetate has fragrance of Jasmine)

(iv) as benzyl benzoate in the treatment of asthma and whooping cough.

(v) in the manufacture of synthetic resins.

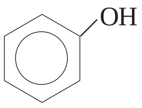
16.7 PHENOLS

Phenols : These form a class of compounds in which one or more hydrogen atom of the benzene nucleus are replaced by hydroxyl group. The simplest members are phenol [C_6H_5OH] and cresols [$CH_3–C_6H_4–OH$].

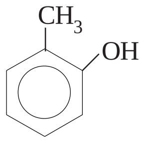
Classification and Nomenclature

1. Phenols may be classified as monohydric, dihydric and trihydric according to the number of hydroxyl groups.

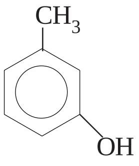
(i) Monohydric phenols :



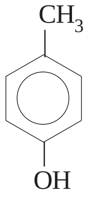
Hydroxy benzene
(Phenol)



o-hydroxy toluene
(o-cresol)



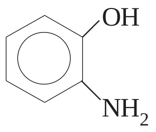
m-hydroxy toluene
(m-cresol)



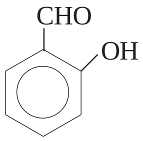
p-hydroxy toluene
(p-cresol)

(ii) Subsituted phenols :

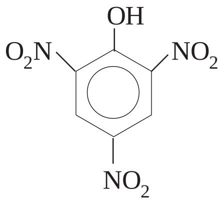
These are named as derivatives of phenol or as hydroxy compounds.



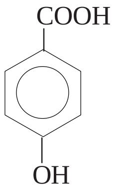
o-aminophenol



o-hydroxy
benzaldehyde

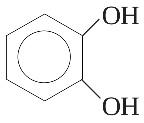


2,4,6-trinitro
phenol

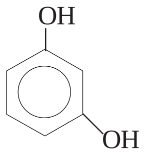


p-hydroxy
benzoic acid

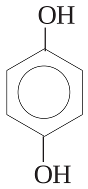
(iii) Dihydric phenols :



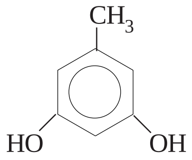
1,2-dihydroxybenzene
or
ortho dihydroxy
benzene
or
Catechol



1,3-dihydroxybenzene
or
meta dihydroxy
benzene
or
Resorcinol

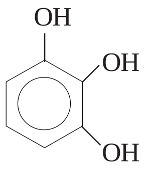


1,4-dihydroxybenzene
or
p-dihydroxy
benzene
or
p-quinol

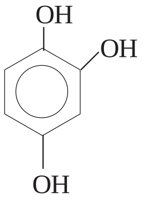


3,5-dihydroxytoluene
or
Orcinol

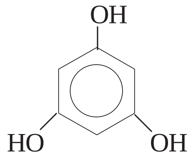
(iv) Trihydric phenols :



1,2,3-trihydroxybenzene
(Pyrogallol)



1,2,4-trihydroxybenzene
(Hydroxy quinol)



1,3,5-trihydroxybenzene
(Phluroglucinol)

Occurence :

Coal tar is the most important source of phenols like phenol, cresol etc., from which they are obtained industrially. Some substituted phenols occur in essential oil of plants like eugenol in clove oil, thymol in mint oil.

16.7.1 Preparation

1. From aryl halides : Phenols can be prepared by heating aryl halide, with caustic soda at high temperature and pressure.

$$\text{Ar-Cl} + \text{NaOH} \xrightarrow[\text{300 atm.}]{\text{623K}} \text{ArOH} + \text{NaCl}$$

$$\underset{\text{Chloro benzene}}{C_6H_5Cl} + \text{NaOH} \xrightarrow[\text{300 atm.}]{\text{623K}} \underset{\text{phenol}}{C_6H_5OH} + \text{NaCl}$$

This reaction is an example of aromatic nucleophilic substitution. The replacement of nuclear halogen is difficult because of the stronger C–Cl bond compared to that in alkyl halides. Yet, this reaction is used for the large scale preparation and is known as **Dow's process.**

2. Phenol is also **manufactured** by heating chlorobenzene with steam in presence of silica as catalyst.

$$C_6H_5Cl + H_2O \xrightarrow{SiO_2} C_6H_5OH + HCl$$

3. From sulphonic acids

Sodium salt of sulphonic acids when fused with sodium hydroxide yield phenoxides. These on treatment with dil. hydrochloric acid give phenols.

$$ArSO_3H + NaOH \longrightarrow ArSO_3Na + H_2O$$

$$ArSO_3Na + 2NaOH \xrightarrow{\text{573 K}} \underset{\text{Sodium phenoxide}}{Ar-ONa} + Na_2SO_3$$

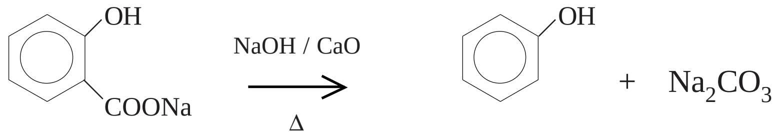
$$ArONa + HCl \longrightarrow ArOH + NaCl$$

4. By boiling weakly acidic aqueous solution of diazonium chloride, phenol is formed.

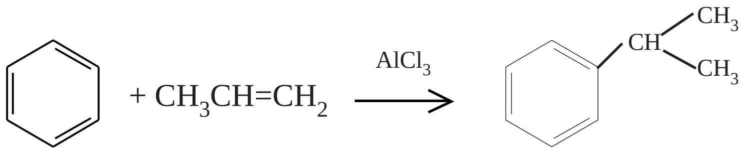
$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + H_2O \xrightarrow{H^+} C_6H_5OH + HCl + N_2$$

This method is useful for the preparation of phenols which cannot be prepared by other methods.

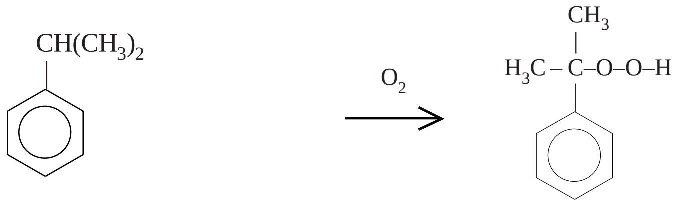
5. By the decarboxylation of phenolic acids. This is carried out by heating sodium salt of phenolic acids with sodalime.



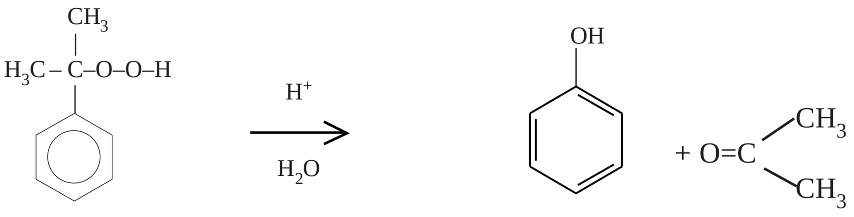
6. Industrially phenol is prepared from cumene. Cumene is prepared from benzene and propylene in presence of Lewis acid like anhydrous aluminium chloride.



This is oxidised to hydro peroxide by oxygen of the air.



This is cleaved to phenol and acetone by aqueous hydrochloric acid.



16.7.2 Properties

1. Pure phenols are colourless liquids or crystalline solids. They turn pink or red on exposure to air and light due to oxidation.
2. Lower phenols have characteristic 'Carbolic acid' - odour.
3. They are insoluble or sparingly soluble in water but dissolve readily in alcohol and ether. Relatively high boiling point of phenols and solubility in alcohols can be explained by intermolecular hydrogen bonding. Insolubility in water is explained by the presence of hydrophobic phenyl group.

16.7.3 General chemical properties

Phenols exhibit reactions of both the hydroxyl group and aromatic ring. They differ from alcohols in having weakly acid character and in not undergoing elimination and substitution reactions.

Reactions of hydroxyl group

In some reactions phenols resemble alcohols. In many others they differ from alcohols.

Reactions different from alcohols

1. They form water soluble coloured complexes with neutral ferric chloride. The colour of the complex vary from violet, red, blue or green. Since different phenols give different colours.

   Phenol itself gives violet colour. It is a characteristic test for phenol.

2. Acidic character

   Phenols are weakly acidic. These are stronger acids than alcohols but weaker than all mineral acids, carboxylic acids and even carbonic acid.

   Hence phenols dissolve in sodium hydroxide (a strong base) but not in sodium bicarbonate (weaker base). This property is used in the separation of phenols from carboxylic acids.

$$C_6H_5OH + NaOH \longrightarrow \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + H_2O$$

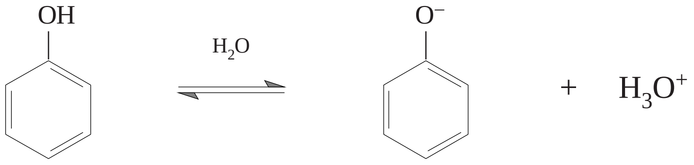
Similarly phenols evolve hydrogen on reaction with electropositive metals like sodium.

$$2C_6H_5OH \ + \ 2Na \longrightarrow 2C_6H_5ONa \ + \ H_2\uparrow$$

16.7.4 Acidic nature of phenols

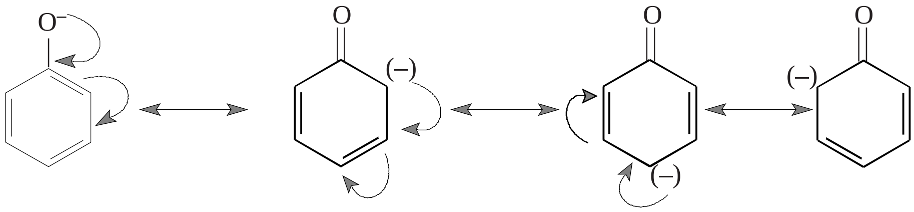
Factors that enhance the stability of the anion of acid and that increase the ease of release of proton, enhance the strength of an acid.

Thus in the case of phenol, the phenolateion is more stabilised by resonance than phenol itself.



Phenol Phenolate ion

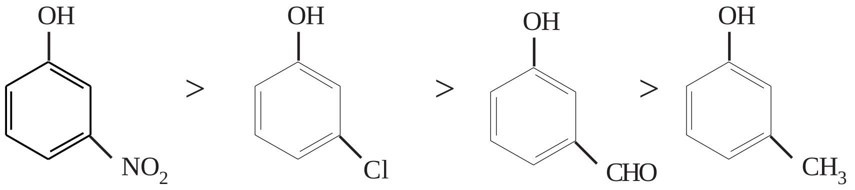
Resonance in phenolate ion



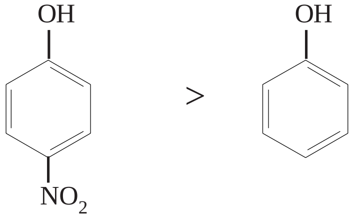
In the case of alcohols there is no stabilisation of the anion.

$$RCH_2–OH \longrightarrow RCH_2–O^{(-)}$$

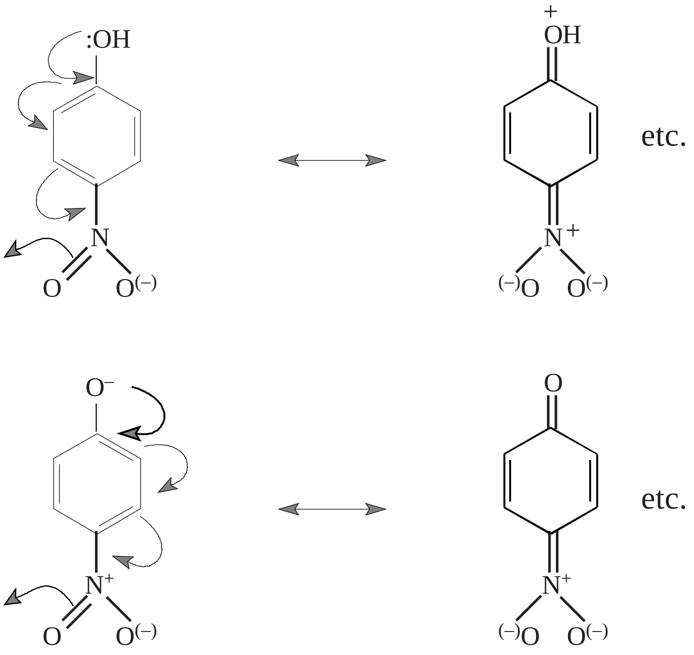
Presence of –I, –M groups in benzene ring enhances its acid strength.



At para position the resonance effect effectively operates.



Resonance in p-nitrophenol and its anion

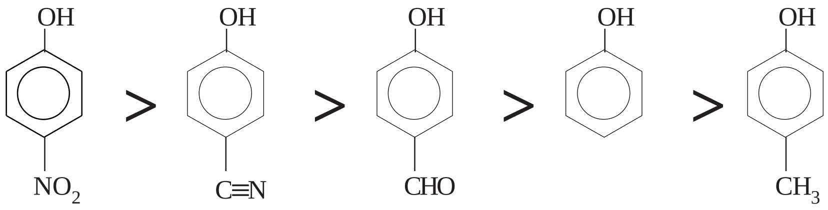


Phenolate ion has no +ve charge on oxygen and hence is more stabilised by resonance than phenol itself.

Consequence of this Resonance

1. Phenols are stronger acid than alcohols (because the RO^--alkoxide ions are not stabilised by resonance).
2. The electron density is increased in the benzene ring and hence the benzene ring is activated towards electrophilic substitution reaction.
3. Ortho and para positions are more electron dense, and the electrophilic substitution takes place at ortho and para positions.
4. Oxygen is strongly bound to the nucleus hence it is not easily removed.

The acid strength of phenols depend on the nature of the substituent present in the benzene ring. Electron withdrawng groups like -Nitro, cyano groups increase the acid strength. Electron donating substituents like $–NH_2$, CH_3- groups decrease the acid strength. (e.g.,) strength of phenol varies in the order.



Reaction with zinc dust

Phenols on distillation with zinc dust give aromatic hydrocarbons.

$$ArOH + Zn \longrightarrow ArH + ZnO$$

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

This reaction is useful in the identification of aromatic ring present in a natural product.

1) Reactions similar to alcohols

The hydrogen of the –OH group of phenol can be replaced by acyl group forming esters.

Direct esterification of phenol using carboxylic acid in presence of dehydrating agent like con. sulphuric acid forms phenol esters but the reaction does not go to completion.

$$C_6H_5OH + CH_3COOH \overset{H^+}{\rightleftharpoons} \underset{\text{Phenyl acetate}}{C_6H_5COOCH_3} + H_2O$$

Acid chlorides and acid anhydrides react with phenols giving esters more easily, especially in presence of a base.

$$C_6H_5 - OH + CH_3 - COCl \xrightarrow{OH^-} C_6H_5OCOCH_3 + HCl$$

$$C_6H_5 - OH + CH_3COOCOCH_3 \xrightarrow{OH^-} C_6H_5OCOCH_3 + CH_3COOH$$

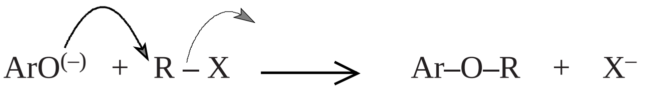
The reaction of phenols with benzoyl chloride in presence of sodium hydroxide to form benzoates is known as **Schotten-Baumann** reaction.

$$C_6H_5OH + C_6H_5COCl \xrightarrow{NaOH} \underset{\text{Phenyl benzoate}}{C_6H_5OCOC_6H_5} + HCl$$

2) Etherification

Phenols react with alkyl halides or alkyl sulphates in presence of alkali to form phenolic ethers. Aryl halides do not react with phenols. This alkylation of phenol is a nucleophilic substitution reaction. This reaction is known as Williamsons synthesis.

$$ArOH \xrightarrow{NaOH} ArO^{(-)} + Na^{+}$$



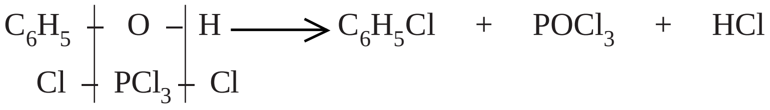
$$ArO^{(-)} + R-X \longrightarrow Ar-O-R + X^{-}$$

$$C_6H_5OH + \underset{\text{Dimethyl sulphate}}{(CH_3)_2\,SO_4} \xrightarrow{NaOH} \underset{\text{Anisole}}{C_6H_5OCH_3} + \underset{\text{Methyl hydrogen sulphate}}{CH_3OSO_2OH}$$

$$C_6H_5OH + C_2H_5Br \xrightarrow{OH^{-}} \underset{\substack{\text{Phenetole or}\\ \text{ethoxy benzene}}}{C_6H_5O\,C_2H_5} + HBr$$

3) Reaction with phosphorous halide

The oxygen of the hydroxyl group in phenol is strongly bound to the benzene ring hence it cannot be easily replaced. Though phenols react with PCl_5 to give chloro benzene, other reagents like HCl, PCl_3, do not give chloro benzene.



$$\begin{matrix} C_6H_5 & | & O & - & H \\ Cl & | & PCl_3 & | & Cl \end{matrix} \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

The yield of chloro benzene is very small and the main product is triphenyl phosphate $(C_6H_5O)_3PO$. (Compare this reaction with alcohol)

4) Diazomethane directly converts phenol to anisole in alkaline medium.

$$\underset{}{C_6H_5OH} + \underset{\text{diazomethane}}{CH_2N_2} \xrightarrow{OH^-} \underset{\text{Anisole}}{C_6H_5OCH_3} + N_2$$

5) Reaction with Ammonia

When heated with NH_3 under pressure in presence of catalysts like anhydrous zinc chloride or calcium chloride, hydroxyl groups of phenols are replaced by amino groups.

$$ArOH + NH_3 \xrightarrow{ZnCl_2/473\ K} ArNH_2 + H_2O$$

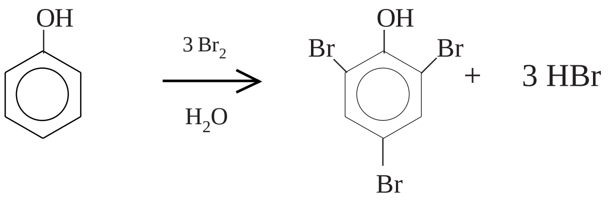
$$\underset{\text{Phenol}}{C_6H_5OH} + NH_3 \xrightarrow{ZnCl_2/473\ K} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

Reactions characteristic of the benzene ring

The phenolic –OH group increases the reactivity of benzene especially with respect to electrophilic substitution reaction. Also it is ortho and para directing group. But due to greater reactivity, phenols undergo poly substitution and oxidation. Hence only under milder conditions mono substitution is expected.

1. HALOGENATION

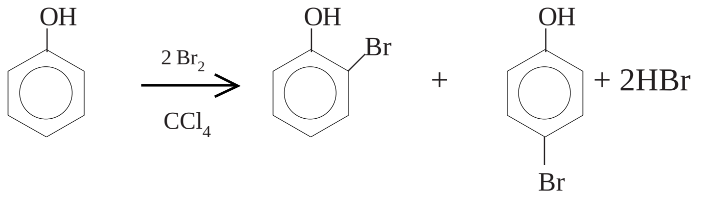
Halogens directly react with phenols, substituting the hydrogen at ortho and para positions. When phenol is treated with bromine water the colour of bromine disappears with the formation of white precipitate. The white precipitate consists of 2, 4, 6-tribromo phenol.



2, 4, 6-tribromo phenol.

This is one of the tests for phenols.

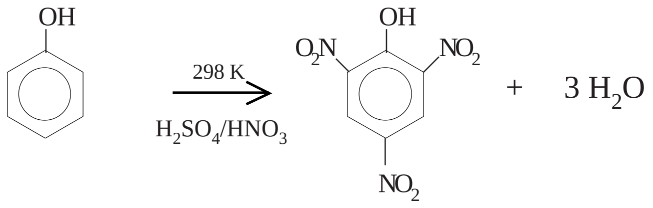
Mono bromoderivative can be prepared at lower temperature and in the presence of non polar solvents like CCl_4 and CS_2.



ortho bromo phenol para bromo phenol

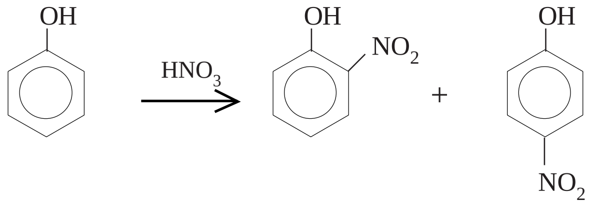
2. NITRATION

Reaction with nitrating mixture - con. H_2SO_4 acid and con. Nitric acid mixture-gives picric acid.



2, 4, 6-trinitro phenol (Picric acid)

With dilute nitric acid, a mixture of ortho and para nitro phenols are formed.

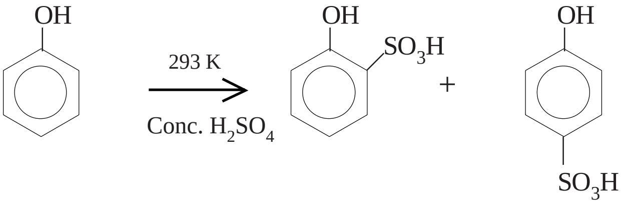


ortho nitro phenol para nitro phenol

NO_2^+ (nitronium ion) is the electrophile in the reaction.

SULPHONATION

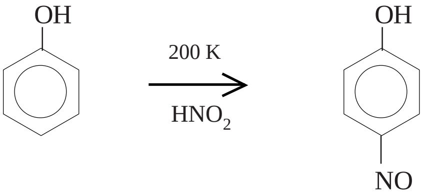
Reaction with con. H_2SO_4. It forms a mixture of ortho and para phenol sulphonic acid.



Ortho hydroxy benzene Sulphonic acid   Para hydroxy benzene Sulphonic acid

NITROSATION

It reacts with nitrous acid (a mixture of sodium nitrite and sulphuric acid) to give *p*-nitrosophenol.

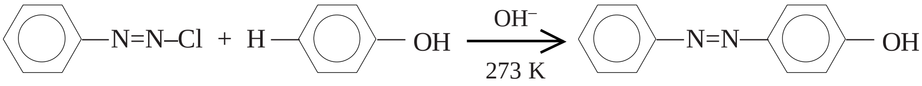


para nitroso phenol

This reaction involves electrophilic attack by NO^+ (nitrosonium ion).

Coupling with diazonium chloride :

Phenol couples with benzene diazonium chloride in alkaline medium to form *p*-hydroxy azobenzene. Diazonium ion $C_6H_5N = N^+$ is the electrophile in this reaction.

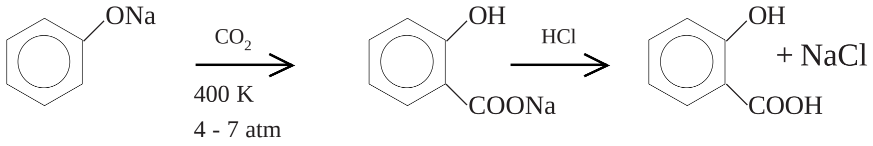


(Benzene diazonium chloride)   (p-hydroxy azobenzene- a red orange dye)

This is also called dye test, which is Characteristic of phenol.

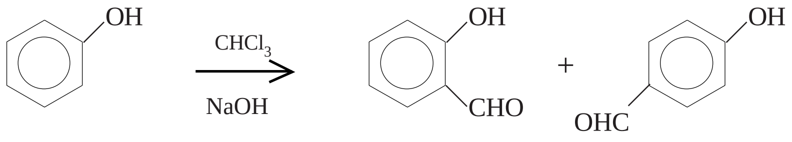
Kolbe schmidt or Kolbe's reaction

When sodium phenoxide is heated with carbon dioxide at 400 K under pressure, sodium salicylate is formed. This is decomposed by dilute hydrochloric acid, when salicylic acid is formed. CO_2 is the electrophile in this reaction.



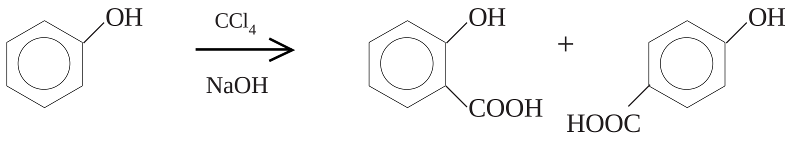
Riemer-Tiemann reaction

This reaction is an example of formylation reaction. When phenol is refluxed with chloroform and sodium hydroxide, a formyl group –CHO is introduced at the ortho or para position to –OH group.



Ortho Para
(Hydroxy benzaldehyde)

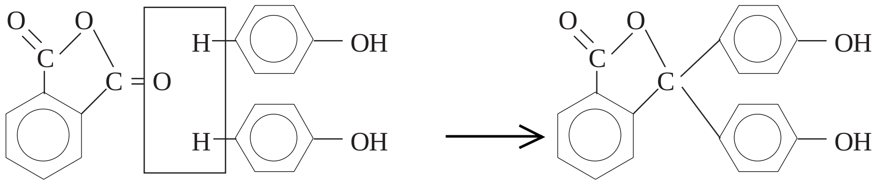
Similarly with CCl_4 and NaOH, hydroxy benzoic acid is formed.



Ortho Para
(Hydroxy benzoic acid)

Phthalein fusion

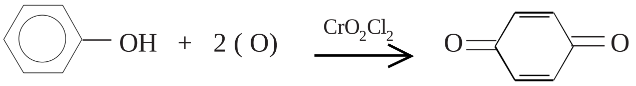
Phenols are heated with phthalic anhydride and con. H_2SO_4 to give Phenolphthalein. This can be tested by the formation of pink colour when it is treated with sodium hydroxide.



Phenolphthalein

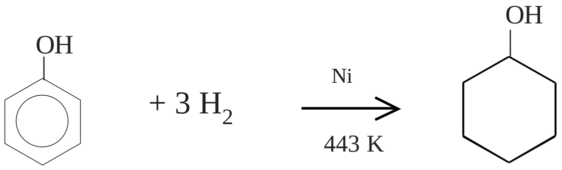
Oxidations

Phenol undergoes oxidation to quinone on treatment with chromyl chloride (CrO_2Cl_2).



Catalytic hydrogenation

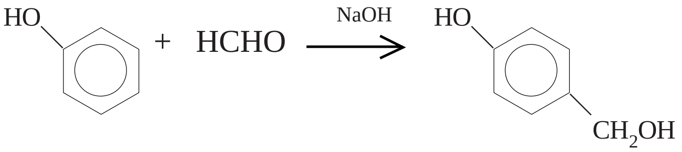
Phenol on hydrogenation in presence of nickel forms cyclohexanol.



(Cyclohexanol)

Condensation :

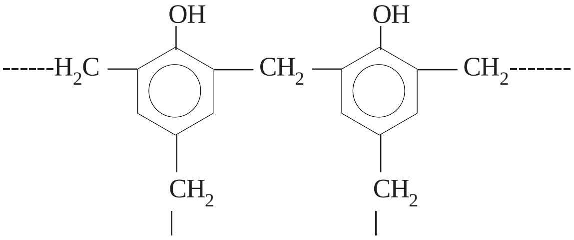
Phenol, when treated with formaldehyde and sodium hydroxide, undergoes condensation reaction.



p-hydroxy phenyl methanol

This is called **'Lederer-Manasse reaction'.**

In presence of excess of formaldehyde, three dimensional polymer called 'Bakelite' is formed.



Bakelite

16.7.4 Uses

Phenol is of much industrial importance. It is used in the manufacture of dyes, drugs, plastics, explosives, pesticides etc. Phenol is an antiseptic and germicide. It is used in some soaps and lotions.

SELF EVALUATION

(A) Choose the correct answer :

1. Which has the highest boiling point ?

   (a) CH_3CH_3 (b) CH_3OH (c) C_2H_5OH (d) C_3H_8

2. Which is soluble in H_2O ?

   (a) Phenol (b) Alkanes (c) Alcohols (d) Alkenes

3. Order of reactivity of alcohol towards sodium metal is

   (a) primary < secondary > tertiary
   (b) primary > secondary > tertiary
   (c) primary < secondary < tertiary
   (d) primary > secondary < tertiary

4. The boiling point of ethyl alcohol should be less than that of

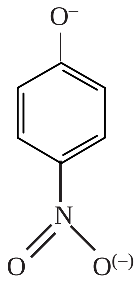
   (a) propane (b) formic acid
   (c) dimethyl ether (d) None of the above

5. Ethyl alcohol cannot be used as a solvent for CH_3MgI because

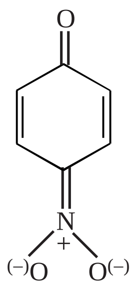
   (a) CH_3MgI reacts with alcohol giving methane
   (b) The reaction between them is explosive in nature
   (c) CH_3MgI is converted to C_2H_5MgI
   (d) Alcohol is immicible with CH_3MgI

6. When alcohols are converted to alkyl chlorides by thionyl chloride in presence of pyridine the intermediate formed is
   (a) sulphonium ion (b) chlorosulphonic acid
   (c) alkyl chlorosulphite (d) chlorosulphite
7. On oxidation of an alcohol gives an aldehyde having the same number of carbon atoms as that of alcohol. The alcohol is
   (a) 1^{o} alcohol (b) 2^{o} alcohol (c) 3^{o} alcohol (d) None
8. A compound that gives a positive iodoform test is
   (a) 1-pentanol (b) 2-pentanone (c) 3-pentanone (d) pentanal
9. The compound that reacts fastest with Lucas reagent is
   (a) butan-1-ol (b) butan-2-ol
   (c) 2-methyl propan-1-ol (d) 2-methyl propan-2-ol
10. The ionization constant of phenol is higher than that of ethanol because
   (a) phenoxide ion is bulkier than ethoxide
   (b) phenoxide ion is stronger base than ethoxide
   (c) phenoxide ion is stablized through delocalisation
   (d) phenoxide ion is less stable than ethoxide ion
11. Among the following compounds strongest acid is
   (a) $HC \equiv CH$ (c) C_6H_6 (c) C_2H_6 (d) CH_3OH
12. The most unlikely representation of resonance structures of p-nitrophenoxide ion is

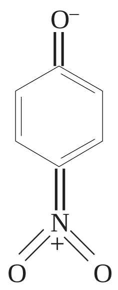
(a)



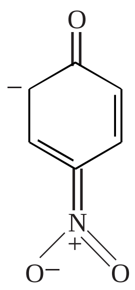
(b)



(c)



(d)



13. p-nitrophenol is having lower pK_a value than phenol because

(a) phenol is more acidic than p-nitro phenol
(b) anion of p-nitrophenol is more stabilised by resonance than that of phenol
(c) degree of ionisation of p-nitro phenol is less than that of phenol
(d) anion of p-nitrophenol is less stable than that of phenol

14. The reaction of Lucas reagent is fast with

(a) $(CH_3)_3COH$ (b) $(CH_3)_2CHOH$
(c) $CH_3(CH_2)_2OH$ (d) CH_3CH_2OH

15. When phenol is distilled with Zn dust it gives

(a) benzaldehyde (b) benzoic acid
(c) toluene (d) benzene

16. A compound that undergoes bromination easily is

(a) benzoic acid (b) benzene
(c) phenol (d) toluene

17. Isomerism exhibited by ethylene glycol is

(a) position isomerism (b) chain isomerism
(c) functional isomerism (d) both (a) and (c)

18. Ethylene diamine is converted to ethylene glycol using

(a) Na_2CO_3 solution (b) nitrous acid
(c) $NaHCO_3$ (aqueous) (d) Baeyer's reagent

19. Ethylene glycol forms terylene with

(a) adipic acid (b) phthalic anhydride
(c) terephthalic acid (d) oxalic acid

20. 1-propanol and 2-propanol can be best distinghished by

(a) oxidation with $KMnO_4$ followed by reaction with Fehling solution
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

21. Glycerol is used

(a) as a sweeteing agent
(b) in the manufacture of good quality soap
(c) in the manufacture of nitro glycerin
(d) in all the above

22. The alcohol obtained by the hydrolysis of oils and fats is

(a) pentanol (b) propanol (c) glycerol (d) glycol

23. The number of secondary alcoholic group in glycerol is

(a) 1 (b) 2 (c) 3 (d) 0

24. The active component of dynamite is

(a) Keiselghur (b) Nitro glycerine
(c) Nitro benzene (d) Trinitro toluene

25. The reaction of ethylene glycol with PI_3 gives

(a) ICH_2CH_2I (b) $CH_2 = CH_2$
(c) $CH_2 = CHI$ (d) $ICH = CHI$

(B) Pick Out the incorrect statements :

1. (a) Secondary alcohol with heated copper at 570 K gives ketone
(b) Isobutyl alcohol in Victor Meyer's test gives blue colour.
(c) Methyl alcohol is more toxic than ethyl alcohol
(d) Methyl alcohol is used in alcoholic beverages

2. (a) The intermediate compound in the preparation of ethylene from ethyl alcohol and con.H_2SO_4 is $C_2H_5.HSO_4$.
(b) An organic acid reacts with alcohol to form an ester.
(c) The acidity of phenol is due to the presence of benzene ring
(d) Tertiary alcohols can not be easily oxidised

3. (a) Benzyl alcohol and phenol can be distinguished by using Br_2/H_2O reagent.

(b) Formation of phenol from chlorobenzene is an example of electrophilic aromatic substitution.
(c) The IUPAC name of ethylene glycol is ethane 1,2-diol
(d) when ethylene glycol is heated to 773 K dehydration reaction takes place.

4. (a) Ethylene glycol reacts with con.H_2SO_4 to form ethylene oxide.
   (b) When acidified potassium permanganate reacts with ethylene glycol C–C bond cleavage takesplace.
   (c) Glycerol on dehydration forms $CH_2=CH–CHO$
   (d) Ethylene decolourises bromine water.

(C) Answer not exceeding sixty words :

1. What are alcohols ? How do they differ from inorganic hydroxides ?
2. Account for the following :
   (a) lower members of alcohols are soluble in water but higher members are not
   (b) Alcohols cannot be used as solvent for grignard reagent.
3. Give reason.
   Methanol is miscible with water while iodo methane is not.
4. Give chemical test to distinguish between ethanol and methanol.
5. Compare the acid strength in 1^o, 2^o and 3^o alcohol giving reason.
6. Write the mechanism briefly when alcohols are treated with anhydrous zinc chloride and HCl.
7. Why is that tertiary alcohols show greater reactivity towards hydrogen halides than secondary and primary alcohols ?
8. How do primary, secondary and tertiary alcohols differ in terms of their oxidation ?
9. How will you convert C_2H_5OH to $C_2H_5OC_2H_5$?
10. Complete the reaction and write the names of products.

$$C_2H_5OH \quad + \quad NH_3 \xrightarrow[360^oC]{Al_2O_3}$$

11. Explain the mechanism of acid catalysed dehydration of ethanol at high temperature.
12. How do primary, secondary and tertiary alcohols differ in terms of their dehydrogenation ?

13. Give chemical tests to distinguish between propan-2-ol and 2-methyl-propan-2-ol.

14. Explain ‘esterification’ reaction with an example.

15. Why is glycol more viscous than ethanol ?

16. What happens when ethylene reacts with alkaline $KMnO_4$ solution ?

17. Explain oxidation reactions of ethylene glycol.

18. How is terylene prepared from glycol ?

19. Write the conversion of ethylene glycol to 1,4-dioxan ?

20. How is glycerol obtained commercially ? State its two uses.

21. How does glycerol react with (i) PCl_5 (ii) $KHSO_4$.

22. Give a brief account of the following reaction. (i) esterification, (ii) Riemer Tiemann reaction.

23. Explain Kolbe’s reaction.

24. Account for the following :

(i) Phenol has a smaller dipole moment than methanol.

(ii) Phenols do not give protonation reaction readily.

25. Explain why phenol does not undergo substitution of the –OH group like alcohol.

26. Complete the following reaction giving names of products.

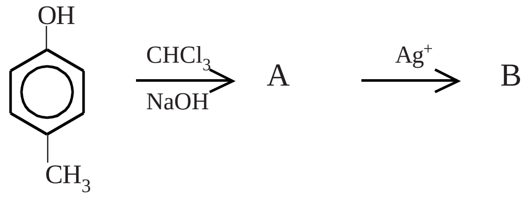
27. Give chemical test to distinguish between methanol and phenol.

28. Give a brief account of coupling reaction.

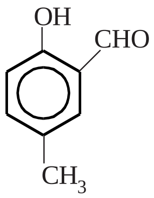
29. What happens when phenol is treated with diazonium chloride in presence of NaOH ?

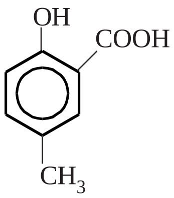
30. Explain Dow’s process.

31. Identify the product A and B.

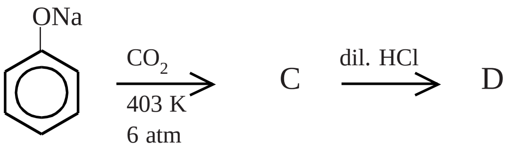


Ans.

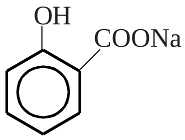
A = 

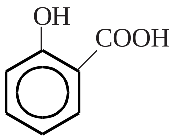
B = 

32. Identify C and D.

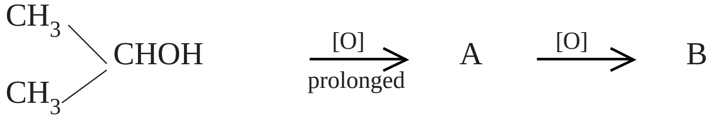


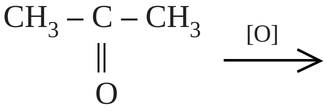
Ans.

C = 

D = 

33. Identify the product. A and B



Ans. A = 

$$CH_3-\underset{\underset{\textstyle O}{\|}}{C}-CH_3 \xrightarrow{[O]} \underset{B}{CH_3\,COOH}$$

34. What are monohydric alcohols ? How are they classified ? Give any three methods of preparing ethyl alcohol.

35. How will you distinguish the primary, secondary and tertiary alcohols by Victor Meyer's method ?

36. Write equation for the following conversions.

(a) Ethyl alcohol $\longrightarrow$ ethylene

(b) Ethyl alcohol $\longrightarrow$ diethyl ether

(c) Ethyl alcohol $\longrightarrow$ ethyl amine

37. Explain the mechanism of esterification.

38. Give short notes on the following :

(a) Kolbe's reaction

(b) Riemer Tiemann reaction

(c) Coupling reaction

39. Explain the action of glycerol with

(i) oxalic acid at 383 K
(ii) oxalic acid at 530 K
(iii) concentrated HNO_3 and H_2SO_4.

40. What are the oxidation products of glycerol ?

41. How is ethylene glycol prepared ? Give three methods.

42. Starting from phenol how would you obtain the following compounds ? (a) p-quinone, (b) picric acid and (c) Anisole.

43. How would you distinguish between

(i) methyl alcohol and ethyl alcohol
(ii) benzyl alcohol and phenol
(iii) ethyl alcohol and benzyl alcohol

44. Give any four methods of preparing benzyl alcohol.

45. Write a note on the 'Acidic nature of phenol'.

Problem.

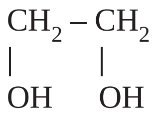
1. How is the following conversion effected ?

   Ethyl alcohol ⟶ Ethylene glycol

   Ans.

$$CH_3CH_2OH \xrightarrow[620K]{Al_2O_3} CH_2 = CH_2 \xrightarrow[KMnO_4]{\text{cold alkaline}}$$

(Baeyer's reagent)



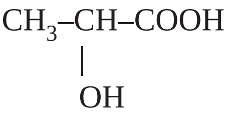
$$\underset{OH}{CH_2} - \underset{OH}{CH_2}$$

2. Give the IUPAC names of

   (i) $CH_3CH(OH)CH_2OH$

   (ii) $HO–CH_2–CH_2–OH$

   (iii)



$$CH_3–\underset{OH}{CH}–COOH$$

   Ans. (i) propane-1, 2-diol

   (ii) ethane-1,2-diol

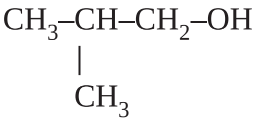
   (iii) 2-hydroxy propanoic acid

3. Identify the isomerism in each of the following pairs.

   (i) $CH_3OCH_2OCH_3$ and $CH_3OC_2CH_2OH$

   (ii) $CH_3CH(OH)CH_2OH$ and $CH_2OHCH_2CH_2OH$

   (iii)



$$CH_3–\underset{CH_3}{CH}–CH_2–OH$$ and $CH_3–CH_2–CH_2–CH_2OH$

Ans. (i) functional isomerism

(a) dimethoxy methane

(b) 2-methoxy ethanol

(ii) position isomerism -diol position is changed

  (a) propane-1,2-diol

  (b) propane-1,3-diol

(iii) chain isomerism - carbon chain is changed.

  (a) isobutyl alcohol

  (b) n-butyl alcohol

4. Complete the following equations by writing the missing A, B, C, D etc.

$$\text{(i) } CH \equiv CH \xrightarrow[\text{HgSO}_4]{\text{dil.H}_2\text{SO}_4} A \xrightarrow{[O]} B \xrightarrow{\text{SOCl}_2} C$$

Ans. A = CH_3CHO

B = CH_3COOH

C = CH_3COCl

$$\text{(ii) } C_2H_5OH \xrightarrow{\text{PCl}_5} A \xrightarrow{\text{KCN}} B \xrightarrow{\text{H}_2\text{O/H}^+} C \xrightarrow[\Delta]{\text{sodalime}} D$$

Ans. A = C_2H_5Cl

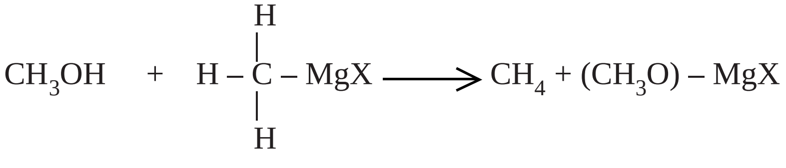
B = C_2H_5CN

C = C_2H_5COOH

D = C_2H_6

5. Why alcohols cannot be used as solvents with (a) Grignard reagent and (b) $LiAlH_4$.

Ans. Alcohols are sufficiently acidic to react with strong bases R^- : and H^- :



$$CH_3OH + H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-MgX \longrightarrow CH_4 + (CH_3O)-MgX$$

$$4CH_3OH + LiAlH_4 \longrightarrow 4H_2 + LiAl(OCH_3)_4$$

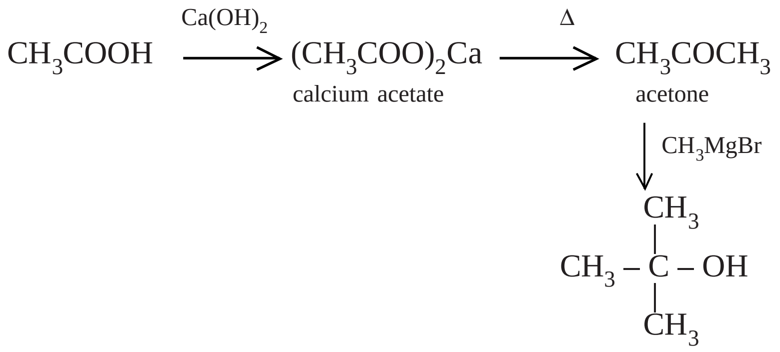
6. When tertiary butyl alcohol and 1-butanol are separately treated with a few drops of $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is that brown precipitate.

Ans. 1-butanol, being primary alcohol gets oxidised by dilute $KMnO_4$. The brown precipitate is due to the formation of manganese dioxide.

$$2KMnO_4 + H_2O \longrightarrow 3KOH + \underset{\substack{\text{manganese dioxide} \\ \text{(brown precipitate)}}}{2MnO_2} + 3\,(O)$$

$$\underset{\text{1-butanol}}{CH_3–CH_2–CH_2–CH_2–OH} + \xrightarrow[\text{room temp.}]{2(O)} \underset{\text{butanoic acid}}{CH_3\,CH_2\,CH_2\,COOH} + H_2O$$

7. Write the conversion of acetic acid to t-butyl alcohol.



$$CH_3COOH \xrightarrow{Ca(OH)_2} \underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} \underset{\text{acetone}}{CH_3COCH_3} \xrightarrow{CH_3MgBr} CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH$$

Tert. butyl alcohol

8. Compound (A) $C_6H_{12}O_2$ on reduction with $LiAlH_4$ yields two compounds B and C. The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave (C). Compound (D) on oxidation gave monobasic acid (molecular formula weight = 60). Deduce the structure of (A), (B), (C), (D) and (E).

Ans. E is monobasic acid (RCOOH) having molecular weight 60 and it is formed from D on oxidation. So E must be acetic acid and D must be acetaldehyde. (B) on oxidation gives CH_3CHO. So (B) must be alcohol (CH_3CH_2OH).

Acetaldehyde (D) on treating with aqueous alkali (NaOH) gives aldol which on heating gives 2-butenal (E).

$$\underset{\text{(D)}}{CH_3CHO} \xrightarrow{NaOH} \underset{\text{aldol}}{CH_3CHOHCH_2CHO} \xrightarrow[-H_2O]{\text{heat}}$$

$$\underset{\text{2-butenal (E)}}{CH_3-CH=CH\ CHO}$$

Compound E on catalytic hydrogenation gives butyl alcohol.

$$CH_3-CH=CHCHO \xrightarrow{H_2} \underset{\text{1-butanol (C)}}{CH_3\ CH_2-CH_2-CH_2\ OH}$$

Hence compound (A) must be an ester. Ester (A) on reduction with $LiAlH_4$ yields two alcohols (B) and (C).

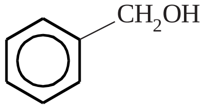
A is ethyl butyrate

$$CH_3CH_2CH_2COOCH_2CH_3 \xrightarrow{LiAlH_4} \underset{\substack{\text{ethyl alcohol} \\ \text{(B)}}}{CH_3CH_2OH} + \underset{\substack{\text{butyl alcohol} \\ \text{(C)}}}{CH_3CH_2CH_2\ CH_2OH}$$

'A' can also be $CH_3CO\text{-}O\text{-}CH_2CH_2CH_2CH_3$. This structure will be answering all the above reactions.

PRACTICE

1. Write the IUPAC names of (i) $CH_3OCH_2CH_2OH$ (ii) $CH_3OCH_2OCH_3$ and (iii)



Ans. (i) 2-methoxy ethanol ; (ii) dimethoxy methane and (iii) phenyl methanol

2. Why sodium metal cannot be used to dry alcohols but it can be used to dry ethers ?

Ans. Alcohols are acidic enough to react with sodium but ethers are inert.

3. An organic compound has the formula $C_4H_{10}O$. It reacts with metallic sodium liberating hydrogen.

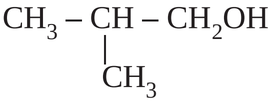
   (i) Write down the formula of three possible isomers of the compound which are similar and react with sodium.

   (ii) What will be the product if any one of the isomers reacts with acetic acid ?

Ans. The three isomers are

(i) $CH_3CH_2CH_2CH_2OH$

$CH_3CH(OH)CH_2CH_3$



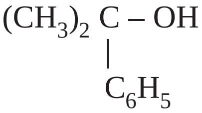
$CH_3-\underset{|}{\underset{CH_3}{CH}}-CH_2OH$

(ii) $CH_3CH_2CH_2CH_2OH + CH_3COOH \longrightarrow CH_3CH_2CH_2CH_2OOCCH_3$

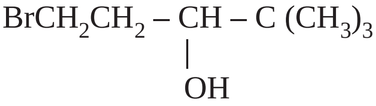
PRACTICE QUESTIONS.

1. Give the IUPAC names of each of the following and classify them as 1°, 2° and 3°.

   (a) $CH_3(CH_2)_3CHOHCH(CH_3)_2$ (b) $(CH_3)_3C–CH_2OH$

   (c) 

   $(CH_3)_2\,\underset{C_6H_5}{\underset{|}{C}}-OH$

   (d) 

   $BrCH_2CH_2-\underset{OH}{\underset{|}{CH}}-C(CH_3)_3$

   (e) $CH_2 = CH–CHOHCH_3$ (f) $PhCH_2OH$

   (g) $HOCH_2CH_2CH_2CH_2C_6H_5$ (h) $(C_2H_5)_3COH$

2. Give all the isomers of alcohols differing only in the position of –OH with molecular formula $C_5H_{10}O$.

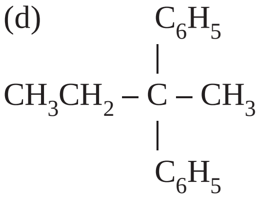
3. Give the structure of all primary alcohols with molecular formula $C_5H_{10}O$.

4. Give the Grignard reagent and carbonyl compound that can be used to prepare

   (a) $CH_3CH_2CH_2OH$ (b) $(CH_3)_2C(OH)CH_2CH_2CH_3$

(c) $C_6H_5\ CH_2CH(OH)CH_3$

(d)



$$CH_3CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}-CH_3$$

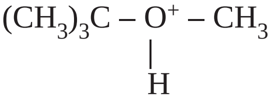
5. Why dry ether is to be used as a solvent for Grignard reagent ?
6. Which of the following does not give Iodoform reaction ?

   CH_3CH_2OH, $CH_3CH(OH)CH_2CH_3$, $CH_3CH(OH)CH_3$, $(CH_3)_3COH$
7. How can ethyl alcohol be converted to isopropyl alcohol ?
8. How can isobutyl alcohol be converted to t-butyl alcohol ?
9. How can 1-butanol be converted to 2-butene ?
10. An organic compound $C_3H_8O_3$ yields on acetylation with acetic anhydride $C_9H_{14}O_6$. How many –OH groups are present in the substance ? What is the possible structure ?
11. Assign $\delta+$and $\delta-$ to each atom joined by the covalent bond shown in the following structures.

    (a) CH_3-Br, (b) CH_3OCH_3, (c) CH_3NH_2, (d) $CH_3-O-SO_2-OCH_3$
12. Predict the species produced during heterolytic fission of the following:

    (a) $(CH_3)_2CHOH$ (b) $(CH_3)_3CBr$

    (c) CH_3CH_2Li (d)



$$(CH_3)_3C-\underset{\underset{\displaystyle H}{|}}{O^+}-CH_3$$

13. Which member of the following pairs would you expect to be more water soluble ?

    (a) $CH_3\ CH_2\ OH$ or $CH_3\ CH_2\ OCH_3$

    (b) $CH_3\ COOH$ or $HCOOCH_3$
14. Which member of the following pairs would you expect to have higher boiling point ?

    $CH_3\ O\ CH_2\ CH_2\ O\ CH_3$ or $CH_2\ OH\ CH_2\ CH_2\ CH_2\ OH$

    $Cl\ CH_2\ CH_2\ OH$ or $CH_2\ OH-CH_2\ OH$

GLYCOLS & GLYCEROLS

1. What happens when - give equation.

   (i) ethylene + alkaline permanganate $\longrightarrow$

   (ii) glycerol $\xrightarrow[\Delta]{KHSO_4}$

   (iii) Ethylene + chlorine $\longrightarrow$ product $\xrightarrow{\text{KOH (aq)}}$

2. How can the following conversion be effected ?

   (i) glycerol $\longrightarrow$ acrolein

   (ii) glycol $\longrightarrow$ dioxan

   (iii) oxalic acid $\longrightarrow$ formic acid

3. What is the action of

   (i) anhydrous $ZnCl_2$ on glycol

   (ii) Con.HI on glycerol

   (iii) heat on a mixture of glycerol and oxalic acid (533 K)

4. Complete the following :

   (i) $C_2H_4 \xrightarrow[\text{523 K}]{O_2/Ag} A \xrightarrow[\text{473K}]{H_2SO_4/H_2O} B$

   (ii) glycerol $\xrightarrow[(O)]{HNO_3} A \xrightarrow[(O)]{HNO_3} B$

   (iii) Allyl chloride $\xrightarrow{Na_2CO_3/H_2O} \quad \xrightarrow{HOCl} \quad \xrightarrow{NaOH}$

5. Convert the following :

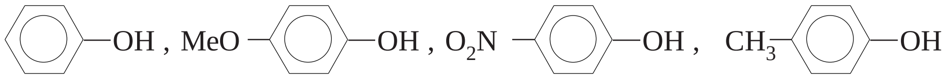
   (i) glycol $\longrightarrow$ Formaldehyde

   (ii) glycerol $\longrightarrow$ TNG

   (iii) glycerol $\longrightarrow$ Glycerol Triacetate

Phenols

1. How can the following be obtained ?
   (a) phenol from benzene diazonium chloride
   (b) 2, 4, 6-tribromo phenol from phenol
2. How will you convert
   (a) chloro benzene to phenol
   (b) phenol to 2-acetoxybenzoic acid
3. How can the following conversion be effected ?
   (a) phenol to phenolphthalein
   (b) phenol to benzene
4. Write the reaction which takes place when
   (i) Sodium phenoxide is treated with CO_2 and the product is acidified
   (ii) Phenol is heated with chloroform and NaOH
   (iii) Phenol is reacted with dilute HNO_3.
5. Account for the following :
   (i) Phenol exhibits acidic character
   (ii) Phenol does not get protonated readily
   (iii) Phenol, Benzendiazonium chloride, NaOH solution gives red dye.
6. How are the following conversions done ?
   (i) phenol to phenyl ethanoate
   (ii) aniline to phenol and (iii) phenol to anisole
7. Arrange the following in the decreasing order of acid strength ?



8. Account for the following :
   (i) phenol is soluble in NaOH and regenerated on adding HCl.
   (ii) phenol is insoluble in $NaHCO_3$ solution while acetic acid is soluble
   (iii) Ethyl alcohol and phenol are miscible in all proportions

9. (i) What happens when phenol is warmed with CCl_4 in presence of NaOH ?

(ii) When phenol is treated with benzoyl chloride in presence of NaOH.

(iii) When phenol is treated with con. H_2SO_4.

10. Distinguish between

(a) Ethanal and phenol

(b) Phenol and acetic acid

(c) Phenol and aniline

(d) Phenol and anisole

SUMMARY :

Structure and isomerism of alcohols - chain isomerism, position isomerism and functional isomerism.

Nomenclature - common system, carbinol system and IUPAC - system of naming alcohols. Classification of hydroxy compounds - alkyl, aryl and aralkyl hydroxy compounds. Classification as primary, secondary and tertiary alcohols.

General methods of preparation - Hydration of olefins, hydrolysis of alkyl halides, reduction of carbonyl compounds and use of Grignard reagents.

Properties : Hydrogen bonding and molecular association and abnormal boiling point.

Chemical properties of alcohols - acidic property, elimination to form olefins, substitution of hydroxy group, to form ethers, alkyl halides, esters and oxidation to carbonyl compounds. Distinction between 1^o, 2^o and 3^o alcohols - uses of methyl alcohol and ethyl alcohol. Preparation and properties of benzyl alcohol. Differences between aliphatic alcohol and benzyl alcohol.

Dihydric alcohol - ethylene glycol

Trihydric alcohol - glycerol - oil and fat - preparation - physical and chemical properties. Special emphasis on oxidation reactions - reaction with HI and dehydration - uses.

Phenols - Substituted phenols - structure and nomenclature - methods of preparation - physical properties - presence of hydrogen bonding. Chemical properties - Acidic property and resonance - properties of hydroxyl group. Properties of benzene ring - activation of benzene ring towards electrophilic substitution - formation of azo dyes and phenolpthalein.

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17. ETHERS

LEARNING OBJECTIVES

- *Ethers - structure, classification, isomerism and nomenclature.*
- *General methods of preparation - properties - physical and chemical properties - uses.*
- *Aromatic ethers - nomenclature.*
- *The methods of preparation of anisole - its physical and chemical properties - uses.*

17.1 ETHERS

These are compounds of the type R–O–R, where oxygen atom is linked to both sides by either saturated, unsaturated or aromatic carbon. Their general formula is R–O–R'.

CLASSIFICATION

Simple ethers :

If the two alkyl groups attached to the oxygen atom are the same (R = R') then it is called **a simple** or **symmetrical ether.**

$CH_3 - O - CH_3$ dimethyl ether $\qquad$ $C_2H_5 - O - C_2H_5$ diethyl ether

Mixed ethers :

If the two alkyl groups are different then they are called as **mixed** or **unsymmetrical ethers.**

(e.g.,) $CH_3 - O - C_2H_5$ ethyl methyl ether

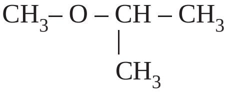
If one or two aryl groups are attached to the oxygen atom then they are called as aromatic ethers. For example

$C_6H_5–O–CH_3$ anisole $\qquad$ $C_6H_5–O–C_6H_5$ diphenyl ether

Nomenclature :

Common system - Ethers are named by prefixing the names of alkyl groups attached to the oxygen atom before the word 'ether'. Thus $CH_3–O–CH_3$ is dimethyl ether $CH_3–O–C_2H_5$ is ethyl methyl ether.

IUPAC name - Here ethers are named as alkoxy derivatives of alkanes.

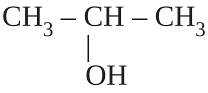
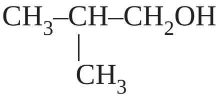
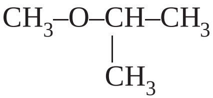
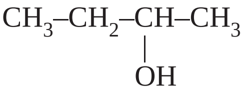
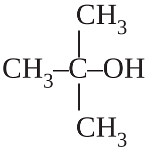
Formula	IUPAC name	Common name
$CH_3 - O - CH_3$	Methoxy methane	Dimethyl ether
$CH_3 - O - C_2H_5$	Methoxy ethane	Ethyl methyl ether
$CH_3 - O - CH_2 - CH_2 - CH_3$	1-methoxy propane	methyl n-propyl ether
 $CH_3 - O - \underset{\underset{CH_3}{\vert}}{CH} - CH_3$	2-methoxy propane	methyl iso propyl ether

Isomerism :

Ethers are functional isomers of alcohols as both have the same general formula $C_nH_{2n+2}O$.

The C_2H_6O stands for both CH_3CH_2OH and $CH_3 - O - CH_3$.

Functional Isomerism

Molecular formula	Ethers	Alcohols
C_3H_8O	$CH_3-O-CH_2-CH_3$ ethyl methyl ether	$CH_3CH_2CH_2OH$ n-propyl alcohol
		 $CH_3 - \underset{\underset{OH}{\vert}}{CH} - CH_3$ isopropyl alcohol
$C_4H_{10}O$	$CH_3CH_2-O-CH_2CH_3$ diethyl ether	$CH_3-CH_2-CH_2-CH_2-OH$ n-butyl alcohol
	$CH_3-O-CH_2-CH_2-CH_3$ methyl-n-propyl ether	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2OH$ isobutyl alcohol
	 $CH_3-O-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$ methyl isopropyl ether	 $CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_3$ sec.butyl alcohol
		 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$ tert. butyl alcohol

Metamerism :

It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

$CH_3 - O - CH_2CH_2CH_3$
methyl-n-propyl ether

$CH_3–CH_2–O–CH_2CH_3$
diethyl ether

$$CH_3–O–\underset{}{\overset{\displaystyle CH_3 \atop |}{CH}}–CH_3$$

methyl isopropyl ether

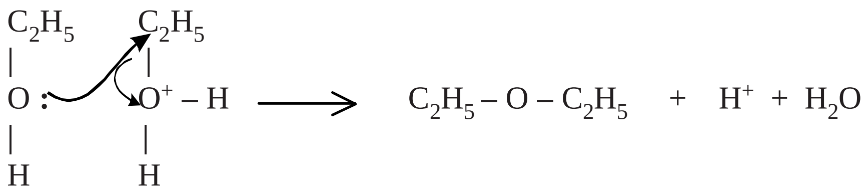
17.2 GENERAL METHODS OF PREPARATION

1. **Intermolecular dehydration of alcohol.** When excess of alcohol is heated with con. H_2SO_4 or H_3PO_4, two molecules condense losing a molecule of water forming ether.

$$R–OH + H – OR \xrightarrow{H_2SO_4} R – O – R + H_2O$$

$$C_2H_5 – O – H + H – O – C_2H_5 \xrightarrow[\text{con. } H_2SO_4]{413K} C_2H_5 – O – C_2H_5$$

This reaction proceeds by a nucleophilic substitution mechanism. The nucleophile alcohol, brings about **nucleophilic attack** on protonated alcohol.



$$C_2H_5–\ddot{O}–H + C_2H_5–\overset{+}{O}H_2 \longrightarrow C_2H_5 – O – C_2H_5 + H^+ + H_2O$$

Dehydration can also be brought about by passing vapours of alcohol over heated Alumina or Thoria.

$$2C_2H_5OH \xrightarrow[Al_2O_3]{250^oC} C_2H_5 – O – C_2H_5 + H_2O$$

2. Williamson's synthesis

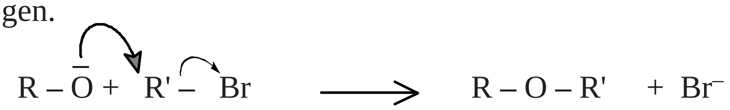
This is the most important method. It consists of heating alkyl halides with **sodium** or **potassium alkoxide.**

$$RX + NaOR' \longrightarrow R\text{–}O\text{–}R' + NaX$$

$$C_2H_5Br + NaOC_2H_5 \longrightarrow C_2H_5 - O - C_2H_5 + NaBr$$

$$\underset{\text{methyl bromide}}{CH_3Br} + \underset{\text{sodium ethoxide}}{NaOC_2H_5} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3 - O - C_2H_5} + NaBr$$

This involves **nucleophilic attack** by RO^- on the carbon atom attached to the halogen.



$$R - \bar{O} + R' - Br \longrightarrow R - O - R' + Br^-$$

This method is suitable to prepare all kinds of ethers - simple and mixed ethers.

3. From alkyl halides

By heating alkyl halides with dry silver oxide, ethers may be prepared.

$$R - X + Ag_2O + X - R \xrightarrow{\Delta} R - O - R + 2AgX$$

$$C_2H_5 - I + Ag_2O + I - C_2H_5 \xrightarrow{\Delta} C_2H_5 - O - C_2H_5 + 2AgI$$

Mixed ethers can be prepared by taking different alkyl halide with dry silver oxide.

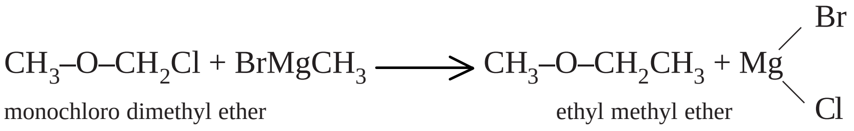
$$\underset{\text{methyl iodide}}{CH_3I} + Ag_2O + \underset{\text{ethyl iodide}}{I - C_2H_5} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3 - O - C_2H_5} + 2AgI$$

$R - O - Ag$ Silver alkoxide may be an intermediate.

4. Using Grignard reagent.

Using Grignard reagent **lower halogenated ether** may be converted to higher ethers.

$$R - O - CH_2\ X + X - Mg\ R' \longrightarrow R - O - CH_2R' + MgX_2$$



$$\underset{\text{monochloro dimethyl ether}}{CH_3\text{–}O\text{–}CH_2Cl} + BrMgCH_3 \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3\text{–}O\text{–}CH_2CH_3} + Mg\begin{smallmatrix} Br \\ Cl \end{smallmatrix}$$

17.2.1 Properties

(i) Lower members are gases, higher members are pleasant smelling volatile liquids.

(ii) insoluble in water, soluble in organic solvents. These can be explained on the basis of the absence of hydrogen bonding.

(iii) Ethers are lighter than water. Lower members are inflammable.

(iv) Lower ethers act as anaesthetics.

Chemical Properties :

These are chemically almost inert and do not react with acids, alkalies, electro positive metals like sodium.

(i) Reaction of the alkyl radicals (substitution reactions)

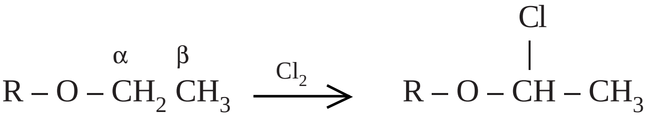
(ii) Ether oxygen-capable of donating a pair of non bonding electrons.

(iii) The C–O bond which is not as stable as C–C bond, is cleaved.

Reaction of alkyl groups :

1. Halogenation

Ethers undergo substitution at the alkyl group when treated with chlorine or bromine **in absence of sunlight.** Usually **α-hydrogen** is substituted more readily.



$$R - O - \overset{\alpha}{CH_2}\ \overset{\beta}{CH_3} \xrightarrow{Cl_2} R - O - \overset{Cl}{\overset{|}{CH}} - CH_3$$

α-chloro ether

$$C_2H_5 - O - C_2H_5 \xrightarrow[\text{dark}]{Cl_2} \underset{\alpha\text{-chloro diethyl ether}}{CH_3 - CHCl - O - CH_2CH_3} \xrightarrow{Cl_2}$$

$$\underset{\alpha,\ \alpha'\text{-dichloro diethyl ether}}{CH_3CHCl - O - CHCl - CH_3}$$

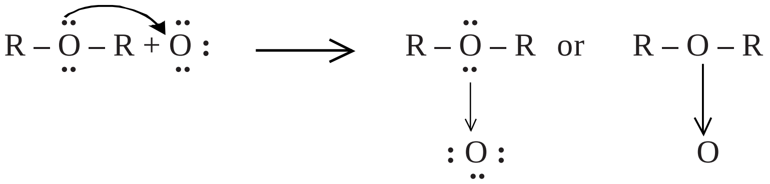
In sunlight, substitution is complete. Thus diethyl ether forms perchloro diethyl ether.

$$C_2H_5-O-C_2H_5 + 10Cl_2 \xrightarrow{\text{light}} C_2Cl_5-O-C_2Cl_5$$

2. Reaction of ether oxygen :

(i) Formation of peroxide :

Ether oxygen is capable of forming a coordinate covalent bond with electron deficient species. Thus it forms peroxide by the action of air or oxygen.



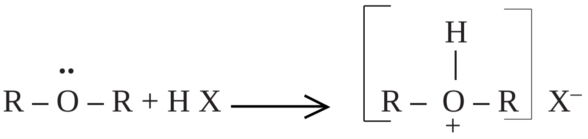
Ether forms Diethyl peroxide

$$C_2H_5-O-C_2H_5 \xrightarrow{(O)} \underset{\text{diethyl peroxide}}{(C_2H_5)_2O_2}$$

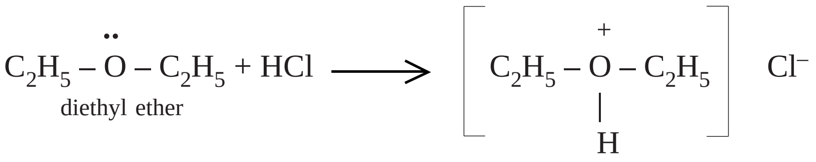
These peroxides are unstable and decomposes violently with explosion on heating. Hence ether should not be evaporated to dryness.

(ii) Formation of oxonium salt.

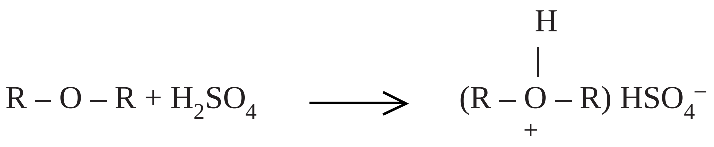
Strong mineral acids protonate the ethereal oxygen forming **oxonium salts.** In this reaction diethyl ether acts as Lewis base.



$$R-\ddot{O}-R + HX \longrightarrow \left[R-\overset{\overset{H}{|}}{\underset{+}{O}}-R\right] X^-$$

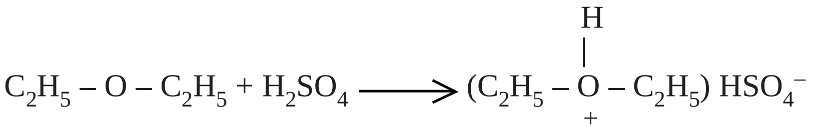


$$\underset{\text{diethyl ether}}{C_2H_5-\ddot{O}-C_2H_5} + HCl \longrightarrow \underset{\text{diethyl oxonium chloride}}{\left[C_2H_5-\underset{\underset{H}{|}}{\overset{+}{O}}-C_2H_5\right]} Cl^-$$



$$R-O-R + H_2SO_4 \longrightarrow (R-\overset{\overset{H}{|}}{\underset{+}{O}}-R)\ HSO_4^-$$

dialkyl oxonium hydrogen sulphate

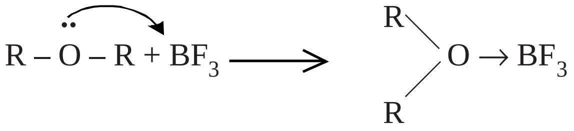


$$C_2H_5-O-C_2H_5 + H_2SO_4 \longrightarrow (C_2H_5-\overset{\overset{H}{|}}{\underset{+}{O}}-C_2H_5)\ HSO_4^-$$

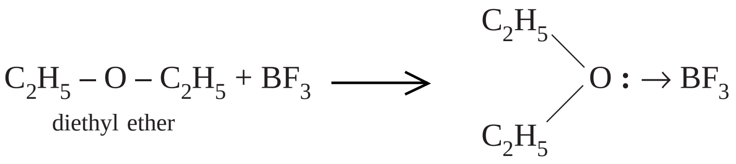
diethyl oxonium hydrogen sulphate

(iii) Reaction with Lewis acids.

Similarly with Lewis acids like BF_3, $AlCl_3$.

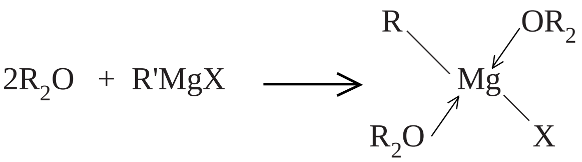


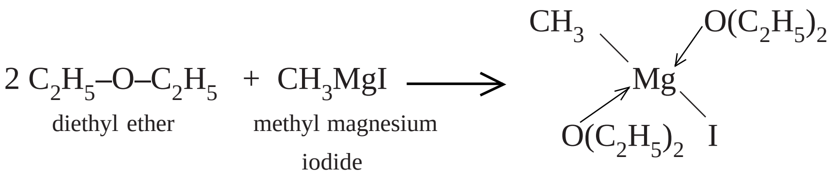
(Boron trifluoride etherate)



(iv) With Grignard reagent

An ether solution of Grignard reagent contains the following complex of ether. Thus the Grignard reagent is stabilised in dry ether.





Hence ether is used as a solvent for Grignard's reagent.

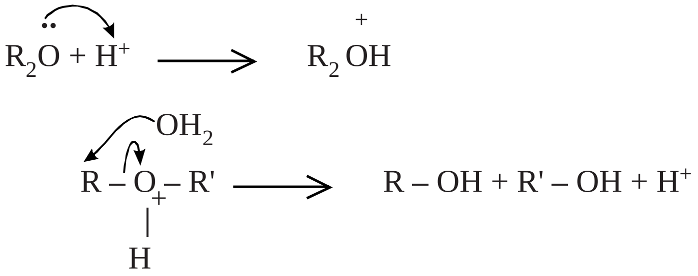
3. Reaction involving C–O bond : Hydrolysis

(i) Ethers on boiling with water in presence dilute acids are hydrolysed to form alcohols.

$$R-O-R \;+\; H-O-H \xrightarrow{H^+} 2R-OH$$

$$C_2H_5-O-C_2H_5 + H-O-H \xrightarrow{H_2SO_4} 2C_2H_5OH$$

This reaction proceeds with **protonation** of ether oxygen.

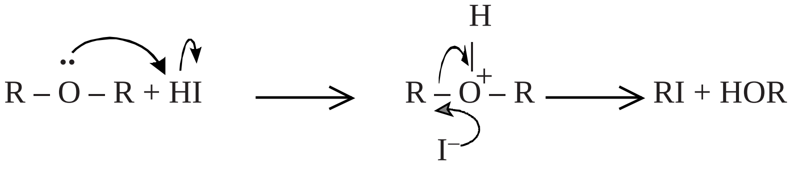


$$R_2\ddot{O} + H^+ \longrightarrow R_2\overset{+}{O}H$$

$$R-\underset{\underset{H}{|}}{\overset{+}{O}}-R' \xrightarrow{OH_2} R-OH + R'-OH + H^+$$

(ii) Reaction with HX

On treating with HBr or HI ether gets cleaved to form alcohol and alkyl halide.



$$R-\ddot{O}-R + HI \longrightarrow R-\overset{\overset{H}{|}}{\overset{+}{O}}-R \longrightarrow RI + HOR$$

Halogen prefers to attack the carbon atom of **the smaller alkyl group.**

$$C_2H_5-O-CH_3 \xrightarrow{HI} C_2H_5OH + CH_3I$$

(iii) With excess hot concentrated hydroidic acid, alkyl iodides are formed.

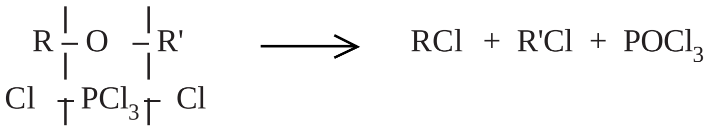
$$CH_3-O-C_2H_5 \xrightarrow{2HI} CH_3I \quad + \quad C_2H_5I \quad + \quad H_2O$$

This reaction also follows the mechanism mentioned in the previous reaction.

This reaction is used in the **Zeisel's method of detection and estimation of alkoxy (especially methoxy) group** in natural products like alkaloids.

4. With PCl_5

Phosphorous pentachloride cleaves the ether into alkyl chlorides.



$$R{-}O{-}R' + PCl_5 \longrightarrow RCl + R'Cl + POCl_3$$

$$C_2H_5{-}O{-}C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

17.2.2 Uses of diethyl ether

Diethyl ether is used as a **refrigerant**, as an **anaesthetic**, as a medium for the preparation of **Grignard reagent,** as a solvent for the **extraction of organic compounds,** mixed with ethanol as **substitute for petrol.**

17.3 AROMATIC ETHERS

Aromatic ethers or phenolic ethers are a class of compounds obtained by the replacement of the phenolic hydrogen by an alkyl or aryl group. The general formula can be Ar–O–R or Ar–O–Ar.

Nomenclature :

Formula	Name in common system	Name in IUPAC system
$C_6H_5OCH_3$	methyl phenyl ether (or) anisole	methoxy benzene
$C_6H_5OC_2H_5$	ethyl phenyl ether (or) phenetole	ethoxy benzene
$C_6H_5 - O - C_6H_5$	diphenyl ether	phenoxy benzene

17.3.1 Preparation

1. Williamsons synthesis :

By heating sodium phenoxide with methyl iodide. This reaction follows **$S_N{}^2$ pathway.** The nucleophile is C_6H_5O- (phenoxide ion) and the substrate is methyl iodide.

$$C_6H_5O^- \ Na^+ + CH_3 - I \longrightarrow C_6H_5 - O - CH_3 \ \text{(Anisole)} + I^- + Na^+$$

$$C_6H_5O^- + C_2H_5I \longrightarrow \underset{\text{(phenetole)}}{C_6H_5 - O - C_2H_5} + I^-$$

In this preparation Iodobenzene as a substrate and sodium ethoxide as the reagent cannot be used to prepare anisole. **Iodine is strongly bonded** to carbon atom of benzene hence it cannot be easily replaced.

2. Using diazomethane :

Phenolic –OH has **acidic hydrogen** atom hence diazomethane could convert this to methyl group.

$$C_6H_5 - \ddot{O} - H + \underset{\text{diazomethane}}{CH_2 - N_2} \longrightarrow C_6H_5 - O - CH_3 + N_2$$

3. Manufacture of ether :

Large scale methylation of phenol is carried out using dimethyl sulphate in presence of sodium hydroxide.

$$C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{NaOH} C_6H_5OCH_3 + CH_3.HSO_4$$

$$C_6H_5\overset{-}{O} + CH_3 - O - SO_2 - OCH_3 \longrightarrow C_6H_5{-}OCH_3 + \overset{-}{O}{-}SO_2{-}OCH_3$$

This reaction involves nucleophilic attack by the phenoxide ion on dimethyl sulphate.

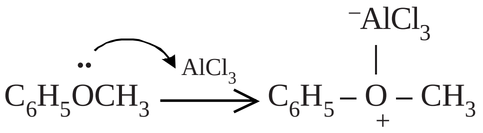
17.3.2 Properties

It is a pleasant smelling liquid insoluble in water, soluble in organic solvents, it gives general reaction of ether though differing in a few reaction.

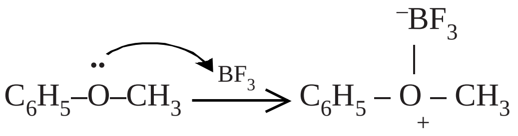
It is not as reactive as phenol or methyl alcohol.

Chemical Properties

1. It forms oxonium compounds with Lewis acids



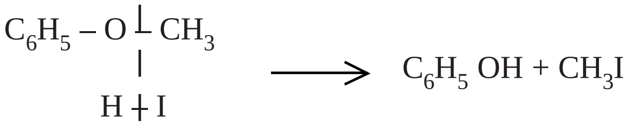
$$C_6H_5\ddot{O}CH_3 \xrightarrow{AlCl_3} C_6H_5-\underset{+}{\overset{{}^{-}AlCl_3}{\overset{|}{O}}}-CH_3$$



$$C_6H_5-\ddot{O}-CH_3 \xrightarrow{BF_3} C_6H_5-\underset{+}{\overset{{}^{-}BF_3}{\overset{|}{O}}}-CH_3$$

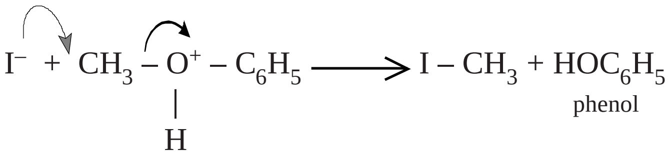
2. Heating with hydroiodic acid cleaves the ether linkage.

Anisole reacts with hydroiodic acid to give phenol and methyl iodide.



$$C_6H_5-O \,|\, CH_3 + H \,|\, I \longrightarrow C_6H_5\,OH + CH_3I$$

anisole



$$I^- + CH_3-\underset{\underset{H}{|}}{O^+}-C_6H_5 \longrightarrow I-CH_3 + HOC_6H_5$$

phenol

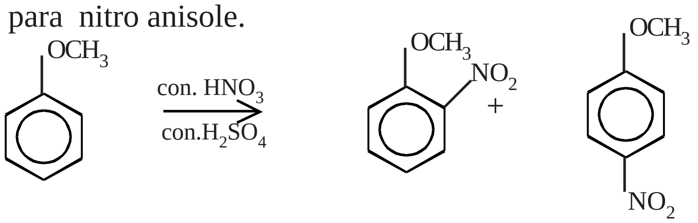
(protonated ether

Here iodide is the nucleophile and the leaving group is ‘phenol’.

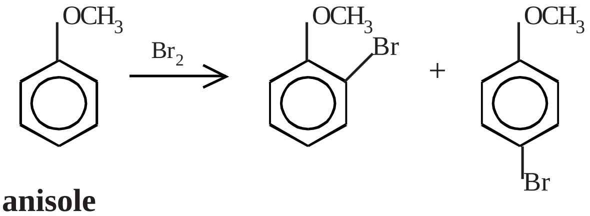
Because of the strong C–O bond in anisole, cleavage of the C–O bond does not occur and iodobenzene, methyl alcohol are never formed.

3. **Reaction due to the benzene ring :**

Similar to –OH group, –OMe, group increase the reactivity of the benzene ring with respect to electrophilic attack and is **ortho, para - directing.** With a mixture of con.HNO_3 and con. H_2SO_4 it gives a mixture of ortho and para nitro anisole.



Bromination yields ortho bromo anisole and p-bromo anisole.



17.3.3 Uses of anisole

It is used in perfumery.

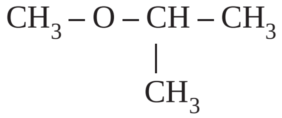
It is used as a starting material in organic synthesis.

Distinction between Aromatic and aliphatic ethers.

Aromatic ethers (Anisole)	Aliphatic ethers (Diethyl ether)
1. Comparatively high boiling liquid.	Volatile liquid
2. Used in perfumery.	Used as anaesthetic.
3. Not used as solvent.	Used as a solvent.
4. Can not be used as a substitute for petrol.	Mixed with alcohol, used as a substitute for petrol.
5. On heating with HI forms phenol and CH_3I only.	It forms C_2H_5OH, and C_2H_5I.
6. With nitrating mixture forms nitro anisoles.	Nitration does not take place.
7. Does not form peroxide easily.	Forms peroxide in air.

SELF EVALUATION

(A) Choose the correct answer :

1. The isomerism exhibited by $C_2H_5OC_2H_5$ and  $CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ is

    (a) Functional (b) metamerism

    (c) position (d) chain

2. Which one of the following is simple ether ?

    (a) $CH_3-O-C_2H_5$ (b) $C_2H_5-O-CH_3$

    (c) $C_2H_5-O-C_2H_5$ (d) $C_3H_7-O-C_2H_5$

3. Diethyl ether can be decomposed with

    (a) HI (b) $KMnO_4$ (c) NaOH (d) H_2O

4. Oxygen atom of ether is

    (a) very active (b) Replacable

    (c) oxidising (d) Comparatively inert

5. According to Lewis concept of acids and bases, ethers are

    (a) Neutral (b) Acidic (c) Basic (d) Amphoteric

6. Intermolecular hydrogen bonds are not present in

    (a) CH_3COOH (b) $C_2H_5OC_2H_5$

    (c) CH_3CH_2OH (d) $C_2H_5NH_2$

7. When ethyl Iodide is treated with dry silver oxide it forms

    (a) Ethyl alcohol (b) diethylether

    (c) silver ethoxide (d) ethylmethyl ether

8. Williamson's synthesis is an example of

    (a) nucleophilic addition (b) electrophilic addition

    (c) electrophilic substitution (d) Nucleophilic substitution reaction

9. When ether is exposed to air for sometime an explosive substance produced is

    (a) peroxide (b) oxide (c) TNT (d) superoxide

10. Ether is formed when alkylhalide is treated with sodium alkoxide. This method is known as

    (a) Hoffmann reaction (b) Williamson's synthesis

    (c) Wurtz synthesis (d) Kolbe's reaction

(B) Pickout the incorrect statement :

1. (a) An example of unsymmetrical ether is $CH_3OC_2H_5$
   (b) Ethers exhibit functional isomerism with alcohols
   (c) Halogenated ether on treating with alcohols forms higher ether
   (d) Ether is lighter than water

2. (a) Diethylether with chlorine in presence of sunlight forms $(C_2Cl_5)_2O$.
   (b) The formula of diethyl oxonium chloride is $(C_2H_5)_2–O^+Cl^-$
   (c) In anisole oxygen is strongly bonded to benzene ring.
   (d) Ether is used as solvent for Grignard reagent.

3. (a) $CH_3OCH_3 \xrightarrow{\text{dry HI}} CH_3I + CH_3OH$
   (b) Ether is used as substitute for petrol
   (c) In Williamson synthesis, ether is formed using alkoxide and alcohol
   (d) Ethers act as Lewis base due to the presence of non-bonding electrons on oxygen.

(C) Answer in one or two sentences :

1. Write the IUPAC names of
   (a) $C_2H_5OCH_3$ (b) $C_6H_5OC_2H_5$

2. Ethers should not be heated to dryness. Why ?

3. Ethers are the best solvents of Grignard reagents- Account for this statement.

4. Write a note on williamson synthesis.

5. Complete and balance

$$C_2H_5OH \xrightarrow[Al_2O_3]{250^oC} ?$$

6. Why are ethers not soluble in water ?
7. Mention the uses of diethyl ether.
8. What happens when anisole is treated with Lewis acid ?
9. What happens when anisole is nitrated ?
10. Write equation for the conversion of phenol to anisole

(D) Answer not exceeding sixty words :

1. Write all possible isomers with the molecular formula $C_4H_{10}O$ and name them.
2. Give any three methods of preparing diethyl ether.
3. Mention the methods of preparation of anisole.
4. How does diethyl ether react with the following reagents ?
   (a) O_2 / long contact　　(b) HI in excess
   (c) PCl_5　　(d) dilute H_2SO_4
5. Give any two chemical differences between anisole and an aliphatic ether.
6. Illustrate electrophilic substitution reactions of anisole.
7. Explain the formation of CH_3I and phenol when anisole is heated with HI.
8. Diethyl ether forms peroxide easily while anisole does not form peroxide easily - Explain.

SUMMARY :

Ethers - aliphatic and aromatic ethers.

Structure - nomenclature - common and IUPAC system.

Preparation - From alcohol, alkoxide and alkyl halide.

Properties - absence of hydrogen bonding - inert nature - formation of oxonium salt - cleavage of ether linkage.

Diethyl ether and anisole - Distinction.

Uses.

REFERENCE :

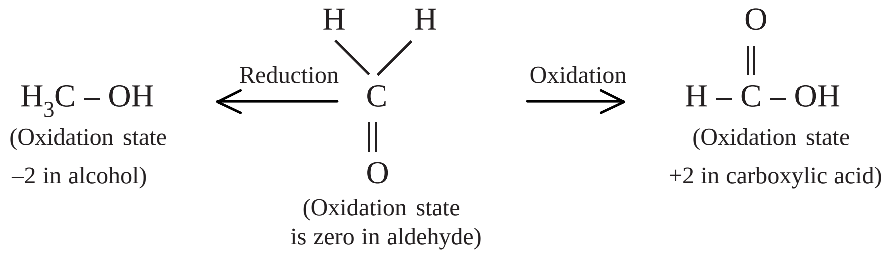
1. Text Book of Organic Chemistry - P.L. Soni.

18. CARBONYL COMPOUNDS

ALDEHYDES AND KETONES

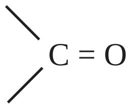
- *Introduction*
- *Structure and classification*
- *Nomenclature and isomers*
- *General methods of preparation*
- *Properties - physical and chemical related to structure*
- *Knowledge of Carbanion addition reactions.*
- *Learn about Condensation reactions.*
- *Distinction between aldehydes and ketones.*
- *Uses.*
- *General methods of preparation of aromatic aldehydes and aromatic ketones.*
- *Properties - Physical and Chemical - related to structure.*
- *Distinction between aliphatic aldehyde and aromatic aldehyde.*
- *Distinction between aliphatic ketones and aromatic ketones.*
- *Uses of aromatic aledhydes and ketones.*

Aldehydes and **ketones** are compounds with the oxidation state of carbon lying in between –2 in alcohol and +2 in carboxylic acid. Hence they are chemically and even biochemically an important class of compounds. Because they can either be oxidised or reduced.



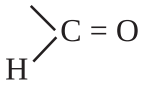
Thus **"Pyridoxal"** an aldehyde derived from the vitamin B_6 (pyridoxine) functions as a coenzyme, because of the dual nature.

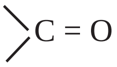
Aldehydes and ketones come under the class of compounds called "carbonyl compounds". They have the carbonyl group.



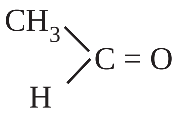
Aldehydes differ from ketones in the presence of a hydrogen atom directly bonded to the carbonyl group.

Aldehydes Ketones

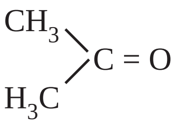




Example

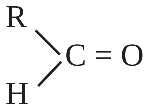


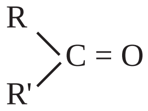
(Acetaldehyde)



(Acetone)

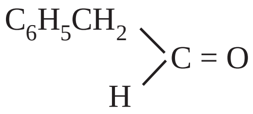
The general formula can be





When R = R' = H that represents formaldehyde, the simplest member of this series. R and R' can be alkyl or aryl.

If R is an aralkyl group we have an aralkyl aldehyde (e.g.,) phenyl acetaldehyde



18.1 NOMENCLATURE

Common names of aldehydes are derived from the common names of carboxylic acid or by adding the suffix "aldehyde" to the prefix that indicates the chain length.

CH_3COOH	CH_3CHO	C_4H_9CHO
Acetic acid	Acetaldehyde	Pentanalehyde

In the IUPAC system, the prefix indicating the length of the carbon chain is followed by the suffix **al** in place of **'e'.**

$CH_3CH_2CH_2CHO$

Butane + al = butanal

Since the aldehyde group is always present in the end it is not shown by any number.

Common name for ketones is arrived at by adding the suffix **"ketone"** to the name of alkyl groups present

$CH_3COCH_2CH_3$

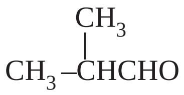
Ethyl methyl ketone

A ketone is named by adding the suffix **‘one’** in place of **‘e’** in the name of the parent hydrocarbon.

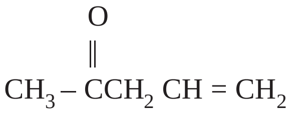
$CH_3CH_2COCH_2CH_3 \longrightarrow$ 3-pentanone

The number of carbon forming the keto group should be mentioned.

For example, ethyl methyl ketone is named as 2-butanone in the IUPAC name.

Formula	**Common name**	**IUPAC name**
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
 $CH_3-\overset{\overset{CH_3}{\vert}}{C}HCHO$	Isobutyraldehyde	2-methyl propanal
$CH_2 = CH–CHO$	Acrolin or acraldehyde	2-propenal
$CH_3\ CH = CH\ CHO$	Crotonaldehyde	2-butenal
C_6H_5CHO	Benzaldehyde	Phenyl methanal
$C_6H_5CH = CH–CHO$	Cinnamaldehyde	3-phenyl-2-propenal
$CH_3CHOH – CH_2\ CHO$	aldol	3-hydroxy butanal

KETONES

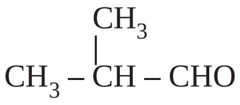
Formula	Common name	IUPAC name
CH_3COCH_3	Acetone	Propanone
$CH_3COCH_2CH_3$	Ethyl methyl ketone	2-butanone
$CH_3CH_2COCH_2CH_3$	Diethyl ketone	3-pentanone
$CH_3\ COCH_2CH_2CH_3$	methyl, n-propyl ketone	2-pentanone
 $CH_3-\overset{\overset{O}{\Vert}}{C}CH_2\ CH=CH_2$	Allyl methyl ketone	4-pentene-2-one

ISOMERISM

Aldehydes exhibit (i) chain isomerism and (ii) functional isomerism.

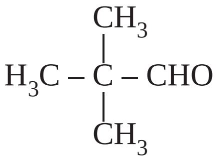
Chain Isomerism arises due to changes in carbon chain.

(i) $\underset{\text{butanal}}{CH_3-CH_2-CH_2-CHO}$ and


$CH_3-\overset{\overset{CH_3}{|}}{C}H-CHO$

2-methyl propanal

(ii) $\underset{\text{Pentanal}}{CH_3\ CH_2\ CH_2\ CH_2\ CHO}$

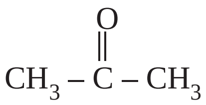

$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO$

2,2-dimethyl propanal

Functional isomerism :

Aldehydes are functional isomers of ketones and unsaturated alcohols.

$CH_3\,CH_2\ CHO$
propanaldehyde

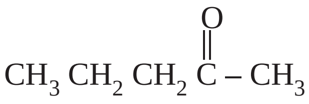

$CH_3-\overset{\overset{O}{\Vert}}{C}-CH_3$

acetone

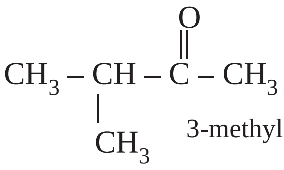
$CH_2=CH-CH_2OH$
unsaturated alcohol
2-propen-1-ol

Ketones exhibit chain isomerism and metamerism.

Chain isomerism :


$CH_3\ CH_2\ CH_2\ \overset{\overset{O}{\Vert}}{C}-CH_3$

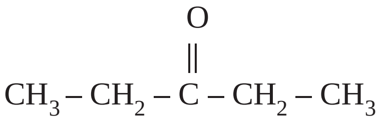
2-pentanone


$CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{O}{\Vert}}{C}-CH_3$

3-methyl-2-butanone

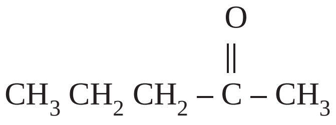
Positional Isomerism :

The carbonyl group may occupy different positions in the carbon chain to give Positional Isomers.



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

3-pentanone



$$CH_3\ CH_2\ CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

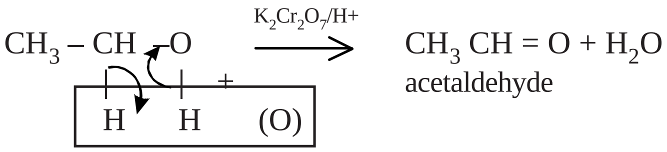
2-pentanone

18.3 GENERAL METHODS OF PREPARATION

1. (a) Oxidation of alcohols with acid dichromate :

Primary alcohols give aldehydes

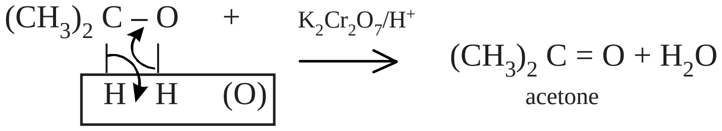
Secondary alcohols give ketones.



$$CH_3-\underset{H}{CH}-\underset{H}{O}\ +\ (O)\xrightarrow{K_2Cr_2O_7/H+}CH_3\ CH=O+H_2O$$

acetaldehyde

primary alcohol
ethyl alcohol



$$(CH_3)_2\ \underset{H}{C}-\underset{H}{O}\ +\ (O)\xrightarrow{K_2Cr_2O_7/H^+}(CH_3)_2\ C=O+H_2O$$

acetone

secondary alcohol (isopropyl alcohol)

(b) Catalytic oxidation : By passing a mixture of alcohol vapours and air over silver catalyst at 520 K aldehyde or ketone is formed.

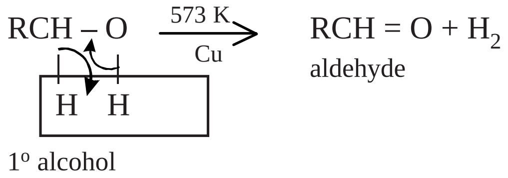
$$CH_3\ CH_2\ OH\ \xrightarrow[520K]{O_2/Ag}\ CH_3CHO$$

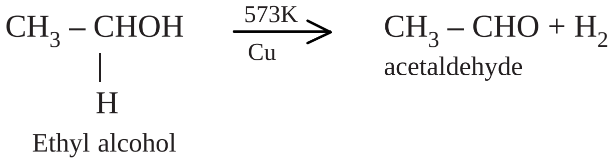
acetaldehyde

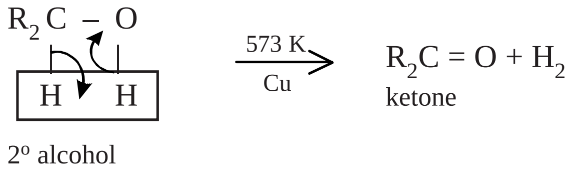
$$(CH_3)_2\ CHOH\ \xrightarrow[520K]{O_2/Ag}\ (CH_3)_2\ CO$$

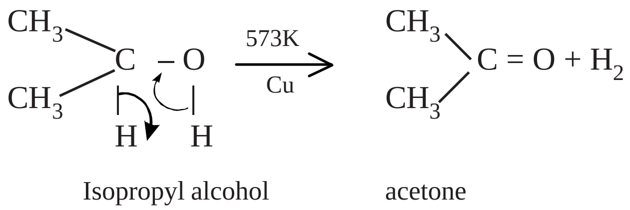
acetone

(c) By the catalytic dehydrogenation of alcohols. The vapours of alcohol are passed over heated copper at 573 K gives aldehyde or ketone.

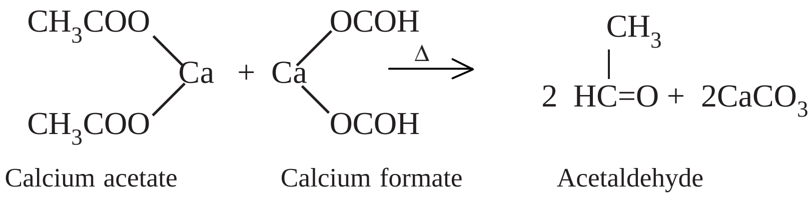



$$\underset{\text{Ethyl alcohol}}{CH_3-\underset{\substack{|\\ H}}{CHOH}} \xrightarrow[Cu]{573K} \underset{\text{acetaldehyde}}{CH_3-CHO+H_2}$$

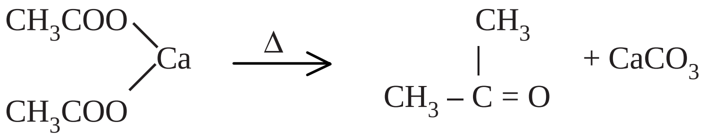




2. Dry Distillation. By the distillation of calcium salt of fatty acids with calcium formate - aldehyde is formed.



By the distillation of calcium salt of fatty acid, ketone is formed.

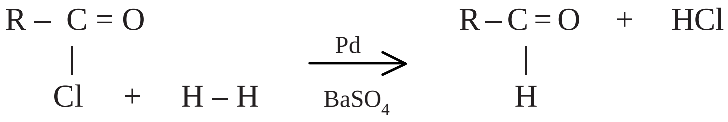


$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-\overset{CH_3}{\overset{|}{C}}=O + CaCO_3$$

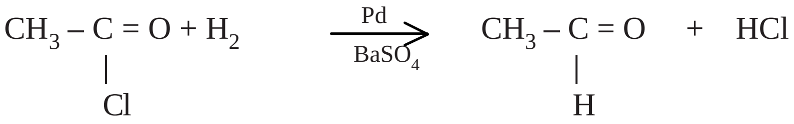
calcium acetate acetone

3. Use of acid chloride :

(i) Rosenmund Reduction. Acid chlorides are reduced to aldehydes by hydrogen in presence of palladium suspended in barium sulphate as catalyst.



$$R-\underset{\underset{Cl}{|}}{C}=O + H-H \xrightarrow[BaSO_4]{Pd} R-\underset{\underset{H}{|}}{C}=O + HCl$$



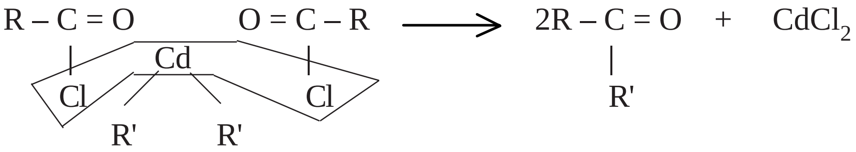
$$CH_3-\underset{\underset{Cl}{|}}{C}=O + H_2 \xrightarrow[BaSO_4]{Pd} CH_3-\underset{\underset{H}{|}}{C}=O + HCl$$

acetyl chloride acetaldehyde

As formyl chloride is unstable at room temperature, formaldehyde cannot be prepared by this method.

This is called **Rosenmund's reduction.** $BaSO_4$ is used as a catalytic poison, to stop the reduction at the stage of aldehyde. **Otherwise**, the aldehyde formed will be further reduced to primary alcohol.

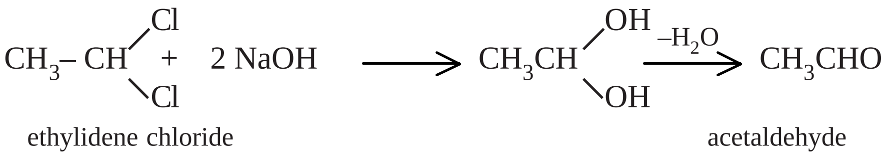
(ii) Using Dialkyl cadmium. Ketones can be prepared by the action of organometallic reagent on acid chlorides. (e.g.,) **Dialkyl cadmium** is the reagent of choice.



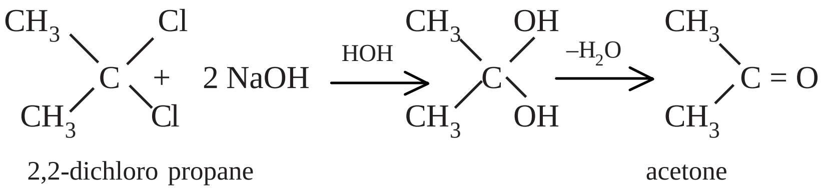
$$R-\underset{\underset{Cl}{|}}{C}=O \quad \underset{R' \quad R'}{Cd} \quad O=\underset{\underset{Cl}{|}}{C}-R \longrightarrow 2R-\underset{\underset{R'}{|}}{C}=O + CdCl_2$$

4. By the hydrolysis of gem dihalides

(i) A **gem dihalide** is a compound in which two halogen atoms are attached to the same carbon. Aldehydes are prepared by hydrolysis of gem dihalides in which two halogen atoms are attached to the terminal carbon atom using alkali.

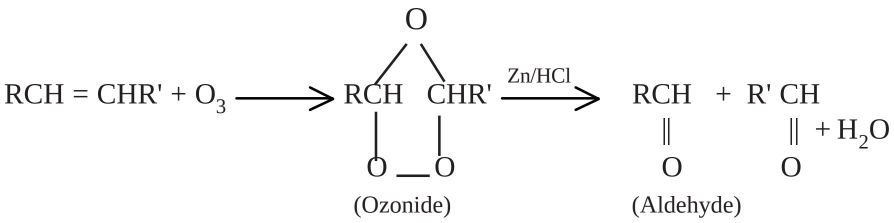


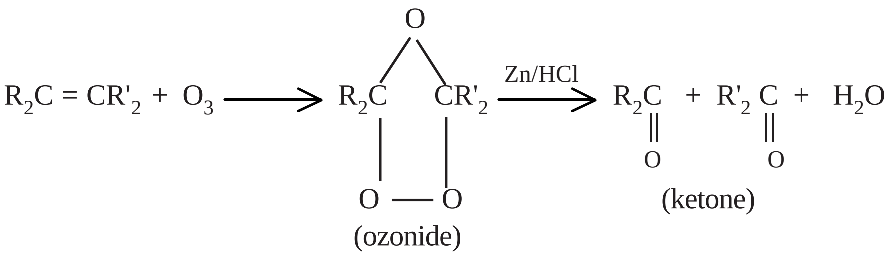
(ii) Ketones are prepared by hydrolysis of a gemdihalides in which two halogens are attached to non terminal carbon atom.



5. By ozonolysis :

Ozone forms addition product with olefin called ozonide, which on reductive cleavage gives aldehyde or ketone.

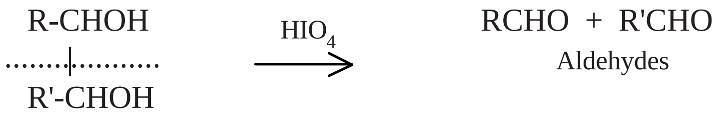




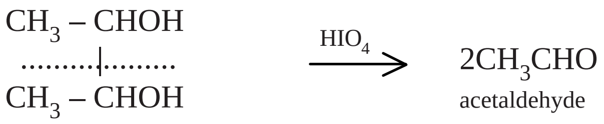
Thus if formaldehyde is obtained, that indicates the **presence of double bond** at the terminal carbon. Hence to **locate the position** of double bond, ozonolysis is helpful.

6. By the **oxidative cleavage** of 1, 2-diols using periodic acid.

   C–C bond in 1,2-diols is cleaved by periodic acid.

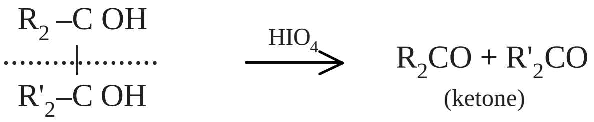


$$\begin{array}{c} \text{R-CHOH} \\ \cdots\cdots|\cdots\cdots \\ \text{R'-CHOH} \end{array} \xrightarrow{HIO_4} \underset{\text{Aldehydes}}{RCHO + R'CHO}$$

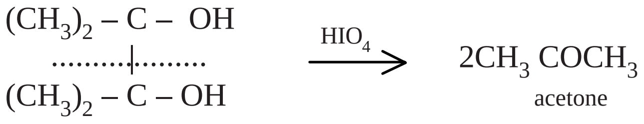


$$\begin{array}{c} CH_3 - CHOH \\ \cdots\cdots|\cdots\cdots \\ CH_3 - CHOH \end{array} \xrightarrow{HIO_4} \underset{\text{acetaldehyde}}{2CH_3CHO}$$

butane-2,3-diol



$$\begin{array}{c} R_2 - C\ OH \\ \cdots\cdots|\cdots\cdots \\ R'_2 - C\ OH \end{array} \xrightarrow{HIO_4} \underset{\text{(ketone)}}{R_2CO + R'_2CO}$$



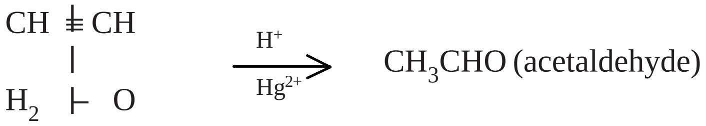
$$\begin{array}{c} (CH_3)_2 - C - OH \\ \cdots\cdots|\cdots\cdots \\ (CH_3)_2 - C - OH \end{array} \xrightarrow{HIO_4} \underset{\text{acetone}}{2CH_3\,COCH_3}$$

butane-2,3-dimethyl-2,3-diol

7. **Hydration of Alkynes**

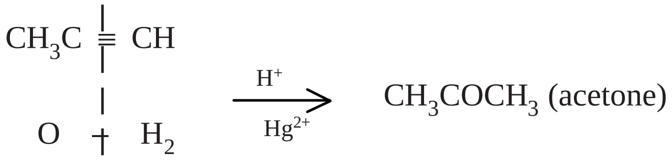
   By the hydration of alkynes in 42% sulphuric acid containing $HgSO_4$ as a catalyst. Acetaldehyde is obtained when acetylene is used. Acetone is obtained using propyne.

(Acetylene)



$$\begin{array}{c} CH \equiv CH \\ | \\ H_2 \vdash O \end{array} \xrightarrow[Hg^{2+}]{H^+} CH_3CHO \text{ (acetaldehyde)}$$

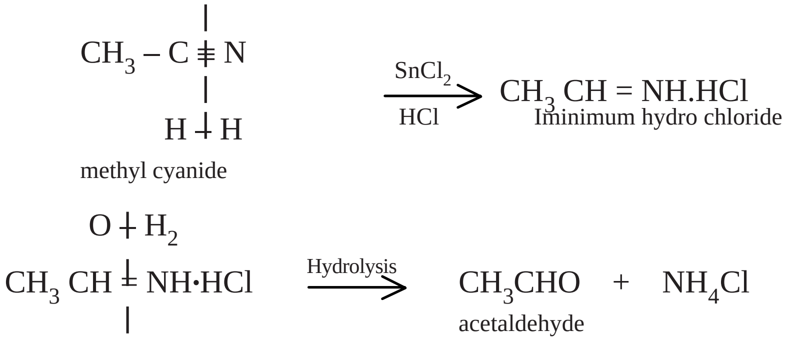
(Propyne)



$$\begin{array}{c} CH_3C \equiv CH \\ | \\ O + H_2 \end{array} \xrightarrow[Hg^{2+}]{H^+} CH_3COCH_3 \text{ (acetone)}$$

8. Stephen's reaction :

Aldehyde can be prepared by **Stephen's reaction,** by the reduction of alkyl cyanide dissolved in ether with Stannous chloride and hydrochloric acid.



$$CH_3-C\equiv N \xrightarrow[HCl]{SnCl_2} CH_3\,CH=NH.HCl$$

methyl cyanide

Iminimum hydro chloride

$$CH_3\,CH=NH\cdot HCl \xrightarrow{\text{Hydrolysis}} CH_3CHO + NH_4Cl$$

acetaldehyde

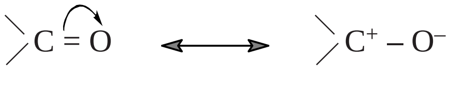
18.3.1 PROPERTIES

Physical properties

Except formaldehyde (a gas) the other lower members of aldehydes and ketones are volatile liquids and the higher members are waxy solids. Ketones have pleasant odour. They have boiling points higher than hydrocarbons (polar nature of carbonyl group) and lower than alcohols (absence of –OH group). Solubility of carbonyl compounds decreases with the increase in their molecular masses. Because with the increase in the length of carbon chain the capacity of the carbonyl group to form hydrogen bonds with water decreases.

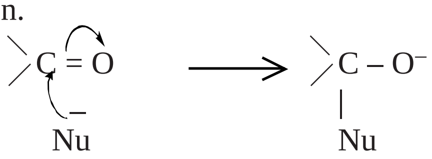
Chemical Characteristics

Aldehydes and ketones contain the carbonyl group >C = O. Oxygen being more electro negative, the >C = O bond is polarised so that oxygen becomes negatively charged and carbon positively charged.



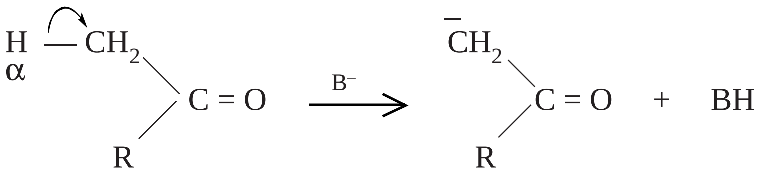
$$>C=O \longleftrightarrow >C^{+}-O^{-}$$

1. Therefore the nucleophilic reagents attack the electron deficient carbonyl carbon.



Both charged and uncharged nucleophiles can attack the carbonyl carbon to form addition products. This is the most common reaction for aldehydes and ketones.

2. Another kind of reaction of aldehydes and ketones which contain atleast one α-hydrogen atom.



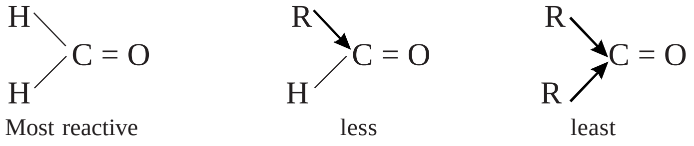
(Deprotonation of α-hydrogen forming carbanion)

α-hydrogen is the hydrogen attached to the α-carbon of the carbonyl group. This hydrogen is acidic, hence a strong base (NaOH, C_2H_5ONa) can remove this hydrogen as a proton, generating a carbanion of the aldehyde or ketone. The carbanion being nucleophile brings forth nucleophilic attack on any **electron deficient carbon**, normally carbonyl carbon leading to condensation reaction.

Reactivity :

Aldehydes are more reactive than ketones for both steric and electronic reasons.

The presence of alkyl group **increases the crowding** near carbonyl group and also increases the electron density at the carbonyl carbon by **Inductive effect**. (+I effect)



Reactions common to aldehydes and ketones.

(a) Reactions of alkyl group. (b) Reaction of carbonyl group.

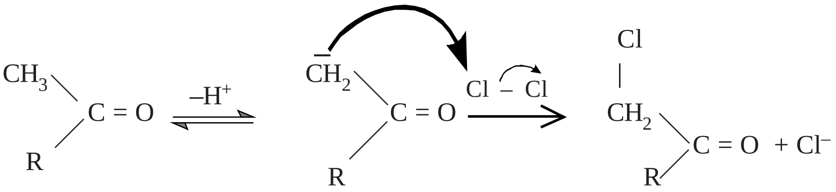
(a) Reactions of alkyl group :

In aldehydes the **α-hydrogen atoms** are more easily replaced than in ketones.

$$\underset{\text{(Acetaldehyde)}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{(Trichloro acetaldehyde)}}{CCl_3\,CHO} + 3HCl$$

$$\underset{\text{(Acetone)}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{(Trichloro acetone)}}{CCl_3\,COCH_3} + 3HCl$$

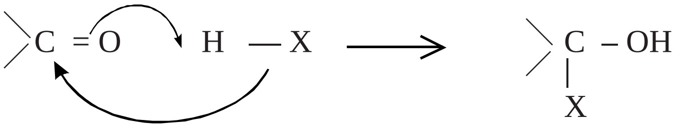
This reaction proceeds with the formation of carbanion.



(ketone) (carbanion) (α-chloroketone)

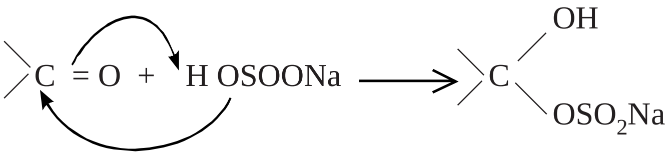
(b) Addition reactions.

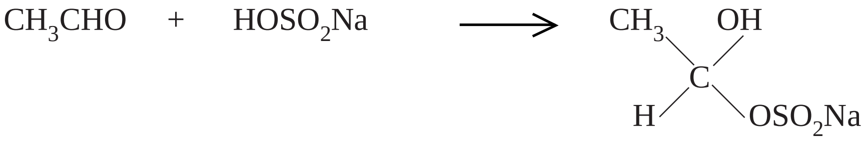
The carbon of the carbonyl group is **the site of** nucleophilic attack. (X^- is a nucleophile).



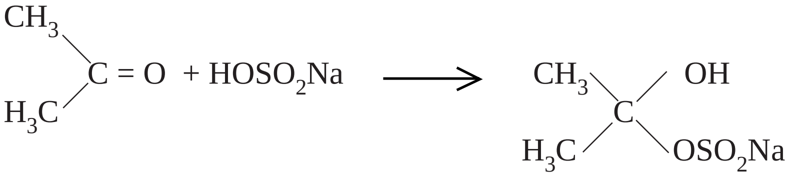
The negative part of the addendum adds to the carbon and the positive part to the oxygen.

In the addition of sodium bisulphite to give bisulphite compound – OSO_2Na anion is the nucleophile.





acetaldehyde bisulphite compound



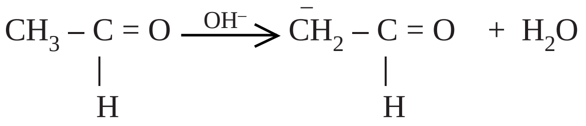
acetone bisulphite

Aldol Condensation :

This reaction is catalysed by base. The carbanion generated is nucleophilic in nature. Hence it can bring about nucleophilic attack on carbonyl group.

Step 1 :

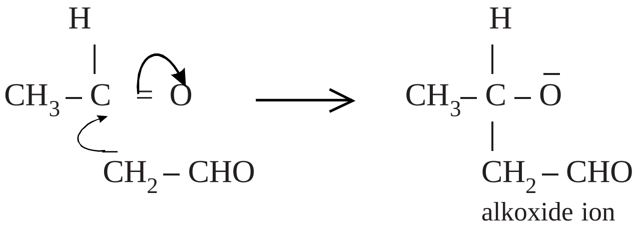
The carbanion is formed as the **α-hydrogen atom** is removed as a proton by the base.



$$CH_3-\underset{\displaystyle H}{\underset{|}{C}}=O \xrightarrow{OH^-} \overset{-}{C}H_2-\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O$$

Step 2 :

The carbanion attacks the carbonyl carbon of another unionised aldehyde molecule.

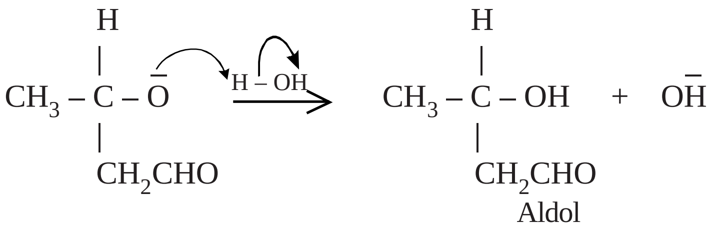


$$CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O \quad \overset{-}{C}H_2-CHO \longrightarrow CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_2-CHO}{\underset{|}{C}}}}-\overline{O}$$

alkoxide ion

Step 3 :

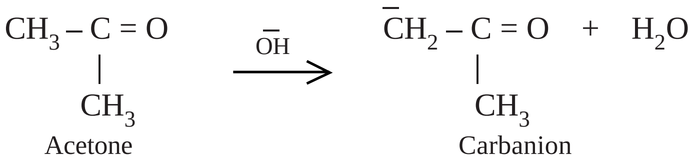
The alkoxide ion formed is protonated by water to give **'aldol'.**



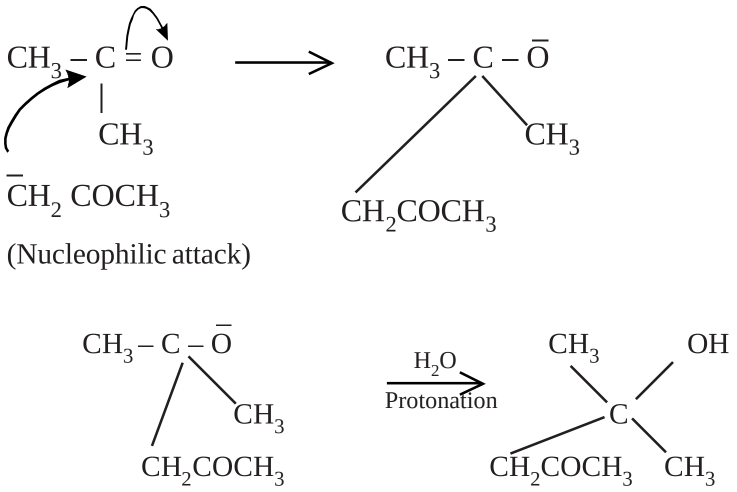
$$CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_2CHO}{\underset{|}{C}}}}-\overline{O} \xrightarrow{H-OH} CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_2CHO}{\underset{|}{C}}}}-OH + \overline{O}H$$

Aldol

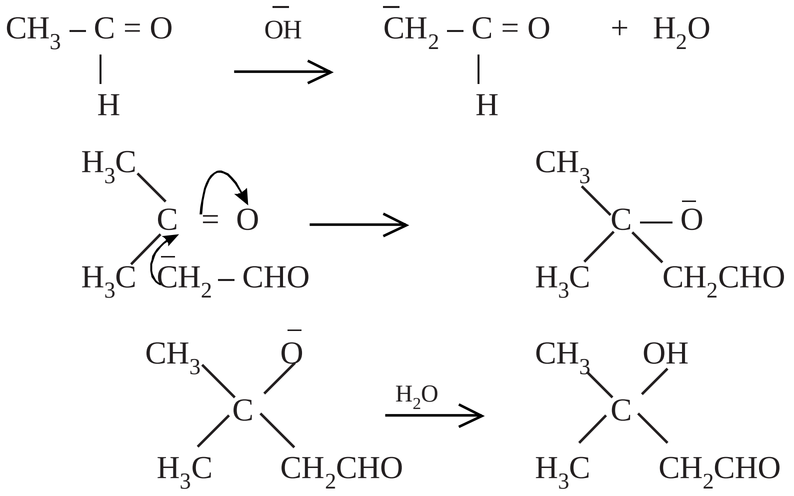
Acetone also undergoes this type of condensation as shown.



$$\underset{\text{Acetone}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O} \xrightarrow{\overline{O}H} \underset{\text{Carbanion}}{\overline{C}H_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=O} + H_2O$$



When an aldehyde and a ketone react in the same way it is called **‘crossed aldol condensation’.**



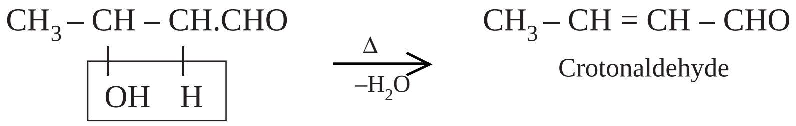
Characteristics of Aldol condensation :

(i) It is an irreversible change.

(ii) It is an addition reaction with or without elimination of water.

(iii) A new carbon to carbon linkage is set up.

(iv) The aldols formed easily eliminate water to form unsaturated compounds. For example aldol on heating gives crotonaldehyde.



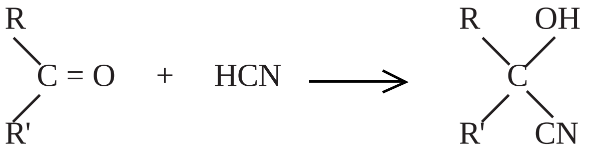
$$CH_3-\underset{\boxed{\underset{OH}{|}}}{CH}-\underset{\boxed{\underset{H}{|}}}{C}H.CHO \xrightarrow[-H_2O]{\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO}$$

(v) This reaction is characteristic of carbonyl compounds having α-hydrogen atom. If there is **no α-hydrogen** atom in the carbonyl compound, aldol condensation does not take place.

$HCHO$,	C_6H_5CHO,	$C_6H_5COC_6H_5$.
Formaldehyde,	Benzaldehyde	Benzophenone

(ii) Addition of hydrogen cyanide

Aldehydes and ketones react with hydrogen cyanide to form cyanohydrin. The reaction is carried out in the presence of **base as a catalyst.**



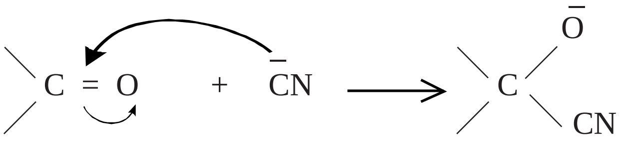
Cyano hydrin

Mechanism : The mechanism involves the following steps :

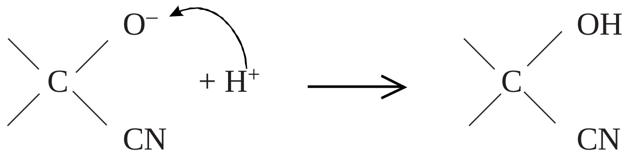
Step 1 : The base removes a proton from hydrogen cyanide to produce cyanide ion.

$$HCN + \overline{O}H \longrightarrow H_2O + \underset{\text{Nucleophile}}{C\overline{N}}$$

Step 2 : The cyanide ion attacks the carbonyl carbon to form an anion.

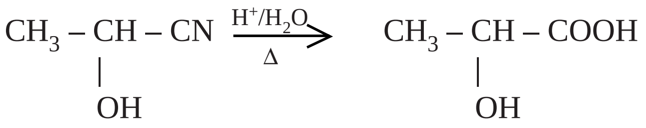


Step 3 : The proton from the solvent combines with the anion to give cyanohydrin.



Cyano hydrin

Like other nitriles cyanohydrin can be hydrolysed to give carboxylic acid.



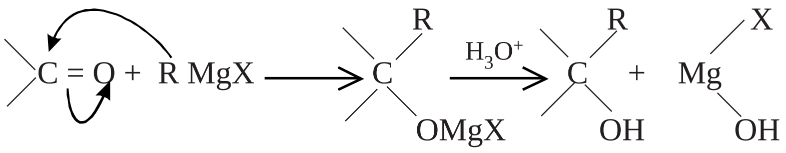
$$CH_3-\underset{\underset{OH}{|}}{CH}-CN \xrightarrow[\Delta]{H^+/H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-COOH$$

Acetaldehyde cyanohydrin　　Lactic acid

This is a very efficient method of preparing lactic acid and other α-hydroxy acids like Mandelic acid ($C_6H_5CHOH\ COOH$).

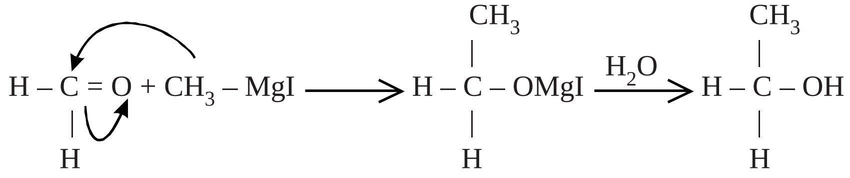
Grignard addition

Grignard addition to aldehydes and ketones are nucleophilic addition. The addition product formed is hydrolysed to alcohols.



Formaldehyde gives primary alcohol and other aldehydes give secondary alcohol with Grignard reagent. Ketones give tertiary alcohol.

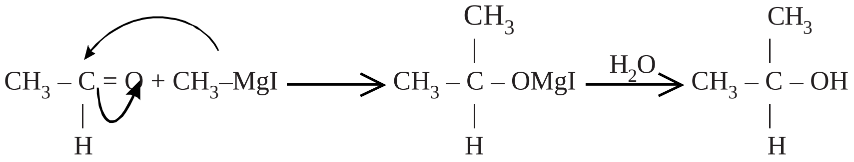
(i)



$$H-\underset{\underset{H}{|}}{C}=O + CH_3-MgI \longrightarrow H-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OMgI \xrightarrow{H_2O} H-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

formaldehyde　　primary alcohol (ethyl alcohol)

(ii)

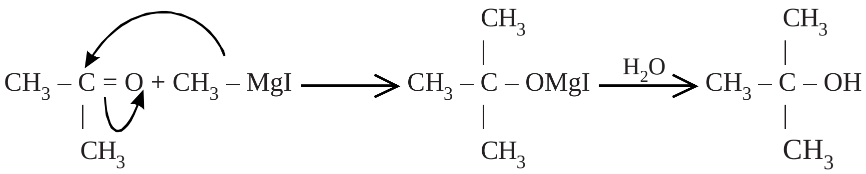


$CH_3-CH(H)=O + CH_3-MgI \longrightarrow CH_3-C(CH_3)(H)-OMgI \xrightarrow{H_2O} CH_3-C(CH_3)(H)-OH$

acetaldehyde

Secondary alcohol
Iso propyl alcohol

(iii)



$CH_3-C(CH_3)=O + CH_3-MgI \longrightarrow CH_3-C(CH_3)_2-OMgI \xrightarrow{H_2O} CH_3-C(CH_3)_2-OH$

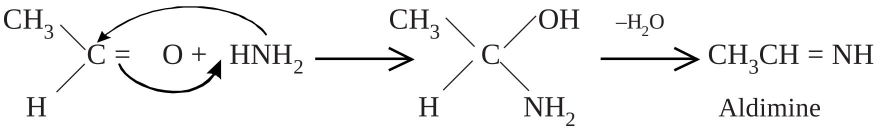
acetone

tertiary butyl alcohol

Addition of ammonia

Formaldehyde and ketones do not form addition compounds with ammonia. They yield complex condensation products. Other aldehydes form addition product with complex structure.

Examples : Acetaldehyde forms simple product while others form products with complex structure with ammonia.



$CH_3CHO + HNH_2 \longrightarrow CH_3CH(OH)NH_2 \xrightarrow{-H_2O} CH_3CH=NH$

Aldimine

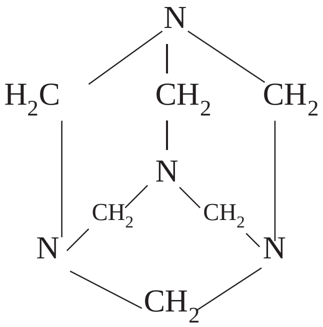
Acetaldehyde ammonia

Formaldehyde forms hexamethylene tetramine with NH_3.

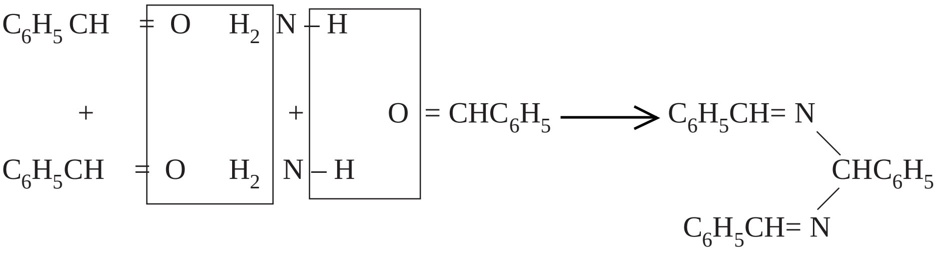
$$6CH_2O \quad + \quad 4NH_3 \longrightarrow (CH_2)_6\,N_4 \quad + \quad 6H_2O$$

hexa methylene tetramine

This is used as Urinary antiseptic in medicine, in the name of ‘Urotropine’.



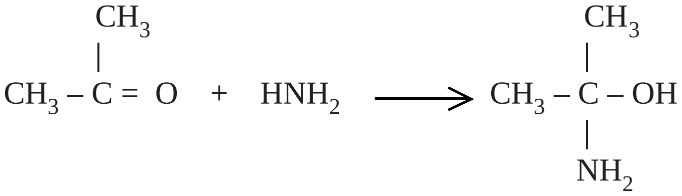
Benzaldehyde undergoes condensation reaction with ammonia to form hydrobenzamide.



$$\begin{array}{l} C_6H_5CH = \boxed{O \quad H_2}\, N \boxed{- H} \\ \qquad + \qquad\qquad\quad + \qquad O = CHC_6H_5 \longrightarrow \begin{array}{l} C_6H_5CH{=}N \\ \qquad\qquad \diagdown \\ \qquad\qquad\quad CHC_6H_5 \\ \qquad\qquad \diagup \\ C_6H_5CH{=}N \end{array} \\ C_6H_5CH = \boxed{O \quad H_2}\, N \boxed{- H} \end{array}$$

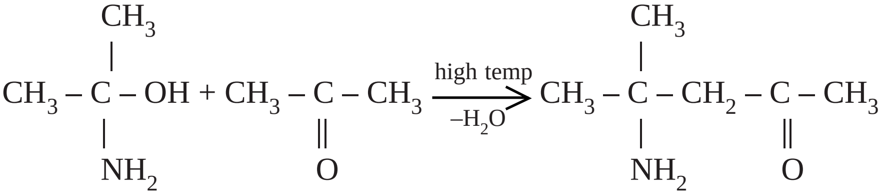
Hydro benzamide

Acetone with ammonia forms acetone ammonia initially at room temperature. On heating it forms diacetone amine.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + HNH_2 \longrightarrow CH_3-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$

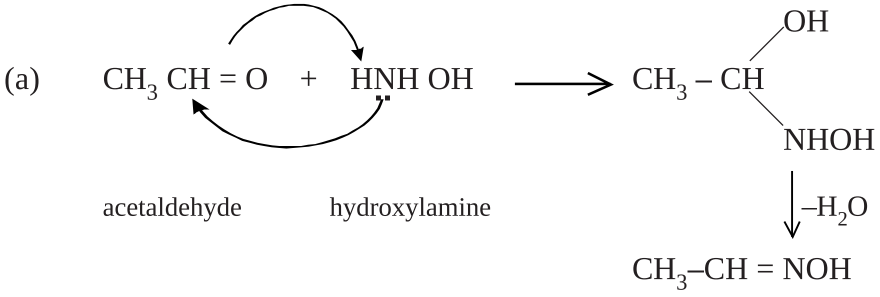
acetone ammonia



$$CH_3-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH + CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{\text{high temp}} CH_3-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$$

diacetone amine

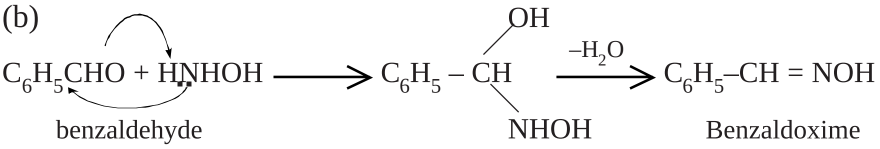
1. Reaction with hydroxylamine : Aldehydes and ketones react with hydroxylamine to form oximes.

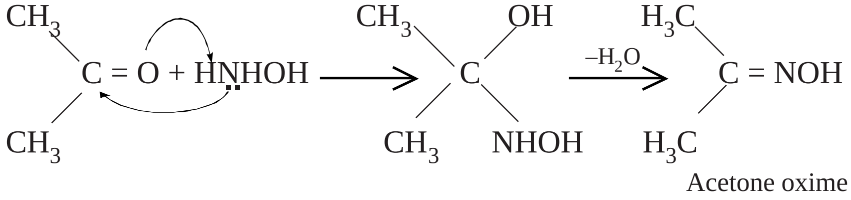


$$CH_3\,CH = O + H\ddot{N}H\,OH \longrightarrow CH_3-CH\begin{array}{l}\diagup OH \\ \diagdown NHOH\end{array} \xrightarrow{-H_2O} CH_3-CH = NOH$$

acetaldehyde oxime

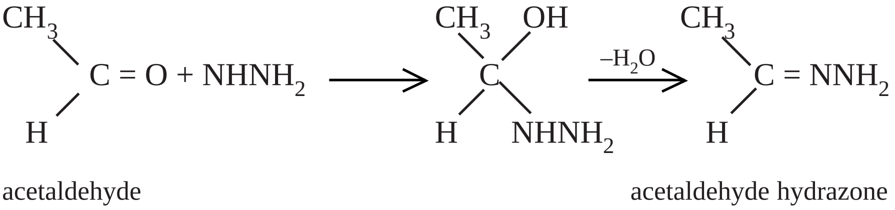
(b)

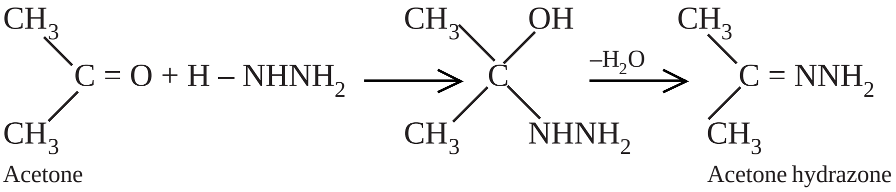




2. Reaction with hydrazine ($NH_2–NH_2$)

Aldehydes and ketones react with hydrazine to form hydrazones.

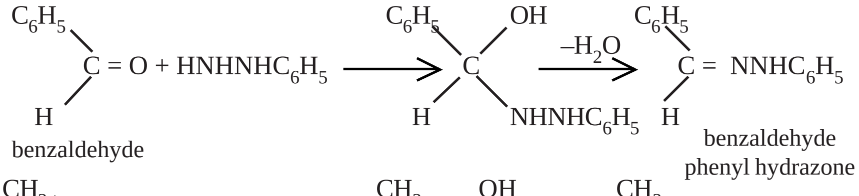




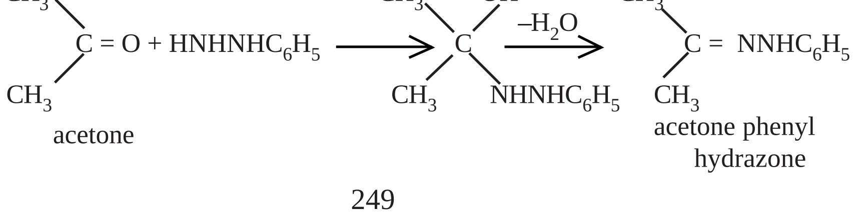
3. Reaction with phenyl hydrazine $C_6H_5NHNH_2$

Aldehydes and ketones react with phenyl hydrazine to form phenyl hydrazones.

(a)



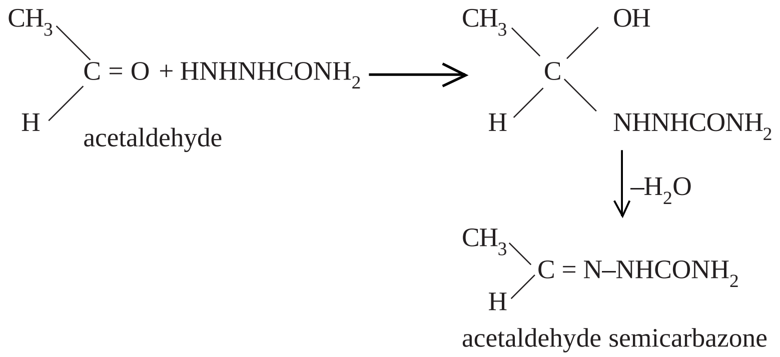
(b)



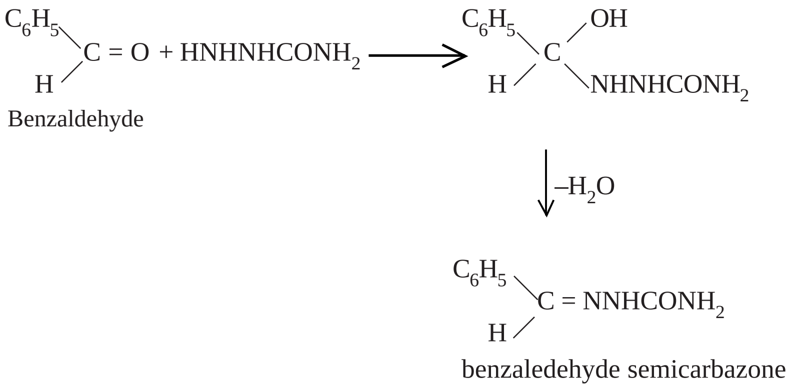
4. Reaction with semicarbazide $NH_2NHCONH_2$

Aldehydes and ketones react with semicarbazide to form semicarbazone.

(a)



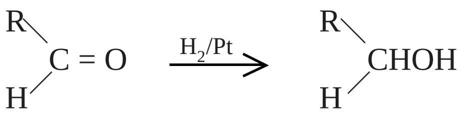
(b)



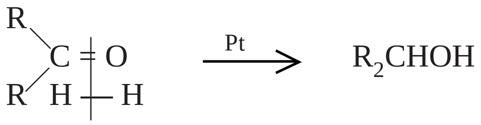
Reduction of aldehydes and ketones

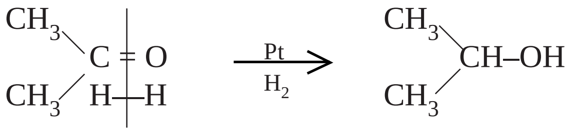
The products of reduction depends upon the reagents used and the conditions of reactions. Hence a variety of reagents are used for reduction.

(i) Catalytic reduction : Aldehydes are reduced to primary alcohols by hydrogen gas in presence of platinum metal as a catalyst.



Ketone on catalytic reduction gives secondary alcohol.





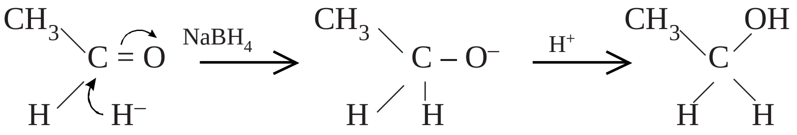
Isopropyl alcohol

It is an example of heterogeneous reaction.

Reduction using metal hydrides :

Metal hydrides like Lithium aluminium Hydride ($LiAlH_4$) Sodium borohydride ($NaBH_4$) reduce them to alcohols.

These are **'Hydride ion'** (H^-) donors. Hydride ion is a nucleophile. Hence it is nucleophilic addition reaction.



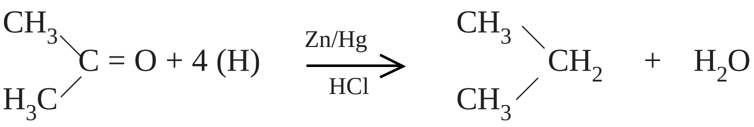
Acetaldehyde

Ethanol

(b) Reduction of carbonyl compounds to hydrocarbons.

(i) Clemmension Reduction :

Aldehydes and ketones can be reduced to hydrocarbons by zinc amalgam and con.HCl.



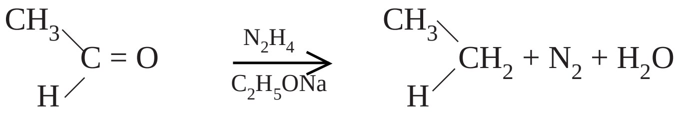
(Propane)

This reaction proceeds by electron addition to carbonyl carbon followed by protonation. **Zinc metal** is the electron source.

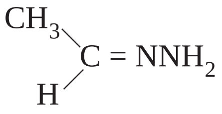
In the absence of mercury, hydrogen gas will be evolved and the reduction is incomplete. This reduction is called **Clemmenson reduction.**

(ii) Reduction under strongly basic condition : Wolff-Kishner Reduction

Aldehydes and ketones are reduced to hydrocarbons by heating with hydrazine and sodium ethoxide.



Hydrazones are formed as intermediates. The base removes the $-NH_2$ hydrogen atoms as protons generating carbanion. Proton addition to carbanion gives alkanes.



Hydrazone

This is called **Wolff-Kishner** reduction.

Oxidation :

Aldehydes have $\underset{\underset{H}{|}}{-C=O}$ bond which is responsible for their reducing properties. Ketones do not have such a structure and are not reducing agents.

All the oxidising agents like acidified potassium dichromate or acidified or alkaline potassium permanganate (powerful oxidising agents) and even milder oxidising agents like **'Tollen's reagent'** and **'Fehling's solution'** oxidise aldehydes to monocarboxylic acids having the same number of carbon atoms.

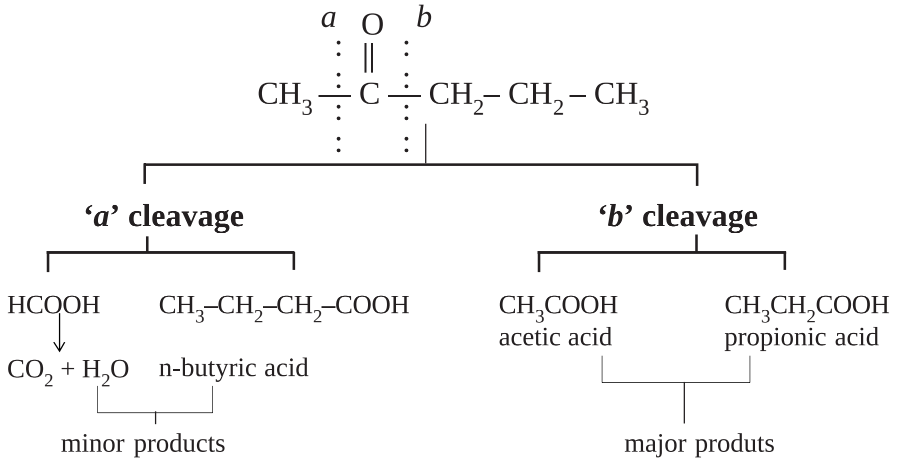
$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{(O)} \underset{\text{Acid}}{RCOOH}$$

Ketones are oxidised only by the strong oxidising agents (acidified potassium dichromate or permanganate) to mono carboxylic acids having lesser number of carbon atoms.

$$\underset{(3c)}{CH_3COCH_3} \longrightarrow \underset{(2c)}{CH_3COOH}$$

Popott's Rule :

During oxidation of unsymmetric ketones with oxidising agent which brings about the cleavage of C–C bond, the smaller alkyl group goes preferentially with the carbonyl group resulting in the carboxylic acids.



Because aldehydes are easily oxidised, they are reducing agents. They reduce ammonical silver nitrate (Tollen's reagent) to metallic silver and Fehling's solution (copper sulphate, sodium potassium tartrate) to red cuprous oxide.

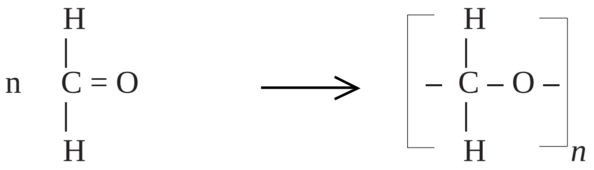
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 2Ag^+ + 3OH^- \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{(silver mirror)}}{2Ag} + 2H_2O$$

$$CH_3CHO + \underset{\substack{\text{(blue)}\\ \text{cupric ion}}}{2Cu^{2+}} + 5OH^- \longrightarrow CH_3COO^- + \underset{\substack{\text{(red precipitate)}\\ \text{cuprous ion}}}{Cu_2O} + 3H_2O$$

Aliphatic aldehydes restore the original colour (red-pink) of the **Schiff's reagent.** (when SO_2 is passed through intensely pink coloured Schiff's reagent in water. It forms a colourless solution. This colourless solution is used for this test). This is characteristic test for aldehydes. Ketones do not restore this colour.

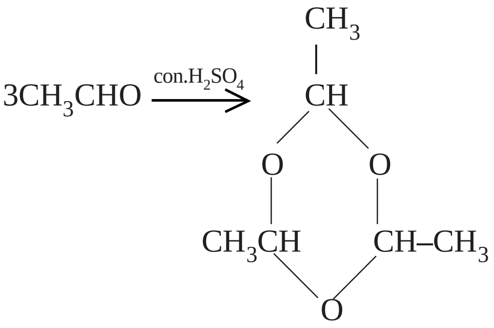
Polymerisation :

(i) When aqueous solution of formaldehyde is evaporated to dryness it forms a white crystalline polymer called **paraformaldehyde.**



$$n\,H-\overset{}{C}(H)=O \longrightarrow \left[-CH_2-O-\right]_n$$

(ii) Acetaldehyde polymerises to a cyclic structure called paraldehyde when a drop of concentrated sulphuric acid is added to it.



Paraldehyde

Benzaldehyde does not undergo polymerisation.

18.3.2 Uses of Aldehydes :

(a) 40% aqueous solution of formaldehyde is known as formalin and is used as a preservative for biological specimens and in leather tanning.

(b) A condensation product with ammonia, known as **'urotropine'** is used in medicine for urinary infection.

(c) In the process of 'Vat dyeing' to decolourise vat dyes by reduction.

(d) In the manufacture of polymeric resin called Bakelite (a condensation polymer with phenol).

Acetaldehyde :

(i) For silvering of mirror.

(ii) Its trimer 'paraldehyde' is hypnotic.

(iii) In the preparation of large number of organic compounds such as chloroform, acetic acid, ethanol, lactic acid etc.

Questions.

1. Which among the following reduces (a) Tollen's reagent only (b) Tollen's and Fehling solution (c) None

C_6H_5CHO, CH_3CHO, CH_3COCH_3, HCHO

Answers. (a) C_6H_5CHO (b) CH_3 CHO, HCHO (c) CH_3COCH_3

2. How can the following be prepared ? Give equations.

2-butenal from acetaldehyde.

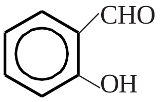
Clue :

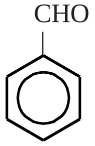
$$CH_3CHO \xrightarrow{OH-} CH_3CHOH\ CH_2CHO \xrightarrow[H_2O]{\Delta} CH_3CH = CHCHO$$

18.4 AROMATIC ALDEHYDES

In aromatic aldehydes, the aldehyde group is directly attached to benzene ring.

Names of Aromatic aldehydes

Formula	Common Name	IUPAC name
C_6H_5CHO	Benzaldehyde	Phenyl methanal
$C_6H_5CH_2CHO$	Phenyl acetaldehyde	Phenyl ethanal
	Salicylaldehyde	2-hydroxy benzaldehyde
$C_6H_5CH = CH–CHO$	Cinnamaldehyde	3-phenyl prop-2-enal

Benzaldehyde :  ***Phenyl methanal* (IUPAC)**

18.5 PREPARATION

1. Toluene is oxidised by chromium trioxide and acetic anhydride or chromyl chloride or air in presence of V_2O_5 at 773 K.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{air}/V_2O_5\ 773K]{(O)} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

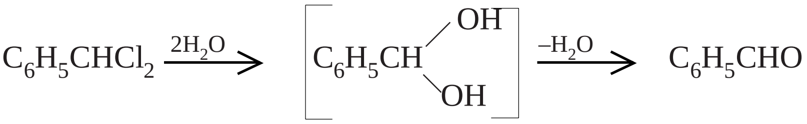
2. Benzyl chloride is oxidised by aqueous lead nitrate.

$$Pb(NO_3)_2 \xrightarrow{H_2O} HNO_3$$

$$C_6H_5CH_2Cl \xrightarrow{HNO_3} C_6H_5CHO$$

Benzyl chloride Benzaldehyde

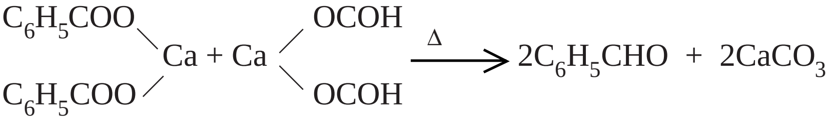
3. By the hydrolysis of benzal chloride. (gem dihalides)



$$C_6H_5CHCl_2 \xrightarrow{2H_2O} \left[C_6H_5CH\begin{matrix} OH \\ OH \end{matrix} \right] \xrightarrow{-H_2O} C_6H_5CHO$$

(unstable)

Distillation of calcium benzoate with calcium formate gives benzaldehyde.



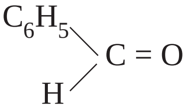
$$\begin{matrix} C_6H_5COO \\ C_6H_5COO \end{matrix} Ca + Ca \begin{matrix} OCOH \\ OCOH \end{matrix} \xrightarrow{\Delta} 2C_6H_5CHO + 2CaCO_3$$

Calcium benzoate (calcium formate)

18.5.1 Properties :

Colourless liquid with boiling point 452 K. It has the smell of bitter almond and known as oil of bitter almonds.

Chemical Properties :



$$\begin{matrix} C_6H_5 \\ H \end{matrix} C = O$$

It resembles aliphatic aldehydes in many properties.

Because of the presence of benzene ring the reactivity towards nucleophilic attack on carbonyl carbon is decreased.

Absence of α-hydrogen atom indicates that a carbanion cannot be generated at the α-carbon. So aldol type of condensation cannot be expected.

Presence of benzene ring makes possible the aromatic electrophilic substitution reaction.

1. It is oxidised to benzoic acid by alkaline permanganate.

$$C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH$$

   It does not reduce Fehling's solution, though it reduces Tollens reagent. Because Ag^+ is more easily reduced to Ag than Cu^{2+} to Cu^+

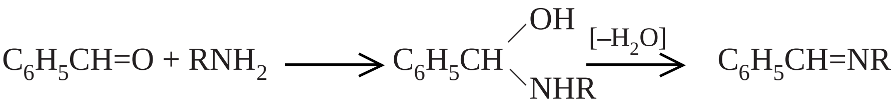
2. It is reduced to benzyl alcohol by $NaBH_4$ or $LiAlH_4$.

$$C_6H_5CHO \xrightarrow{[H^-]} C_6H_5CH_2OH$$

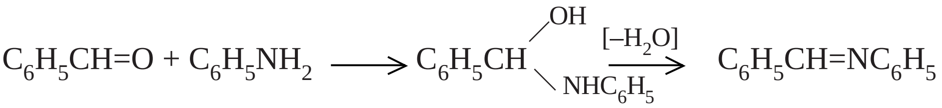
3. It can be reduced to toluene by Clemmenson or Wolff Kishner procedure.

$$C_6H_5CHO \xrightarrow[\text{or}\ N_2H_4\ /\ KOH]{Zn/Hg/HCl} C_6H_5CH_3$$

4. It condenses with ammonia forming hydrobenzamide.
5. It undergoes addition and addition elimination reactions with HCN, $NaHSO_3$, RMgX and with NH_2OH, $C_6H_5NHNH_2$, $NH_2CONHNH_2$.
6. Benzaldehyde reacts with primary amines to form **"aldimine"** type of compound called Schiffs base.



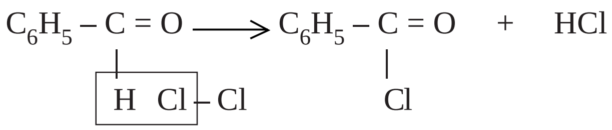
$$C_6H_5CH{=}O + RNH_2 \longrightarrow C_6H_5CH\begin{matrix} OH \\ NHR \end{matrix} \xrightarrow{[-H_2O]} C_6H_5CH{=}NR$$



$$C_6H_5CH{=}O + C_6H_5NH_2 \longrightarrow C_6H_5CH\begin{matrix} OH \\ NHC_6H_5 \end{matrix} \xrightarrow{[-H_2O]} C_6H_5CH{=}NC_6H_5$$

   Recognise the nucleophilic addition followed by elimination - pathway in this reaction.

7. In **the absence of catalyst,** chlorine displaces aldehydic hydrogen forming benzoyl chloride.



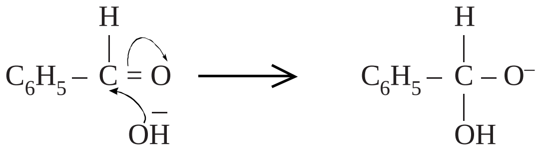
$$C_6H_5-\underset{\boxed{H\;\;Cl}-Cl}{\underset{|}{C}}=O \longrightarrow C_6H_5-\underset{Cl}{\underset{|}{C}}=O \;+\; HCl$$

8. **Cannizaro reaction :** Benzaldehyde undergoes Cannizaro reaction because of the **absence α-hydrogen.** It involves self oxidation and reduction of benzaldehyde when heated with concentrated NaOH.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaOH} \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

The mechanism involves the transfer of hydride ion from one molecule of benzaldehyde to the other molecule.

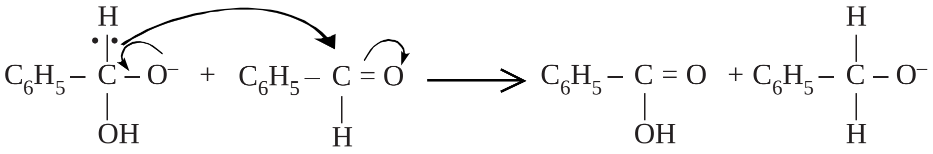
I step.



$$C_6H_5-\overset{H}{\overset{|}{C}}=O \quad \overset{-}{O}H \longrightarrow C_6H_5-\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-O^-$$

Nucleophilic attack by $\overset{-}{O}H$ ion on carbonyl carbon.

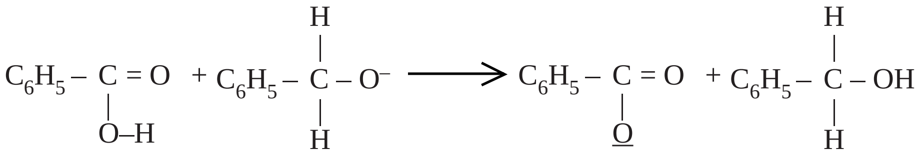
II step.



$$C_6H_5-\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-O^- + C_6H_5-\underset{\underset{H}{|}}{C}=O \longrightarrow C_6H_5-\underset{\underset{OH}{|}}{C}=O + C_6H_5-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-O^-$$

Transfer of hydride ion from the anion to carbonyl carbon of another molecule.

III step.



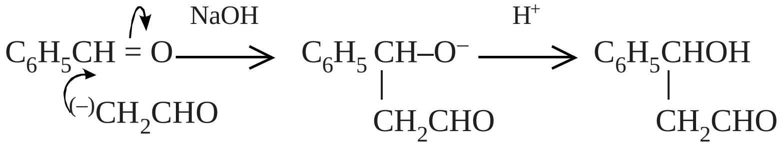
$$C_6H_5-\underset{\underset{O-H}{|}}{C}=O + C_6H_5-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-O^- \longrightarrow C_6H_5-\underset{\underset{\underline{O}}{|}}{C}=O + C_6H_5-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-OH$$

The benzyloxide ion picks up the acidic proton from benzoic acid to give benzyl alcohol.

9. **Claisen or Claisen Schmidt reaction**

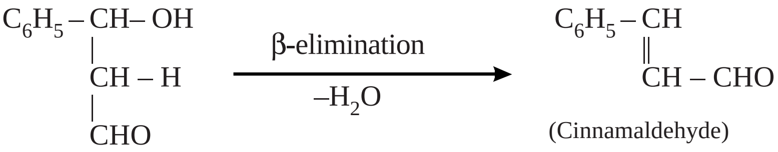
It reacts with aliphatic aldehydes or ketones in presence of NaOH forming α, β unsaturated aldehyde or ketone.

$$CH_3CHO \xrightarrow{NaOH} \overset{-}{C}H_2CHO \text{ (Carbanion)}$$



$$C_6H_5CH=O + {}^{(-)}CH_2CHO \xrightarrow{NaOH} C_6H_5\underset{\displaystyle CH_2CHO}{CH}-O^- \xrightarrow{H^+} C_6H_5\underset{\displaystyle CH_2CHO}{CHOH}$$

(Nucleophilic attack)



$$C_6H_5-\underset{\underset{\displaystyle CHO}{|}}{\underset{\displaystyle CH-H}{\underset{|}{CH}}}-OH \xrightarrow[-H_2O]{\beta\text{-elimination}} C_6H_5-CH=CH-CHO$$

(Cinnamaldehyde)

Similarly,

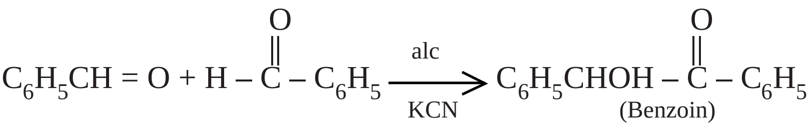
$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{NaOH} C_6H_5CH=CHCOCH_3$$

The carbanion formed from acetaldehyde or acetone brings forth a nucleophilic attack on the carbonyl carbon of benzaldehyde. The aldol type of product undergoes **β-elimination** (of water). This reaction is known as **Claisen Schmidt reaction.**

10. Benzoin Condensation :

This is another reaction, which is characteristic of aromatic aldehydes. When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide - α-hydroxy ketone called benzoin is formed. Cyanide ion (CN^-) is the specific catalyst in this reaction.

Benzoin can be considered as dimer of benzaldehyde.



$$C_6H_5CH=O + H-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow[KCN]{alc} C_6H_5CHOH-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$$

(Benzoin)

In presence of cyanide ion, one molecule of benzaldehyde **behaves as a carbanion.** That brings forth nucleophilic attack on the carbonyl group of another molecule of benzaldehyde. This results to Benzoin.

11. Perkins reaction :

When benzaldehyde is heated with sodium salt of acetic acid in presence of acetic anhydride, it forms cinnamic acid.

$$C_6H_5CH = O \;+\; \underset{\text{Acetic anhydride}}{CH_3\text{–}CO\text{–}O\text{–}COCH_3} \xrightarrow[\Delta]{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH = CH\text{–}COOH}$$

$$+\; CH_3COOH$$

Sodium acetate is the base that generates a carbanion at the α-carbon in the acetic anhydride. This brings forth nucleophilic attack on the carbonyl carbon forming **β-hydroxy acid,** water gets removed from this by β-elimination.

12. Knoevenagal reaction :

Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, pyridine is the basic catalyst here. This mechanism is quite similar to the previous reaction, involving carbanion, from the malonic acid.

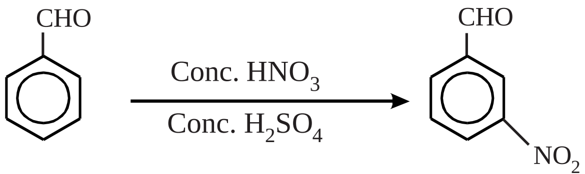
$$C_6H_5CH = O \;+\; H_2C(COOH)_2 \xrightarrow{\text{Pyridine}} \underset{\text{Malonic acid}}{C_6H_5CH = C(COOH)_2}$$

$$\xrightarrow[\Delta]{CO_2} \underset{\text{(Cinnamic acid)}}{C_6H_5CH{=}CHCOOH}$$

Reactions of the benzene ring :

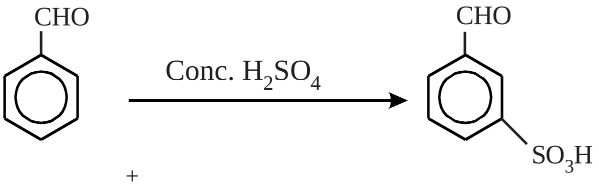
The reaction characteristic of benzene ring is electrophilic substitution. The aldehyde group (CHO) reduces the activity of benzene with respect to the attack by an electrophile. It is a **meta-directing group.** Hence meta substituted products are formed.

Nitration :



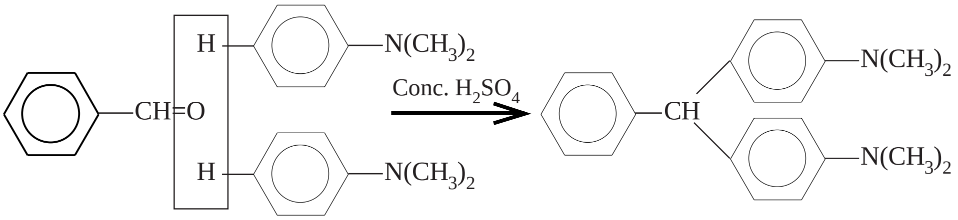
(The electrophile being NO_2^+)

Sulphonation :



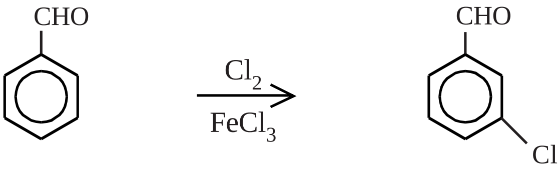
(The electrophile $\overset{+}{SO_3}H$) (m-benzaldehyde sulphonic acid)

In presence of con. H_2SO_4 benzaldehyde condenses with two molecules of N,N-dimethyl aniline forming triphenyl methane dye called **Malachite green.**



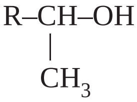
Triphenyl methane dye

Halogenation :



($FeCl_3$ is the Lewis acid catalyst that forms the electrophile Cl^+)

Comparison of Formaldehyde and Acetaldehyde

Reactions	HCHO	CH_3CHO
1. Iodoform test	does not undergo	gives iodoform
2. With Ammonia	forms 'urotropine' a condensation product	gives simple addition product.
3. With alkaline solution	undergoes Cannizzaro reaction	undergoes aldol condensation.
4. With phenol	forms thermosetting plastic-bakelite	does not form resin.
5. With RMgX	forms RCH_2OH	 $R{-}\underset{\substack{\vert \\ CH_3}}{CH}{-}OH$ is formed.

Comparison of Aliphatic aldehyde and aromatic aldehyde

Reactions	CH_3CHO	C_6H_5CHO
1. Heating with Fehling's solution.	gives a red precipitate	no reaction.
2. With ammonia	forms simple addition product.	forms complex condensation product.
3. With caustic soda	undergoes Aldol condensation	undergoes Cannizzaro reaction.
4. With primary amines	does not form Schiff's base	forms Schiff's base.
5. With chlorine	does not form acetyl chloride	forms benzoyl chloride.
6. Polymerisation	undergoes polymerisation.	does not polymerise.
7. Electrophilic substitution.	does not undergo.	undergoes at the meta position.
8. With Schiff's reagent.	gives pink colour in cold.	gives pink colour.

Uses

Benzaldehyde is used

(a) In the preparation of cinnamaldehyde, cinnamic acid and mandelic acid.

(b) Benzoin prepared from benzaldehyde is used as **'tincture benzoin'** in medicine for throat infection.

(c) With phenols and aromatic tertiary amines, it forms triphenyl methane dyes.

(d) In perfumery, as a flavouring agent.

Questions.

1. What happens when the following is heated with 50% NaOH ?

(a) HCHO (b) C_6H_5CHO (c) a mixture of (a) and (b)

Ans. (a) $CH_3OH + HCOOH$

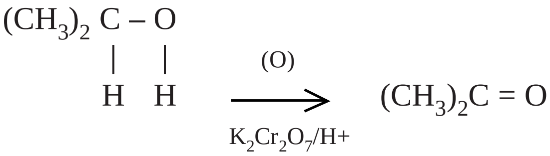
(b) $C_6H_5CH_2OH + C_6H_5COOH$

(c) $C_6H_5CH_2OH + HCOOH$ (HCHO is more easily oxidised than benzaldehyde) Crossed Cannizzaro reaction.

18.6 KETONES

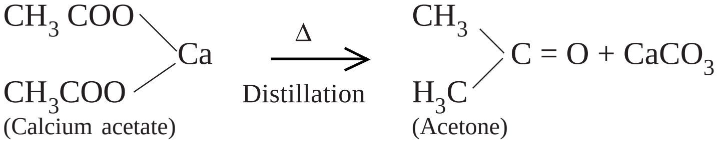
Preparation of ketones - Acetone

1. By the oxidation of isopropyl alcohol with acid dichromate acetone is formed.

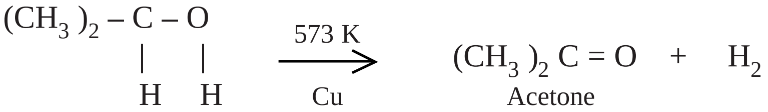


$$(CH_3)_2\underset{|\atop H}{C}-\underset{|\atop H}{O} \xrightarrow[K_2Cr_2O_7/H^+]{(O)} (CH_3)_2C=O$$

2. Dry distillation of calcium acetate.



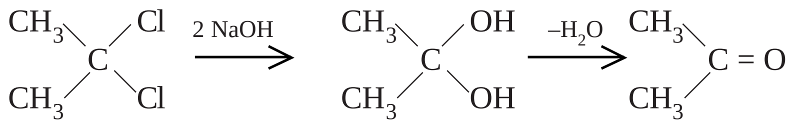
3. Passing the vapours of isopropyl alcohol over heated copper - catalytic dehydrogenation takes place.



$$(CH_3)_2 - \underset{H}{C} - \underset{H}{O} \xrightarrow[Cu]{573\ K} (CH_3)_2 C = O + H_2$$

(Isopropyl alcohol) Acetone

4. By the hydrolysis of isopropylidene chloride.



(Isopropyl alcohol) (Unstable) Acetone

18.6.1 Properties :

Colourless, volatile liquid, soluble in water and solubility is explained by its polar nature.

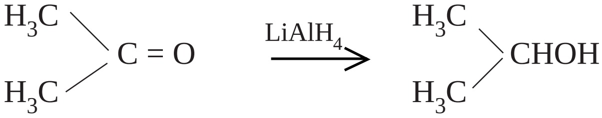
Chemical properties :

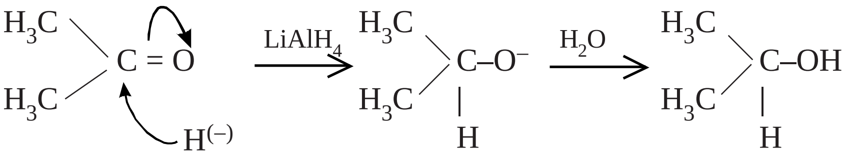
It resembles acetaldehyde in many reactions - especially reactions due to $CH_3 - \underset{|}{C} = O$ group.

1. It is not easily oxidised - hence it does not reduce Tollen's reagent and Fehling's solution. It does not restore the colour of Schiff's reagent.
2. Strong oxidising agents ($H_2SO_4 + K_2Cr_2O_7$) oxidise acetone to acetic acid.

$$CH_3COCH_3 \xrightarrow{(O)} CH_3COOH$$

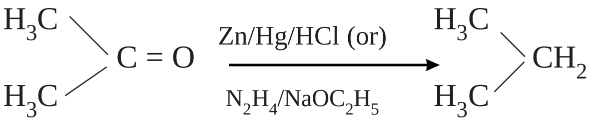
3. It can be reduced to isopropyl alcohol by sodium amalgam and water or Lithium Aluminium Hydride.





Lithium aluminium hydride donates hydride ion (a nucleophile).

4. **Clemmenson reduction or Wolff-kishner reduction** converts acetone to propane.



(Acetone) (Propane)

5. **Haloform reaction**

The compounds having $CH_3CHOH–$ or $CH_3CO–$ group undergoes haloform reaction.

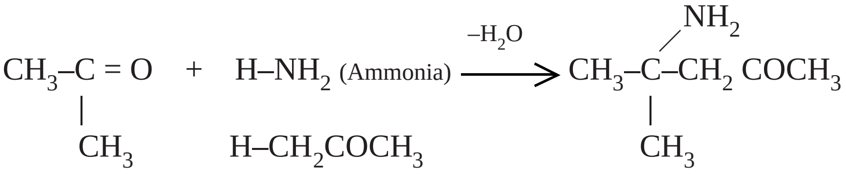
It undergoes halogenation at α-carbon atom.

$$CH_3–CO–CH_3 + 3\,Cl_2 \longrightarrow CCl_3 – CO – CH_3 + 3\,HCl$$

In the presence of NaOH, chloroform is formed.

6. It undergoes addition reaction with HCN, $NaHSO_3$, RMgX and condensation (addition followed by elimination) with NH_2OH, $NH_2–NH_2$, $C_6H_5NHNH_2$, $NH_2\ NHCONH_2$.

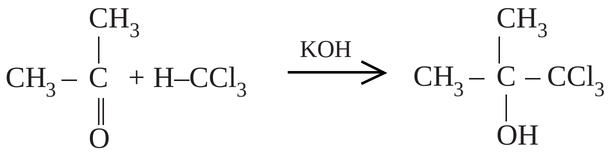
7. With ammonia its forms an addition product.



$$\underset{\underset{CH_3}{|}}{CH_3–C = O} + \underset{H–CH_2COCH_3}{H–NH_2}\ \text{(Ammonia)} \xrightarrow{-H_2O} CH_3–\overset{\overset{NH_2}{/}}{\underset{\underset{CH_3}{|}}{C}}–CH_2\ COCH_3$$

(Diacetone amine)

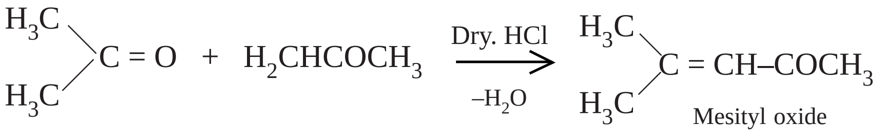
8. With chloroform acetone forms an addition products.



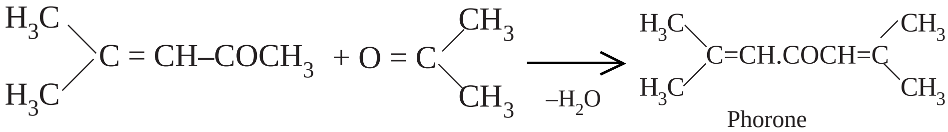
$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + H-CCl_3 \xrightarrow{KOH} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CCl_3$$

(Chloretone)

9. With dry hydrogen chloride first it forms mesityl oxide and then phorone. This reaction follows aldol type condensation followed by dehydration.

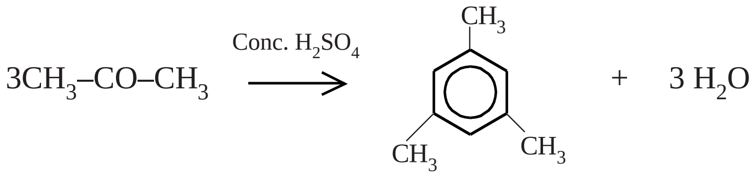


Mesityl oxide
4-methyl pent-3-ene-2-one



Phorone
2,6-dimethyl hept-2,5-diene-4-one

In presence of con. H_2SO_4 three molecules of acetone condense to give mesitylene (1, 3, 5 trimethyl benzene)



18.6.2 Uses.

1. A very good laboratory and industrial solvent.
2. In the preparation of Tranquilizers like sulphonal, in medicine.
3. In the manufacture of cordite.

Comparison of Aldehyde and Ketone.

Reactions	CH_3CHO	CH_3COCH_3
1. With Fehling's solution.	gives a red precipitate	does not react.
2. With Tollen's reagent.	gives silver mirror.	no silver mirror.
3. Oxidation	gives acetic acid	gives acetic acid with loss of one carbon atom.
4. Reduction with $NaBH_4$	ethanol (primary alcohol)	isopropyl alcohol (secondary alcohol)
5. With NH_3	simple addition product is formed.	forms complex ketonic amine.
6. Iodoform reaction	forms iodoform and formic acid.	forms iodoform and acetic acid.
7. Polymerisation	forms paraldehyde	forms condensation products.
8. With Schiff's reagent.	pink colour appears in cold.	no pink colour in cold.
9. Warming with NaOH	a brown resinons mass.	no resinous mass.

18.7 AROMATIC KETONES

IUPAC name of acetophenone and benzophenone

Formula	**Common name**	**IUPAC name**
$CH_3COC_6H_5$	methyl phenyl ketone	acetophenone
$C_6H_5COC_6H_5$	diphenyl ketone	benzophenone

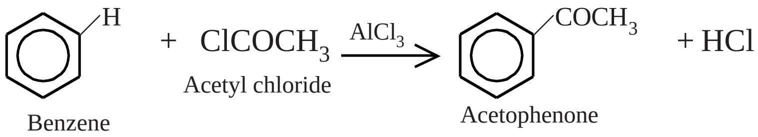
Methyl phenyl ketone: $CH_3COC_6H_5$

IUPAC name : Acetophenone

18.7.1 ACETOPHENONE

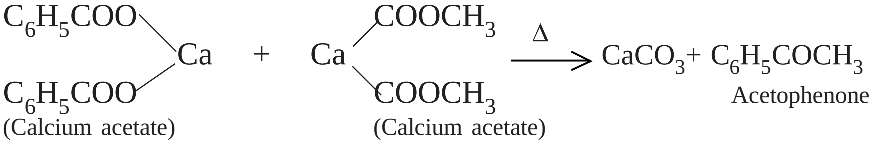
Preparation

1. Friedel Crafts acetylation of benzene with CH_3COCl / $AlCl_3$.



This is an electrophilic substitution reaction. The electrophile $CH_3\overset{+}{C}O$ is generated by the Lewis acid $AlCl_3$ from acetyl chloride.

2. Dry distillation of calcium benzoate with calcium acetate.



18.7.2 Properties

Colourless liquid, sparingly soluble in water readily soluble in ethanol and ether.

Chemical properties :

1. Oxidation :

Acid permanganate oxidises aceto phenone to benzoic acid.

$$\underset{\text{(Acetophenone)}}{C_6H_5COCH_3} \xrightarrow{(O)} \underset{\text{Phenyl glyoxalic acid}}{C_6H_5COCOOH} \longrightarrow \underset{\text{benzoic acid}}{C_6H_5COOH} + CO_2$$

2. **Reduction :** Reagents like sodium and ethanol, sodium borohydride, lithium aluminium hydride reduce acetophenone to phenyl methyl carbinol.

(a) $C_6H_5COCH_3 \xrightarrow{2(H)} C_6H_5CHOHCH_3$

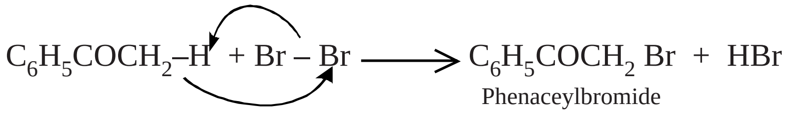
(b) Clemmenson reduction or Wolff-kishner reduction converts aceto phenone to ethyl benzene.

$$C_6H_5COCH_3 \xrightarrow{4(H)} C_6H_5CH_2CH_3 + H_2O$$

Halogenation :

At 273 K bromine in ether reacts with acetophenone to form phenacyl bromide.

One α-hydrogen is removed as a proton to the remaining carbanion, bromine addition takes place.



$$C_6H_5COCH_2{-}H + Br - Br \longrightarrow C_6H_5COCH_2\,Br + HBr$$

Phenaceylbromide

A small amount of anhydrous aluminium chloride catalyses this reaction.

Haloform reaction :

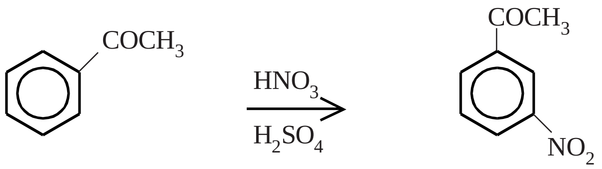
Because of the presence of CH_3CO- group it undergoes haloform reaction.

$$CH_3COC_6H_5 \xrightarrow[NaOH]{Cl_2} CHCl_3 + C_6H_5COONa$$

Electrophilic substitution :

Acetyl group deactivates the benzene ring and is meta directing group.

Nitration :



m-nitroacetophenone

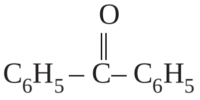
18.7.3 Uses

1. Used as a hypnotic (sleep inducing) by name hypnone

2. In perfumary.

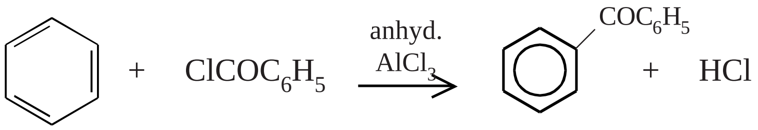
18.8 Benzophenone :

Diphenyl ketone



$$C_6H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - C_6H_5$$

1. **By Friedel Crafts reaction :** Benzoylation of benzene takes place in presence of **anhydrous aluminium chloride** as a catalyst. Benzoyl cation ($C_6H_5CO^+$) is the electrophile.

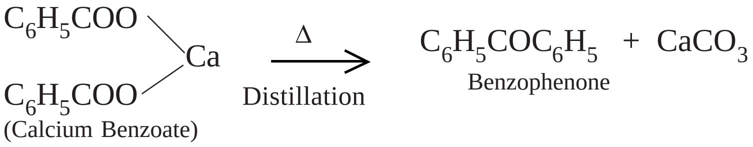


2. By the reaction of excess of benzene with carbonyl chloride (phosgene) in presence of anhydrous aluminium chloride as a catalyst, Benzoyl chloride may be formed initially.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Phosgene}}{Cl-CO-Cl} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{4(H)} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5}$$

Thus involves two Friedel craft's acylation reactions.

3. By the dry distillation of calcium benzoate.



$$\underset{\text{(Calcium Benzoate)}}{(C_6H_5COO)_2Ca} \xrightarrow[\text{Distillation}]{\Delta} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + CaCO_3$$

18.8.1 Properties

1. It is a colourless, sweet smelling solid (m.pt. 323 K).
2. It is insoluble in water but soluble in alcohol and ether.
3. Though it gives all reactions of carbonyl compound, it does not form addition product with sodium bisulphite because of steric hindrance and lowered reactivity due to the presence of two phenyl groups.
4. Oxidation with $K_2Cr_2O_7$ and con. H_2SO_4, it gives benzoic acid.

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{(O)} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

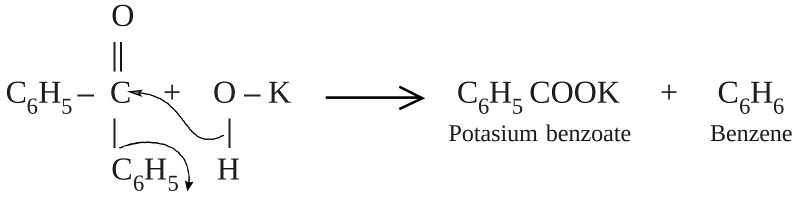
5. Reduction with sodium amalgam and water or lithium aluminium hydride, diphenyl carbinol is formed.

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{2(H)} \underset{\text{diphenyl carbinol}}{C_6H_5CHOHC_6H_5}$$

Diphenyl carbinol is also called **‘benzhydrol’**. Reduction wtih zinc amalgam and con. HCl gives Diphenyl methane.

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{4(H)} \underset{\text{diphenyl methane}}{C_6H_5CH_2C_6H_5}$$

6. On fusion with potassium hydroxide, it undergoes disproportionation reaction.



$$C_6H_5-\underset{\underset{C_6H_5}{|}}{\overset{\overset{O}{\|}}{C}} + \underset{\underset{H}{|}}{O}-K \longrightarrow \underset{\text{Potasium benzoate}}{C_6H_5\,COOK} + \underset{\text{Benzene}}{C_6H_6}$$

18.8.2 Uses :

Benzophenone is used in perfumery and in the preparation of benzhydrol drop and diphenyl methane.

SELF EVALUATION

(A) Choose the correct answer :

1. The chain isomer of 2-methyl propanal is

(a) 2-butanone	(b) butanal
(c) 2-methyl propanol	(d) but-3-ene-2-ol

2. Schiffs reagent gives pink colour with

(a) acetone	(b) acetaldehyde
(c) ethyl alcohol	(d) methyl acetate

3. Isopropyl alcohol vapours with air over silver catalyst at 520 K give

(a) tert.butyl alcohol (b) acetaldehyde
(c) acetone (d) 2-propanol

4. Methyl ketones are usually characterised by

(a) the Fehling's solution (b) the iodoform test
(c) the Schiff's test (d) the Tollen's reagent

5. Which of the following compounds is oxidised to give ethyl methyl ketone ?

(a) 2-propanol (b) 2-pentanone
(c) 1-butanol (d) 2-butanol

6. Formaldehyde polymerises to give

(a) paraldehyde (b) paraformaldehyde
(c) formalin (d) formic acid

7. Tollen's reagent is

(a) ammoniacal cuprous chloride (b) ammoniacal cuprous oxide
(c) ammoniacal silver nitrate (d) ammoniacal silver chloride

8. When acetaldehyde is heated with Fehling solution, it gives a precipitate of

(a) Cu_2O (b) CuO (c) $CuO + Cu_2O$ (d) Cu

9. The compound that does not undergo Cannizzaro reaction is

(a) formaldehyde (b) acetaldehyde
(c) benzaldehyde (d) trimethyl acetaldehyde

10. The formation of cyanohydrin from a ketone is an example of

(a) electrophilic addition (b) nucleophilic addition
(c) nucleophilic substitution (d) electrophilic substitution

11. Hydrogenation of benzoyl chloride in the presence of Pd on $BaSO_4$ gives

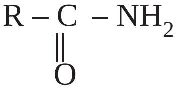
(a) phenol (b) benzoic acid
(c) benzyl alcohol (d) benzaldehyde

12. From which of the following, tertiary butyl alcohol is obtained by the action of methyl magnesium iodide ?

(a) HCHO (b) CH_3CHO (c) CH_3COCH_3 (d) CO_2

13. During reduction of aldehydes with hydrazine and C_2H_5ONa the product formed is

(a) $R-CH=N-NH_2$ (b) $R-C\equiv N$

(c) 
$R-\underset{\underset{O}{\|}}{C}-NH_2$ (d) $R-CH_3$

14. Aldol is

(a) 2-hydroxy butanol (b) 3-hydroxy butanol

(c) 3-hydroxy butanal (d) 2-hydroxy butanal

15. In the reduction of acetaldehyde using $LiAlH_4$ the hydride ion acts as

(a) electrophile (b) nucleophile

(c) both (a) and (b) (d) a free radical

16. Which of the following statement is wrong ?

(a) 2-pentanone and 3-pentanone are position isomers

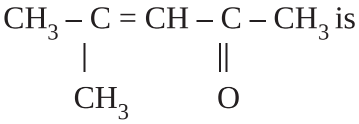
(b) aqueous solution of formaldehyde is known as formalin

(c) aldehydes and ketones undergo nucleophilic substitution

(d) aldehydes act as reducing agents

17. A cyanohydrin of a compound X on hydrolysis gives lactic acid. The X is

(a) HCHO (b) CH_3CHO (c) $(CH_3)_2\,CO$ (d) $C_6H_5CH_2CHO$

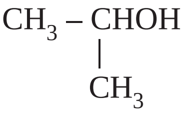
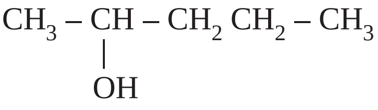
18. The IUPAC name of 
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$ is

(a) 4-methylpent-3-en-2-one (b) 2-methylpent-3-en-2-one

(c) 3-methyl pent-2-en-1-one (d) None of these

19. Which of the following does not give iodoform test ?

(a) aceto phenone (b) benzophenone

(c) 
$CH_3-\underset{\underset{CH_3}{|}}{CHOH}$ (d) 
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2\,CH_2-CH_3$

20. The compound which does not reduce Fehling solution is

(a) formaldehyde (b) acetaldehyde

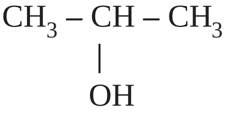
(c) benzaldehyde (d) propionaldehyde

21. $CH_3COCH_3 \xrightarrow{\text{Conc. } H_2SO_4}$ The product is

(a) mesitylene (b) mesityl oxide

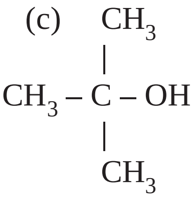
(c) phorone (d) paraldehyde

22. Which compound on strong oxidation gives propionic acid ?

(a) 

$$CH_3 - \underset{\substack{| \\ OH}}{CH} - CH_3$$

(b) $CH_3 - CO - CH_3$

(c) 

$$CH_3 - \underset{\substack{| \\ CH_3}}{\overset{\substack{CH_3 \\ |}}{C}} - OH$$

(d) $CH_3\ CH_2\ CH_2\ OH$

23. The compound used in the preparation of the tranquilizer, sulphonal is

(a) acetone (b) acetophenone

(c) isopropyl alcohol (d) glycol

24. Calcium acetate + calcium benzoate $\xrightarrow{\text{distillation}}$ gives

(a) benzophenone (b) benzaldehyde

(c) acetophenone (d) phenyl benzoate

25. Bakelite is a product of reaction between

(a) formaldehyde and NaOH (b) phenol and methanal

(c) aniline and NaOH (d) phenol and chloroform

(B) Answer in one or two sentences :

1. Give the structural formulae of

   (a) mesitylene (b) phorone and (c) mesityl oxide

2. What is Rosenmund's reduction ? What is the purpose of adding $BaSO_4$ in it ?

3. Name one reagent used to distinguish acetaldehyde and acetone.

4. Give four examples of carbonyl compounds ?

5. Does formaldehyde undergo aldol condensation ? Justify your answer.
6. What type of aldehydes undergo Cannizzaro reaction ?
7. What is urotropine ? Give its use.
8. What happens when calcium acetate is dry distilled ?
9. What is formalin - write its use.
10. Ethanal is more reactive towards nucleophilic addition reaction than propanone. Why ?
11. How is acetophenone prepared by Friedel-Crafts method ?
12. Write a note on haloform reaction.
13. How will you convert acetophenone to phenacyl bromide ?
14. Though benzophenone gives all reactions of carbonyl compounds, it does not form addition product with $NaHSO_3$ - give reasons.
15. Arrange the following in increasing order of reactivity towards nucleophilic addition. HCHO ; CH_3CHO and CH_3COCH_3
16. Predict the formulae of the products in the following reactions.

    (i) $CH_3COCH_3 + HCN \longrightarrow$

    (ii) $C_6H_5COCH_3 + NH_2OH \longrightarrow$
17. Formaldehyde and benzaldehyde give Cannizzaro reaction but acetaldehyde does not - Account for this
18. Give two tests for aldehydes.
19. Mention the industrial uses of formaldehyde.
20. How will you distinguish between formaldehyde and acetaldehyde.

(C) Answer not exceeding sixty words :

1. Write any three methods of preparing formaldehyde from alcohol.
2. How does formaldehyde react with (i) NH_3, (ii) CH_3MgI followed by hydrolysis and (iii) NaOH.
3. Illustrate the reducing property of acetaldehyde with examples.

4. How is acetone converted to
   (i) mesitylene (b) mesityl oxide, (iii) phorone and (iv) isopropyl alcohol.

5. Write giving chemical equations, a brief account of the following :
   (i) Rosenmund Reduction, (ii) Cannizzaro reaction
   (iii) Clemmenson reduction, and (iv) Aldol condensation

6. Give nucleophilic addition reaction of acetaldehyde with (a) $NaHSO_3$, and (b) $LiAlH_4$.

7. Discuss aldol condensation.

8. How are the following conversions carried out ?

   (i) benzaldehyde from Toluene, (ii) acetophenone from benzene, and (iii) benzoin from benzaldehyde.

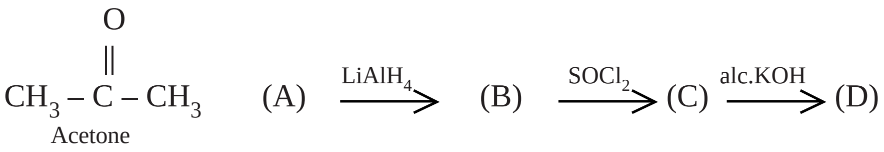
9. Distinguish acetaldehyde from acetone.

10. Write a note on (i) Perkins reaction, and (ii) Knoevenagal reaction.

11. How will you distinguish between formaldehyde and acetaldehyde.

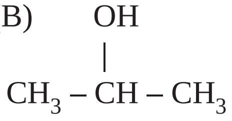
12. Write the differences between acetophenone and benzophenone.

13. Identify (B), (C) and (D)



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}\qquad (A)\xrightarrow{LiAlH_4}(B)\xrightarrow{SOCl_2}(C)\xrightarrow{alc.KOH}(D)$$

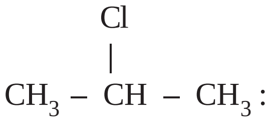
Answers (B)



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

: Isopropyl alcohol

(C)



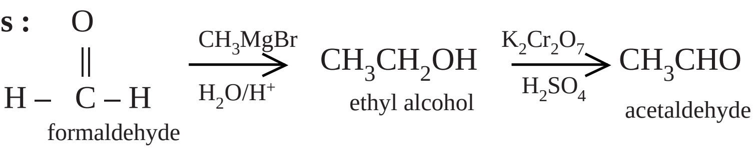
$$CH_3-\overset{\overset{Cl}{|}}{CH}-CH_3$$

: Isopropyl chloride

(D) $CH_3-CH=CH_2$: propylene

14. How will you synthesise acetaldehyde from formaldehyde ?

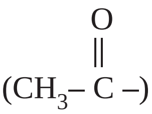
Answers :



$$\underset{\text{formaldehyde}}{H-\overset{\overset{O}{\|}}{C}-H} \xrightarrow[H_2O/H^+]{CH_3MgBr} \underset{\text{ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{acetaldehyde}}{CH_3CHO}$$

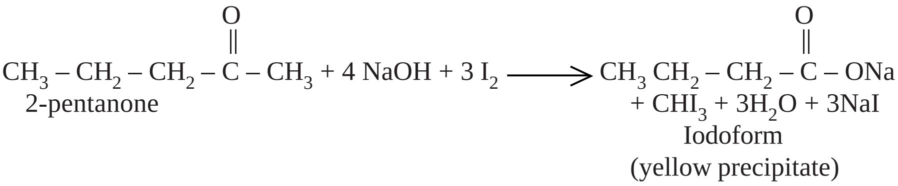
15. How will you distinguish between 2-pentanone and 3-pentanone.

Answers : Since 2-pentanone contains methyl ketone



$(CH_3-\overset{\overset{O}{\|}}{C}-)$

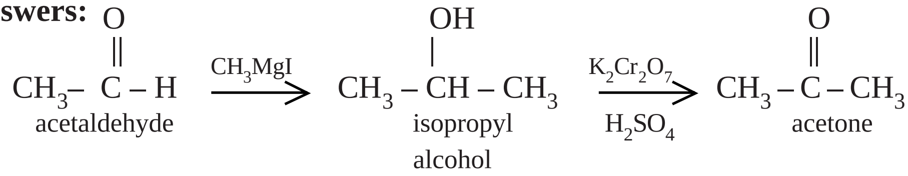
it undergoes iodoform test with an alkaline solution of iodine and forms yellow precipitate of iodoform But-3-pentanone does not give this test.



$$\underset{\text{2-pentanone}}{CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + 4\,NaOH + 3\,I_2 \longrightarrow CH_3\,CH_2-CH_2-\overset{\overset{O}{\|}}{C}-ONa + \underset{\substack{\text{Iodoform}\\ \text{(yellow precipitate)}}}{CHI_3} + 3H_2O + 3NaI$$

16. How will you synthesise acetone from acetaldehyde ?

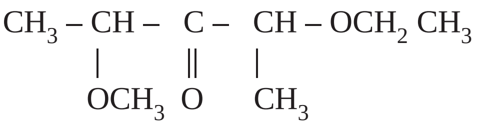
Answers:



$$\underset{\text{acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{CH_3MgI} \underset{\text{isopropyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

17. Give the IUPAC names of

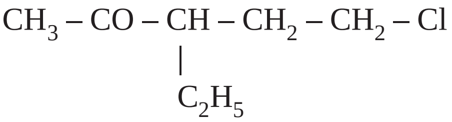
(i)



$$CH_3-\underset{\underset{OCH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-OCH_2\,CH_3$$

and

(ii)



$$CH_3-CO-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_2-Cl$$

Answers :

(i) 2-ethoxy-4-methoxy-3-pentanone and

(ii) 3-ethyl-5-chloro-2-pentanone.

18. An organic compound, C_2H_4O gives a red precipitate when warmed with Fehling's solution. It also undergoes aldol condensation in presence of alkali.

(i) Write IUPAC name of the compound.

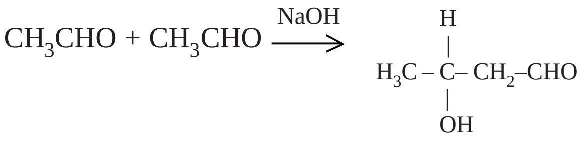
(ii) What is the hybridization of carbon atoms in the compound ?

(iii) Write equation for the reaction.

Answers : (i) Ethanal

(ii) sp^2 and

(iii) $CH_3CHO + 2Cu^{2+} + 3OH^- \longrightarrow CH_3COO^- + 2Cu^+ + 2H_2O$

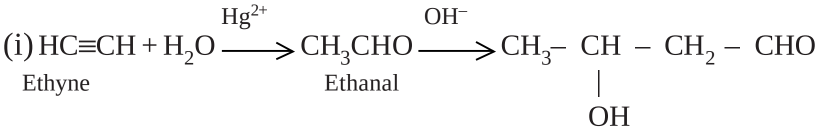


$$CH_3CHO + CH_3CHO \xrightarrow{NaOH} H_3C-\underset{\displaystyle OH}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-CH_2-CHO$$

aldol

19. Write the structural formula of the main product formed when ; (i) The compound obtained by hydration of ethyne is treated with dilute alkali. (ii) Methanal reacts with ammonia.

Answers: (i)



$$\underset{\text{Ethyne}}{HC\equiv CH} + H_2O \xrightarrow{Hg^{2+}} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{OH^-} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CHO$$

aldol

(ii) $6CH_2O + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$

20. How will you synthesise 2-butanone from ethyl alcohol ?
Clue : Steps are (i) $SOCl_2$ (ii) Mg/ether (iii) CH_3CHO, (iv) H_2O/H^+ and (v) $Na_2Cr_2O_7$ / H_2SO_4.

21. What happens when the following alcohol vapours are passed over heated copper ? (a) n-butyl alcohol, (b) isobutyl alcohol, (c) 2-butanol and (d) 2-methyl-2-propanol.

22. How can the following conversions be effected ?

(a) $CH_3COCl \longrightarrow CH_3CHO$

(b) $CH_3COCl \longrightarrow CH_3COCH_3$

(c) $CH_3CN \longrightarrow CH_3CHO$

(d) $CH_3CN \longrightarrow CH_3CH_2OH$

23. Which compounds on Clemmenson reduction give (a) 2-methyl propane, (b) ethyl benzene, (c) propane and (d) diphenyl methane.

24. What happens when the following compounds are treated with dilute NaOH solution in cold ?

(a) propanal, (b) $(CH_3)_3C\text{-}CHO$, (c) mixture of $(CH_3)_3$ CCHO and acetone.

25. Identify the atoms that has undergone change in hybridisation in the following reactions.

(a) $CH_3\ CHO + HCN \longrightarrow CH_3COOH$

(b) $CH_3C \equiv N \longrightarrow CH_3CH_2CH_3$

(c) $CH_3COCH_3 \longrightarrow CH_3CH_2CH_3$

(d) $CH \equiv CH \longrightarrow CH_2 = CH_2$

26. Draw resonance structures for the following :

(a) CH_3COO^-, (b) CH_3CONH_2, (c) C_6H_5CHO, (d) $C_6H_5COO^-$

27. Which of the following pairs is more resonance stabilised ?

(a) C_6H_5CHO and $C_6H_{13}CHO$

(b) CH_3COCH_3 and $CH_3\ COC_6H_5$,

(c) p-hydroxy benzaldehyde and m-hydroxy benzaldehyde,

(d) $C_6H_5CH_2OH$ and $CH_3–C_6H_4–OH$ (para)

SUMMARY :

Functional group of aldehyde and ketone.

Structure, isomerism involved and nomenclature - common name and IUPAC name.

Preparation - by the oxidation or dehydrogenation of alcohols ozonolysis of olefins, hydration of alkynes, catalytic reduction of acid chloride, distillation of calcium salt of fatty acid and hydrolysis of gem dihalide.

Properties - Higher boiling point of polar molecules than hydro carbons - carbon of the carbonyl group is the site of nucleophilic attack - Most of the addition reactions - nucleophilic - addition product eliminates water forming condensation product. Reactions with $NaHSO_3$, HCN, NH_3, RMgX, NH_2OH, $C_6H_5NHNH_2$, $NH_2NHCONH_2$, reductions with $NaBH_4$, $LiAlH_4$, also nucleophilic in nature, that give alcohols.

Some reductions - Zn/Hg/HCl or heating with $N_2H_4/NaOC_2H_5$ - gives hydrocarbon.

Mild oxidising agents like Fehling’s solution, Tollen’s reagent - oxidise aldehydes to mono carboxylic acids. Ketones require more powerful oxidising agents like acidified $K_2Cr_2O_7$ or $KMnO_4$ in which carbon-carbon bond is cleaved to give carboxylic acids having lesser number of carbon atoms.

Aldehydes and ketones having α-hydrogen atom form carbanions in presence of base. These take part in condensation reactions with other carbonyl compounds. Aldehydes and ketones having CH_3CO- group undergo haloform reaction.

Formaldehyde undergoes condensation with Ammonia to form urotropine and phenol to form Bakelite.

Acetone and acetaldehyde undergo aldol condensation while formaldehyde undergoes Cannizaro reaction.

Distinction between formaldehyde and acetaldehyde and acetaldehyde and acetone.

Structure and nomenclature of aromatic aldehydes - preparation and properties - Reactivity of carbonyl group - decreased by benzene ring.

Absence of α-hydrogen - cannot form carbanion. But carbanion formed from other carbonyl compounds attack the carbonyl group of benzaldehyde. Hence it takes part in all the nucleophilic addition reactions and condensation reactions.

In addition it undergoes aromatic electrophilic substitution reactions. The benzene ring - deactivated and meta-products formed.

Distinction between aliphatic and aromatic aldehydes.

Aromatic ketones - acetophenone and benzophenone, preparation - Friedel Crafts acylation.

Properties - Resemblance of acetophenone with acetone. Benzophenone - least reactive - absence of α-hydrogen - uses.

Name reactions
Rosenmund reduction
Clemmenson reduction
Wolff-kishner reduction
Aldol condensation
Cannizaro reaction
Fehling's test
Tollen's test
Claisen condensation
Perkins reaction
Knoevenagel reaction
Benzoin condensation
Friedel Crafts acylation

REFERENCES :

1. Organic Chemistry by Finar (Vol. I)
2. Text book of Organic Chemistry by P.L. Soni.
3. Text book of Organic Chemistry by Cram, Hammond & Hendrickson

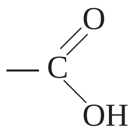
19. CARBOXYLIC ACIDS

LEARNING OBJECTIVES

- *To know about carboxylic acids and their derivatives.*

19.1 CARBOXYLIC ACIDS

Organic compounds containing the carboxyl group,



$$-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup\!\!\diagdown}}$$

are called carboxylic acids. The acid may be monocarboxylic acid, if it contains one –COOH group ; a dicarboxylic acid if it contains two –COOH groups ; a tricarboxylic acid if it contains three –COOH groups etc.

The aliphatic mono carboxylic acids are called fatty acids and the higher members like Stearic acid ($C_{17}H_{35}COOH$), palmitic acid ($C_{15}H_{31}COOH$), oleic acid ($C_{16}H_{33}COOH$) etc., occur as glycerides in oils and fats.

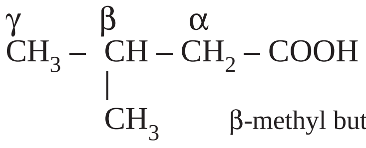
Nomenclature :

(a) Trivial system :

The names of lower members are derived from the **source** of individual acids.

Formula	Source	Trivial name
HCOOH	Red ant (formica)	formic acid
CH_3COOH	Vinegar (acetum)	acetic acid
C_3H_7COOH	Butter (Butyrum)	butyric acid
C_4H_9COOH	Root of valarion plant	valeric acid
$C_{11}H_{23}COOH$	Laurel oil	lauric acid

In case of substituted acids the **position of the substituent** is represented by α, β, γ, δ etc. Thus



$$\overset{\gamma}{CH_3} - \underset{\displaystyle |\atop CH_3}{\overset{\beta}{CH}} - \overset{\alpha}{CH_2} - COOH$$

β-methyl butyric acid

Derived names :

Sometimes fatty acids are named as alkyl derivatives of acetic acid.

(e.g.,)	$MeCH_2COOH$	Methyl acetic acid
	$Me_2CHCOOH$	Dimethyl acetic acid
	$Me_2CH.CH_2COOH$	Isopropyl acetic acid

IUPAC names :

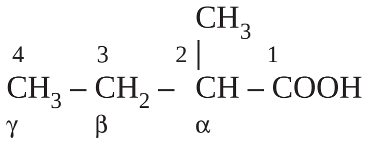
Acids are named after the alkane by replacing the ending ***'e'*** by ***'oic'*** acid.

HCOOH	Methanoic acid
CH_3COOH	Ethanoic acid
CH_3CH_2COOH	Propanoic acid
$CH_3CH_2CH_2COOH$	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	Pentanoic acid

In case of substituted acid the longest carbon chain including the carboxyl group is taken as the parent chain.

Position of the substituent is indicated by either 1, 2, 3, etc., (or) **α, β, γ, ...**

When it is done by numbers the carbon of the carboxyl group is numbered as (1) when it is done by Greek letters the carbon next to the –COOH group is **designated as 'α'.**



$$\underset{\gamma}{\overset{4}{CH_3}} - \underset{\beta}{\overset{3}{CH_2}} - \underset{\alpha}{\overset{\overset{CH_3}{|}}{\overset{2}{CH}}} - \overset{1}{COOH}$$

2-methyl butanoic acid (IUPAC)

α-methyl butyric acid (Common)

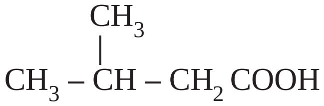
Isomerism :

1. Chain isomerism :

This arises due to the difference in the carbon chain of alkyl group attached to carboxyl group.

$CH_3\,CH_2\,CH_2\,CH_2\,COOH$

(pentanoic acid)



$$CH_3-\underset{}{\overset{\displaystyle CH_3\atop|}{CH}}-CH_2\,COOH$$

(3-methyl butanoic acid)

2. Functional isomerism :

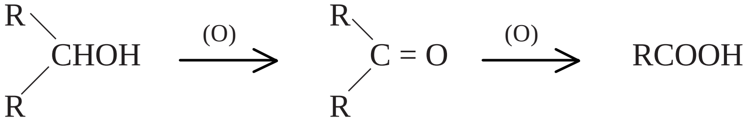
Carboxylic acids may be functional isomers of esters.

$CH_3\,CH_2\,COOH$ propanoic acid	and	$CH_3\,COOCH_3$ methyl acetate	$HCOOC_2H_5$ ethyl formate

19.2 Preparation of monocarboxylic acids :

1. **Oxidation :** Carboxylic acids are prepared by the oxidation of alcohols, aldehydes or ketones with $K_2Cr_2O_7$ and H_2SO_4. Primary alcohol is first oxidised to aldehyde and then to carboxylic acid. On the otherhand secondary alcohols are first oxidised to ketone and then to acid with lesser number of carbon atoms.

$$RCH_2OH \xrightarrow{(O)} RCHO \xrightarrow{(O)} RCOOH$$

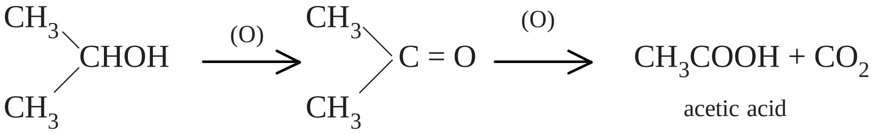


$$R_2CHOH \xrightarrow{(O)} R_2C=O \xrightarrow{(O)} RCOOH$$

(i) $CH_3CH_2OH \xrightarrow{(O)} CH_3CHO \xrightarrow{(O)} CH_3COOH$

ethyl alcohol — acetaldehyde — acetic acid

(ii)



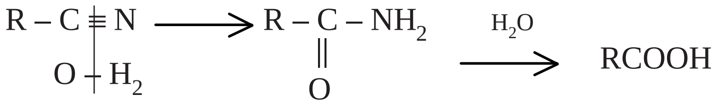
$$(CH_3)_2CHOH \xrightarrow{(O)} (CH_3)_2C=O \xrightarrow{(O)} CH_3COOH + CO_2$$

Isopropyl alcohol — acetone — acetic acid

2. Hydrolysis methods :

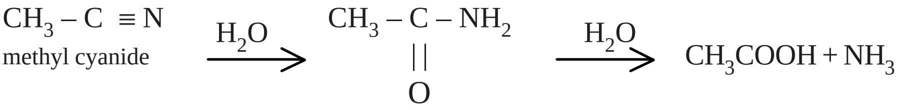
(a) Hydrolysis of cyanides, amides and esters : Alkyl cyanides, amides, esters are hydrolysed with aqueous acid or alkali to give carboxylic acid.

(i)



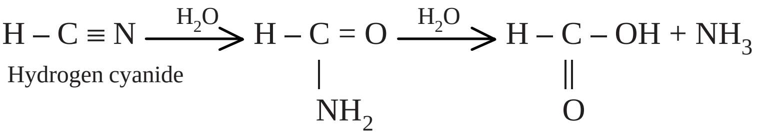
$$\underset{\text{alkyl cyanide}}{R-C\equiv N} \xrightarrow{H_2O} \underset{\text{amide}}{R-\underset{\underset{O}{\|}}{C}-NH_2} \xrightarrow{H_2O} RCOOH$$

alkyl cyanide amide



$$\underset{\text{methyl cyanide}}{CH_3-C\equiv N} \xrightarrow{H_2O} \underset{\text{acetamide}}{CH_3-\underset{\underset{O}{\|}}{C}-NH_2} \xrightarrow{H_2O} CH_3COOH + NH_3$$

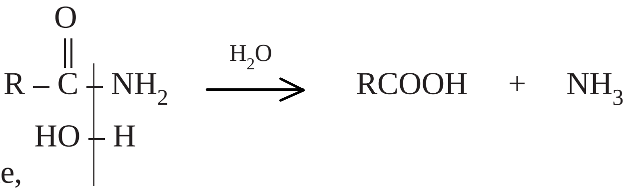
methyl cyanide acetamide



$$\underset{\text{Hydrogen cyanide}}{H-C\equiv N} \xrightarrow{H_2O} \underset{\text{Formamide}}{H-\underset{\underset{NH_2}{|}}{C}=O} \xrightarrow{H_2O} H-\underset{\underset{O}{\|}}{C}-OH + NH_3$$

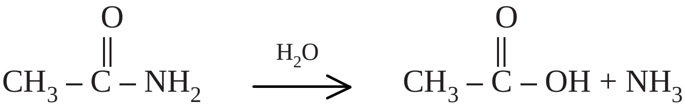
Hydrogen cyanide Formamide

(ii)



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + HO-H \xrightarrow{H_2O} RCOOH + NH_3$$

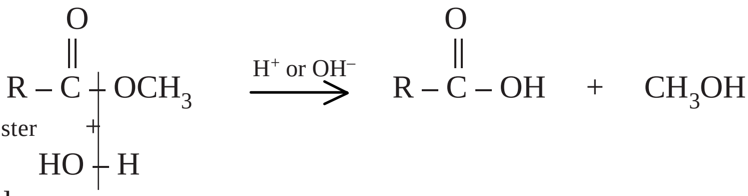
Example,



$$\underset{\text{acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{H_2O} CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_3$$

acetamide

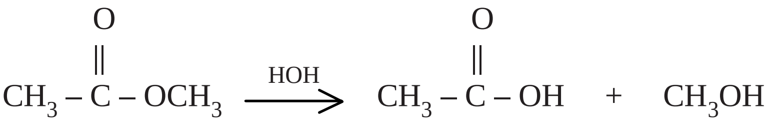
(iii)



$$\underset{\text{ester}}{R-\overset{\overset{O}{\|}}{C}-OCH_3} + HO-H \xrightarrow{H^+ \text{ or } OH^-} R-\overset{\overset{O}{\|}}{C}-OH + CH_3OH$$

ester

Example,

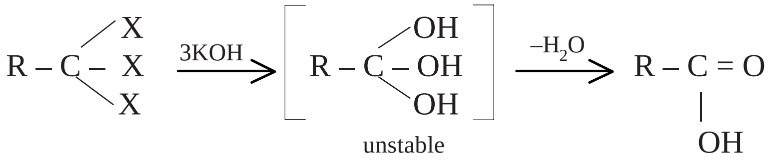


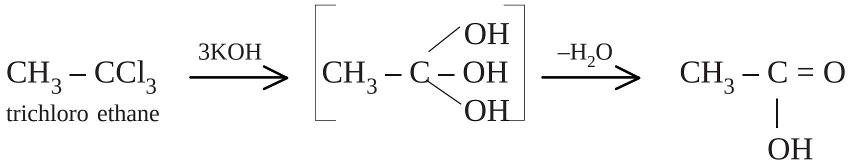
$$\underset{\text{methyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OCH_3} \xrightarrow[H^+ \text{ or } OH^-]{HOH} \underset{\text{acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + CH_3OH$$

methyl acetate acetic acid

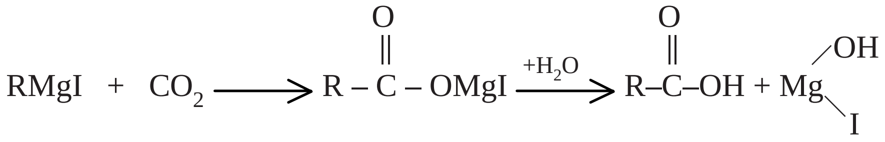
(acid or alkaline hydrolysis)

(b) Hydrolysis of trihalides : By the hydrolysis of trihalides containing three halogen atoms attached to the same carbon atom, carboxylic acids are formed.

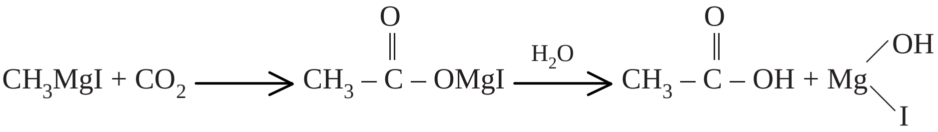




3. From Grignard reagent :



Methyl magnesium iodide with carbondioxide gives acetic acid.



Formic acid cannot be prepared by Grignard reagent since the acid contains only one carbon atom.

Preparation of formic acid

4. From CH_3OH or HCHO

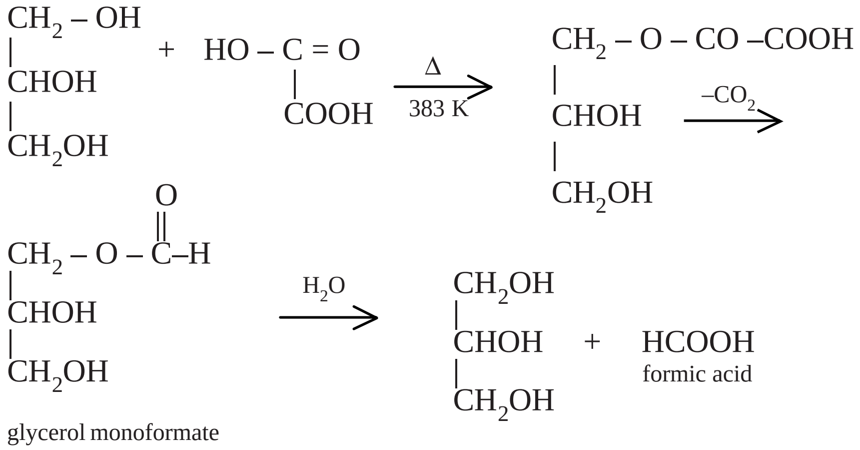
By the oxidation of methyl alcohol or formaldehyde with $K_2Cr_2O_7/H_2SO_4$.

$$CH_3OH \xrightarrow{3(O)} HCOOH$$

$$HCHO \xrightarrow{(O)} HCOOH$$

5. From glycerol

By heating glycerol with oxalic acid at 373 K – 383 K

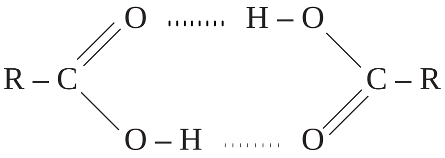


$$\begin{matrix} CH_2-OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} + \begin{matrix} HO-C=O \\ | \\ COOH \end{matrix} \xrightarrow[383\text{ K}]{\Delta} \begin{matrix} CH_2-O-CO-COOH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow{-CO_2}$$

$$\underset{\text{glycerol monoformate}}{\begin{matrix} CH_2-O-\overset{\overset{O}{\|}}{C}-H \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \xrightarrow{H_2O} \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} + \underset{\text{formic acid}}{HCOOH}$$

19.2.1 Properties

1. Lower members are pleasant smelling liquids with higher boiling points. The higher members are waxy solids. The higher boiling points are explained on the basis of **association by hydrogen bonding.**



2. The first few members are highly soluble in water and higher members are insoluble. This can also be explained on the basis of hydrogen bonding between acids and water. With higher members the size of the alkyl group is increased which repels the hydrophilic groups.

Chemical Properties :

1. Fatty acids react with alkalies to form salt and water and liberates CO_2 with carbonates (stronger than carbonic acid).

$$CH_3COOH + NaOH \longrightarrow \underset{\text{(sodium acetate salt)}}{CH_3COONa} + H_2O$$

$$2\ HCOOH + 2Na_2CO_3 \longrightarrow \underset{\text{(sodium formate)}}{2\ HCOONa} + H_2O + CO_2$$

2. They liberate hydrogen, when react with electropositive metals like zinc or magnesium.

$$2CH_3COOH + Zn \longrightarrow \underset{\text{(zinc acetate)}}{(CH_3COO)_2\,Zn} + H_2$$

$$2HCOOH + Mg \longrightarrow \underset{\text{(magnesium formate)}}{(HCOO)_2\,Mg} + H_2$$

3. **Reaction involving - hydroxyl group :** carboxylic acid reacts with alcohols in presence of mineral acid as catalyst and forms esters. This reaction is called **esterification.**

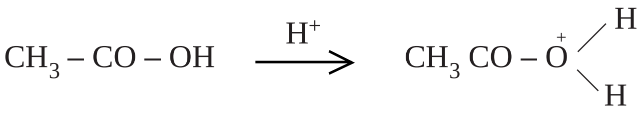
$$CH_3COOH + C_2H_5OH \xrightarrow{H^+} \underset{\text{(ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

$$HCOOH + CH_3OH \xrightarrow{H^+} \underset{\text{(methyl formate)}}{HCOOCH_3} + H_2O$$

Mechanism of esterification

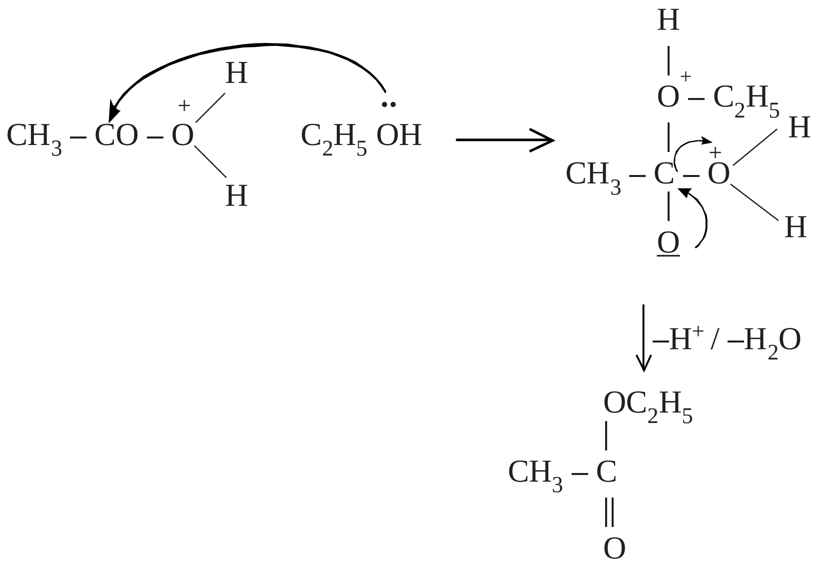
Protonation of the –OH group of the acid, enhances the nucleophilic attack by alcohol to give the ester.

Step 1. Protonation of carboxylic acid



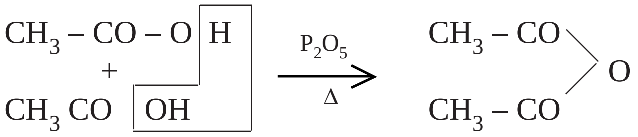
$$CH_3 - CO - OH \xrightarrow{H^+} CH_3\,CO - \overset{+}{O}\begin{smallmatrix} \diagup H \\ \diagdown H \end{smallmatrix}$$

Step 2. Attack by nucleophile.

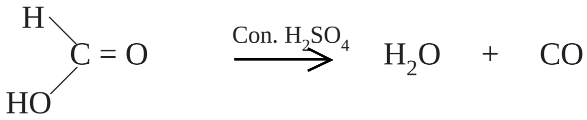


4. Dehydration

Except formic acid others undergo intermolecular dehydration on heating with P_2O_5 forming anhydride.

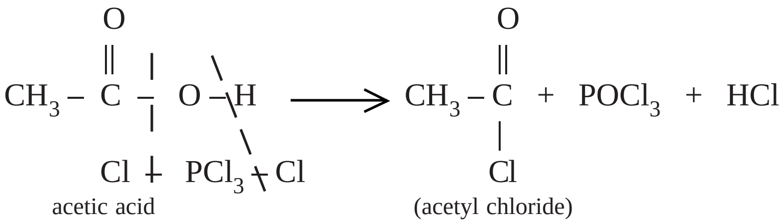


HCOOH on dehydration forms carbon monoxide.



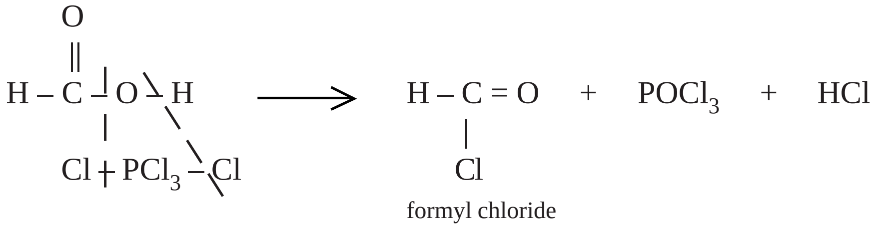
5. With phosphorous pentachloride or thionyl chloride.

(i) Acid chloride is formed.

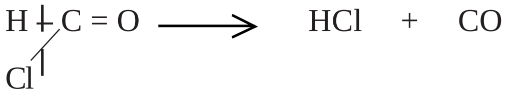


(ii) Formic acid forms formyl chloride.

Formyl chloride being unstable decomposes to carbon monoxide and hydrogen chloride.

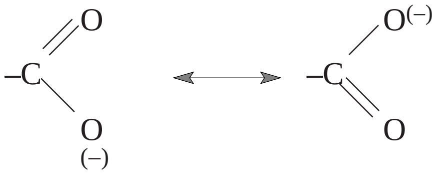


$$H-\overset{\overset{O}{\|}}{\underset{\underset{Cl-PCl_3-Cl}{|}}{C}}-O-H \longrightarrow H-\underset{\underset{Cl}{|}}{C}=O + POCl_3 + HCl$$



$$H-\underset{\underset{Cl}{|}}{C}=O \longrightarrow HCl + CO$$

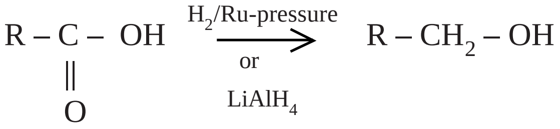
The carboxyl group is involved in resonance.



Hence reactions characteristic of $>$**C=O is almost absent with acids.** They do not form addition product with HCN, N_2H_4 etc.

6. Reduction

(i) Carboxylic acid group is not reduced easily. But it is reduced to primary alcoholic group by $LiAlH_4$ or H_2/Ru under pressure. This reaction works under higher pressure.



$$R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{or } LiAlH_4]{H_2/\text{Ru-pressure}} R-CH_2-OH$$

(ii) Heating with HI/P converts the carboxylic acid to alkane.

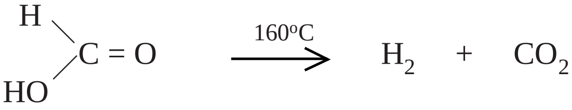
$$CH_3COOH \xrightarrow[\Delta]{HI/P} CH_3-CH_3$$

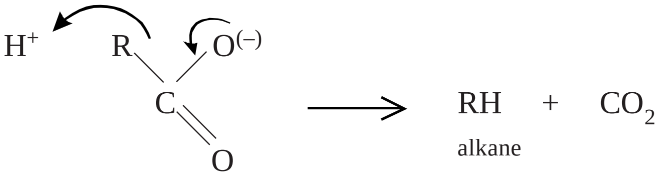
7. **Decarboxylation :** When anhydrous sodium salt of carboxylic acids are heated with sodalime, carboxyl group is removed with the formation of hydrocarbon containing one carbon atom less.

$$\mathrm{RCOONa} \xrightarrow[\Delta]{\mathrm{NaOH/CaO}} \underset{\text{(Hydrocarbon)}}{\mathrm{RH}} + \mathrm{Na_2CO_3}$$

$$\underset{\text{sodium acetate}}{\mathrm{CH_3COONa}} \xrightarrow{\mathrm{NaOH/CaO}} \underset{\text{methane}}{\mathrm{CH_4}} + \mathrm{Na_2CO_3}$$

Formic acid gets decarboxylated on heating.





Carboxylate anion

8. Halogenation :

(i) Fatty acids having α-hydrogen atoms, can be **converted** to **α-halo acids** by halogen in presence of **halogen carrier** like red phosphorous.

$$\underset{\text{propionic acid}}{\mathrm{CH_3CH_2COOH}} \xrightarrow{\mathrm{Br_2/P}} \underset{\alpha\text{-bromo propionic acid}}{\mathrm{CH_3CHBr\ COOH}} \longrightarrow \underset{\alpha,\ \alpha,\ \text{di bromopropionic acid}}{\mathrm{CH_3CBr_2COOH}}$$

(ii) **HVZ - reaction :** When the halogenation is carried out with halogen and phosphorous trihalide, this reaction is known as **Hell-Volhard Zelinsky** reaction. (HVZ-reaction).

$$\mathrm{RCH_2COOH} \xrightarrow{\mathrm{Br_2/PBr_3}} \mathrm{RCH_2COBr} \longrightarrow \mathrm{RCHBrCOBr} \xrightarrow{\mathrm{H_2O}} \mathrm{RCHBrCOOH}$$

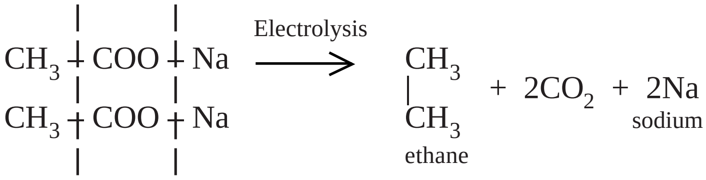
9. **Reactions with ammonia :** Carboxylic acid reacts with NH_3 to form

ammonium salt which on heating undergoes dehydration to amides, ultimately alkyl cyanide results.

$$RCOOH + NH_3 \longrightarrow \underset{\text{(Ammonium Salt)}}{RCOONH_4} \xrightarrow[\Delta]{-H_2O} \underset{\text{(Amide)}}{RCONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{(Cyanide)}}{RCN}$$

$$HCOOH + NH_3 \longrightarrow \underset{\text{(Ammonium formate)}}{HCOONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{(Formamide)}}{HCONH_2}$$

10. **Kolbe's electrolytic reaction :** Electrolysis of concentrated aqueous solution of sodium salt of acids gives hydrocarbon.

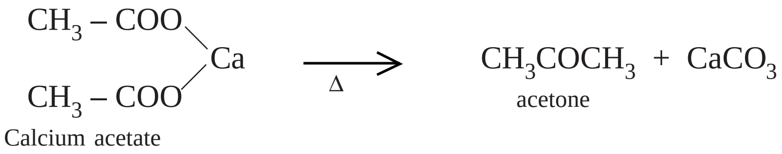


$$\begin{matrix} CH_3 - COONa \\ CH_3 - COONa \end{matrix} \xrightarrow{\text{Electrolysis}} \underset{\text{ethane}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}} + 2CO_2 + \underset{\text{sodium}}{2Na}$$

Under this condition Formic acid gives hydrogen.

11. Dry distillation of calcium salt of fatty acids.

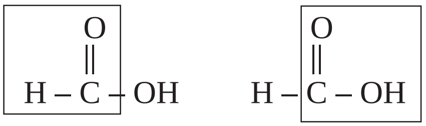
Calcium acetate on dry distillation gives acetone.



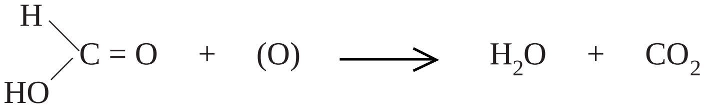
$$\underset{\text{Calcium acetate}}{(CH_3-COO)_2Ca} \xrightarrow[\Delta]{} \underset{\text{acetone}}{CH_3COCH_3} + CaCO_3$$

12. Reducing property

Formic acid is unique because it contains both an aldehyde group and carboxyl group also. Hence it **can act as a reducing** agent. It reduces Fehling's solution, Tollens reagent and decolourises pink coloured $KMnO_4$ solution.



In all cases formic acid is oxidised to CO_2 and water.



$$HCOOH + (O) \longrightarrow H_2O + CO_2$$

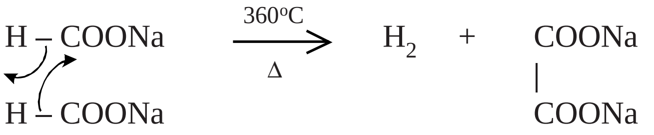
(a) Formic acid reduces ammoniacal silver nitrate solution (Tollen's reagent) to metallic silver.

$$HCOOH + Ag_2O \longrightarrow H_2O + CO_2 + 2Ag\downarrow \text{ (metallic silver)}$$

(b) Formic acid reduces Fehling's solution. It reduces blue coloured cupric ions to red coloured cuprous ions.

$$HCOO^- + \underset{\text{(blue)}}{2Cu^{2+}} + 5OH^- \longrightarrow CO_3^{2-} + \underset{\text{(red)}}{Cu_2O} + 3H_2O$$

(c) On the otherhand when sodium formate is heated to 360°C it decomposes to hydrogen and sodium oxalate.



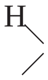
$$\begin{matrix} H-COONa \\ H-COONa \end{matrix} \xrightarrow[\Delta]{360^oC} H_2 + \begin{matrix} COONa \\ | \\ COONa \end{matrix}$$

Sodium formate Sodium oxalate

Problems for Practice

Formic acid gives a red precipitate when heated with Fehling solution but acetic acid does not - reason out.

Answer.

Formic acid has  C = O group an aldehyde group but **acetic acid has no aldehydic group.** Hence formic acid reduces - Fehling's solution.

19.2.2 Uses of formic acid

(a) In Textile Industry for preparing **"mordants".**

(b) In leather tanning for removing lime from the hides.

(c) In coagulating rubber latex.

(d) Nickel formate as hydrogenation catalyst.

(e) As a stimulant for the growth of yeast.

(f) As an antiseptic and in preservation of fruits.

(g) In the treatment of gout.

19.2.3 Tests for carboxylic acid

1. Aqueous solution of carboxylic acids turn blue litmus into red colour.
2. Carboxylic acids give **brisk effervescence** with sodium bi-carbonate due to the evolution of carbon-di-oxide.
3. On warming carboxylic acids with alcohol and concentrated sulphuric acid it forms ester which is identified from its **fruity odour.**

19.3 Monohydroxy carboxylic acids

$CH_3CH(OH)\ COOH$ α-hydroxy propionic acid (or) lactic acid	$CH_2(OH)CH_2COOH$ β-hydroxy propionic acid

19.3.1 Lactic acid

Lactic acid is the main constituent of milk that has gone sour.

Natural Source : Pyruvic acid is the precursor in organism. It is also present in gastric juice, cucumbers, or opium.

19.3.2 Manufacture

Industrially it is made by the Fermentation of solution of cane sugar (or) glucose.

(a) To a dilute solution of cane sugar (or) glucose (or) maltose a little of sour milk (or) decayed cheese is added. Temperature is maintained at 40 – 45^o C for six days. The **Bacillus acidi lacti** brings forth fermentation. Methyl glyoxal forms as intermediate compound. Acid is removed by the addition of $CaCO_3$ which precipitates calcium lactate. It is filtered and decomposed with dilute sulphuric acid. The filterate is distilled under reduced pressure.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{BAL} \underset{\text{Methyl glyoxal}}{2CH_3COCHO} \longrightarrow \underset{\text{Lactic acid}}{2CH_3CHOHCOOH}$$

(b) Synthesis from acetylene

Acetylene is prepared by striking an electric arc using carbon electrodes in an atomsphere of hydrogen. This is passed through dilute sulphuric acid containing mercuric ion catalyst. Acetaldehyde is formed. It is converted to cyanohydrin on treatment with HCN, which is then hydrolysed to get lactic acid.

$$2C + H_2 \xrightarrow[\text{Arc}]{\text{electric}} CH{\equiv}CH \xrightarrow[\substack{\text{1\%Hg} \\ 80}]{\text{dil. } H_2SO_4} CH_3CHO \xrightarrow{\text{HCN}}$$

$$\underset{\text{(acetaldehyde cyano hydrin)}}{CH_3CH(OH)CN} \xrightarrow{\text{dil. HCl}} \underset{\text{lactic acid}}{CH_3CH(OH)COOH}$$

(c) From propene :

Propene is treated with chlorine to get 1,2-dichloropropane. This on treatment with aqueous alkali solution gives propane 1,2-diol. This on oxidation with mild oxidising agent, gives lactic acid.

$$\underset{\text{propylene}}{CH_3CH = CH_2} \xrightarrow{Cl_2} \underset{\text{1,2-dichloro propane}}{CH_3CHCl - CH_2Cl} \xrightarrow{\text{dil/NaOH}} \underset{\text{propane 1,2-diol}}{CH_3CH(OH)CH_2OH}$$

$$\xrightarrow{(O)} \underset{\text{lactic acid}}{CH_3CH(OH)COOH}$$

(d) Hydrolysis of α-bromo propionic acid :

Hydrolysis of α-bromo propionic acid using moist Ag_2O gives lactic acid.

$$\underset{\alpha\text{-bromo propionic acid}}{2CH_3CH(Br)COOH} \xrightarrow[H_2O]{Ag_2O} \underset{\text{lactice acid}}{2CH_3CH(OH)COOH}$$

Properties :

Colourless syrupy liquid, hygroscopic and extremely soluble in water.

Chemical properties :

Reactions characteristic of both –OH and –COOH group.

1. Oxidation :

(i) Mild oxidising agent like Fenton's reagent Fe^{2+}/H_2O_2 forms **pyruvic acid** with lactic acid

$$\underset{\text{Lactic acid}}{CH_3CH(OH)COOH} \xrightarrow[H_2O_2/Fe^{2+}]{(O)} \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

(ii) With dilute acidified permanganate it decomposes forming acetaldehyde.

$$CH_3CH(OH)COOH + (O) \longrightarrow CH_3CHO + H_2O + CO_2$$

2. With dilute H_2SO_4 :

With dil. H_2SO_4 acid it dissociates to acetaldehyde and formic acid.

$$CH_3CH(OH)COOH \xrightarrow{\text{dil. } H_2SO_4} CH_3CHO + HCOOH$$

3. Haloform reaction :

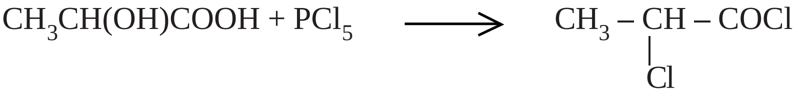
It undergoes **haloform** reaction with I_2 and caustic soda.

$$CH_3CH(OH)COOH \xrightarrow{(O)} \underset{\text{pyruvic acid}}{CH_3COCOOH} \xrightarrow{I_2} \underset{\text{tri iodo pyruvic acid}}{CI_3COCOOH}$$

$$\xrightarrow{NaOH} \underset{\text{iodoform}}{CHI_3} + \underset{\text{sodium oxalate}}{(COONa)_2}$$

4. With PCl_5

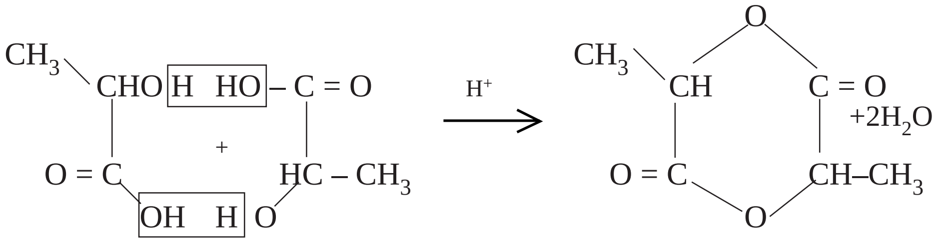
With PCl_5 it forms lactyl chloride.



$$CH_3CH(OH)COOH + PCl_5 \longrightarrow \underset{\text{lactyl chloride}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{C}H}-COCl}$$

5. Formation of cyclic ester :

Formation of cyclic diester - by heating in presence of catalytic amount of con. H_2SO_4.



lactide

Uses of lactic acid :

1. In tanning industry.
2. In soft drinks.
3. In the treatment of digestive disorder in children.
4. Preparation of lactates, ethyl lactate as a solvent.
5. Silver lactate as an antiseptic and astringent.

19.4 Dicarboxylic acids

They contain two carboxyl groups, one at each end of a saturated hydrocarbon chain. Their general formula is

$HOOC - (CH_2)_n - COOH$ where n = 0, 1, 2, 3, etc.

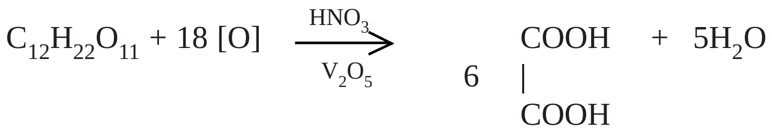
Dicarboxylic acids are named as Alkane dioic acid in IUPAC system. Most simple dicarboxylic acids have common names.

Formula	Common name	IUPAC name
$HOOC - COOH$	Oxalic acid	Ethane dioic acid
$HOOC - CH_2 - COOH$	Malonic acid	Propane dioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butane dioic acid
$HOOC\ (CH_2)_4\ COOH$	Adipic acid	Hexane dioic acid

19.4.1 Methods of preparation

Oxalic acid : ethane dioic acid, $HOOC - COOH$

1. **Laboratory method.** Oxalic acid is made by oxidation of sucrose or molasses with concentrated nitric acid in the presence of vanadium pentoxide as catalyst.



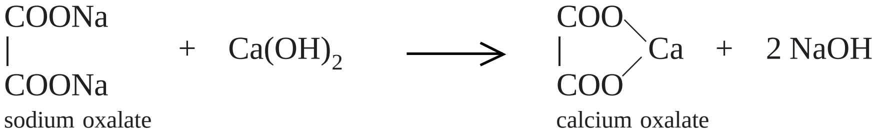
$$C_{12}H_{22}O_{11} + 18\,[O] \xrightarrow[V_2O_5]{HNO_3} 6\begin{array}{l}COOH\\ |\\ COOH\end{array} + 5H_2O$$

The –CHOH–CHOH - units present in sucrose molecule are split and oxidised to oxalic acid.

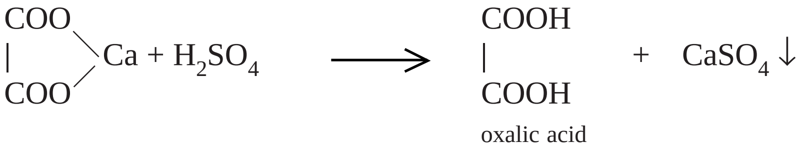
2. **Manufacture :** Oxalic acid is made industrially by heating sodium formate to 673 K.

$$\underset{\text{sodium formate}}{2HCOONa} \xrightarrow{673\ K} \underset{\text{sodium oxalate}}{NaOOC-COONa} + H_2$$

The sodium oxalate thus formed is dissolved in water and calcium hydroxide added to precipitate calcium oxalate. The solution is filtered and the precipitate is treated with calculated quantity of dilute sulphuric acid to liberate the oxalic acid.



$$\underset{\text{sodium oxalate}}{\begin{array}{l}COONa\\|\\COONa\end{array}} + Ca(OH)_2 \longrightarrow \underset{\text{calcium oxalate}}{\begin{array}{l}COO\\|\\COO\end{array}\!\!>Ca} + 2\,NaOH$$

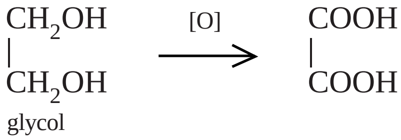


$$\begin{array}{l}COO\\|\\COO\end{array}\!\!>Ca + H_2SO_4 \longrightarrow \underset{\text{oxalic acid}}{\begin{array}{l}COOH\\|\\COOH\end{array}} + CaSO_4\downarrow$$

Calcium sulphate precipitates and oxalic acid is crystallised as the hydrate $(COOH)_2.2H_2O$.

3. From glycol :

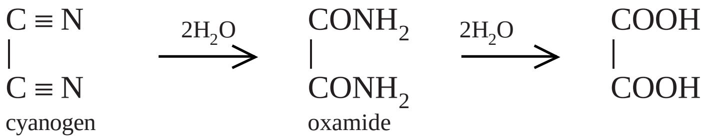
It is prepared by oxidising glycol with con.HNO_3.



$$\underset{\text{glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}} \xrightarrow{[O]} \begin{array}{l}COOH\\|\\COOH\end{array}$$

4. From Cyanogen :

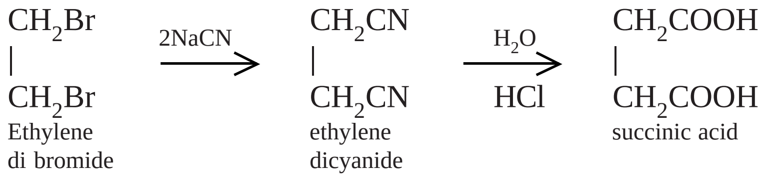
By passing **cyanogen** through an aqueous solution of acid or alkali.



$$\underset{\text{cyanogen}}{\begin{array}{l}C\equiv N\\|\\C\equiv N\end{array}} \xrightarrow{2H_2O} \underset{\text{oxamide}}{\begin{array}{l}CONH_2\\|\\CONH_2\end{array}} \xrightarrow{2H_2O} \begin{array}{l}COOH\\|\\COOH\end{array}$$

Succinic acid, Butanedioic acid $HOOC–CH_2–CH_2–COOH$

Preparation : Succinic acid is prepared from ethylene dibromide by treating with sodium cyanide and subsequent hydrolysis of ethylene dicyanide.



$$\underset{\substack{\text{Ethylene}\\ \text{di bromide}}}{\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}} \xrightarrow{2NaCN} \underset{\substack{\text{ethylene}\\ \text{dicyanide}}}{\begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array}} \xrightarrow[HCl]{H_2O} \underset{\text{succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}}$$

19.4.2 Properties

Oxalic acid occurs as potassium hydrogen oxalate in the wood sorrel, and tomatoes. The insoluble calcium oxalate is found in some stony deposits in kidneys and bladder in human body. Oxalic acid is an active poison depressing the central nervous system.

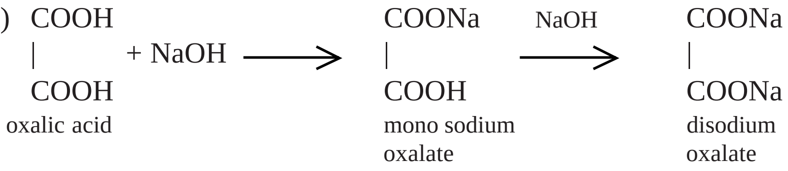
Chemical Properties

Dicarboxylic acid gives all the usual reactions of COOH group twice.

1. **With alkali :** With NaOH it gives two kinds of salts.

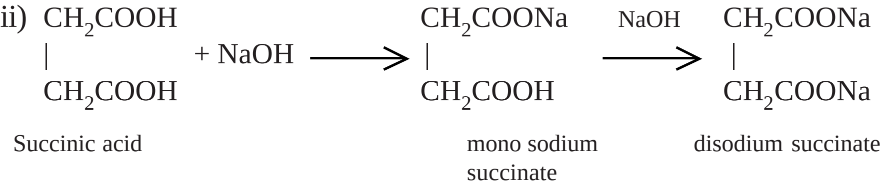
(e.g.,)

(i)



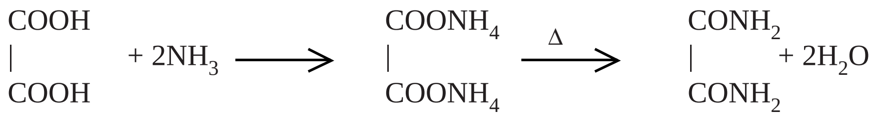
$$\underset{\text{oxalic acid}}{\begin{array}{l}COOH\\ |\\ COOH\end{array}} + NaOH \longrightarrow \underset{\substack{\text{mono sodium}\\ \text{oxalate}}}{\begin{array}{l}COONa\\ |\\ COOH\end{array}} \xrightarrow{NaOH} \underset{\substack{\text{disodium}\\ \text{oxalate}}}{\begin{array}{l}COONa\\ |\\ COONa\end{array}}$$

(ii)



$$\underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}} + NaOH \longrightarrow \underset{\substack{\text{mono sodium}\\ \text{succinate}}}{\begin{array}{l}CH_2COONa\\ |\\ CH_2COOH\end{array}} \xrightarrow{NaOH} \underset{\text{disodium succinate}}{\begin{array}{l}CH_2COONa\\ |\\ CH_2COONa\end{array}}$$

2. **With ammonia :** Dicarboxylic acid gives ammonium salts first which then loses water molecule to give amide.

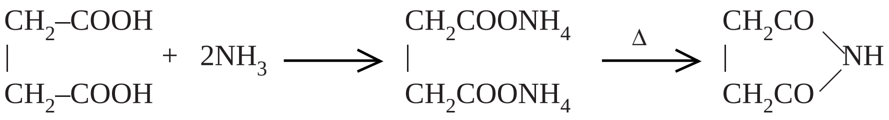


$$\begin{array}{l}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} + 2\mathrm{NH_3} \longrightarrow \begin{array}{l}\mathrm{COONH_4}\\|\\\mathrm{COONH_4}\end{array} \xrightarrow{\Delta} \begin{array}{l}\mathrm{CONH_2}\\|\\\mathrm{CONH_2}\end{array} + 2\mathrm{H_2O}$$

ammonium oxalate

oxamide

Succinic acid forms its ammonium salt. On strong heating it forms succinimide.



$$\begin{array}{l}\mathrm{CH_2{-}COOH}\\|\\\mathrm{CH_2{-}COOH}\end{array} + 2\mathrm{NH_3} \longrightarrow \begin{array}{l}\mathrm{CH_2COONH_4}\\|\\\mathrm{CH_2COONH_4}\end{array} \xrightarrow{\Delta} \begin{array}{l}\mathrm{CH_2CO}\\|\\\mathrm{CH_2CO}\end{array}\!\!\!\!\!>\mathrm{NH}$$

Succinic acid

Ammonium succinate

Succinimide

3. With PCl_5 :

With PCl_5, these form the acid chlorides.

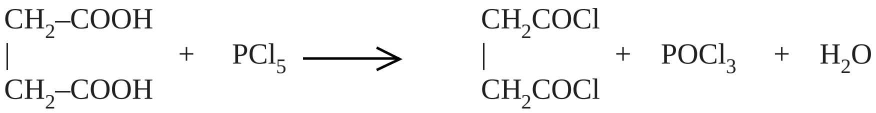
(i) 

$$\begin{array}{l}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} + \mathrm{PCl_5} \longrightarrow \begin{array}{l}\mathrm{COCl}\\|\\\mathrm{COCl}\end{array} + \mathrm{POCl_3} + \mathrm{H_2O}$$

oxalic acid

oxalylchloride

phosphorous oxy chloride

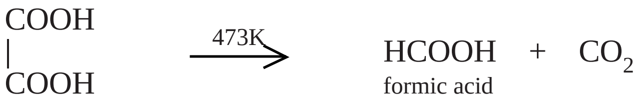


$$\begin{array}{l}\mathrm{CH_2{-}COOH}\\|\\\mathrm{CH_2{-}COOH}\end{array} + \mathrm{PCl_5} \longrightarrow \begin{array}{l}\mathrm{CH_2COCl}\\|\\\mathrm{CH_2COCl}\end{array} + \mathrm{POCl_3} + \mathrm{H_2O}$$

succinoyl chloride

4. Action of heat :

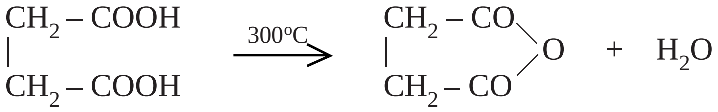
(i) Oxalic acid on heating at 373 K – 378 K loses water of hydration. On further heating it decomposes to formic acid and carbon dioxide.



$$\begin{array}{l}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} \xrightarrow{473\mathrm{K}} \mathrm{HCOOH} + \mathrm{CO_2}$$

formic acid

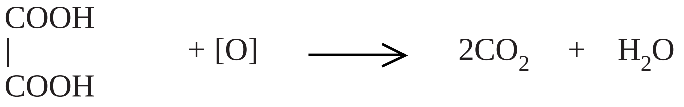
(ii) Succinic acid on heating to 300ºC loses a molecule of water to form anhydride.



$$\begin{array}{l}\mathrm{CH_2-COOH}\\|\\\mathrm{CH_2-COOH}\end{array} \xrightarrow{300^{\circ}\mathrm{C}} \begin{array}{l}\mathrm{CH_2-CO}\\|\\\mathrm{CH_2-CO}\end{array}\!\!\!\!\!>\mathrm{O} + \mathrm{H_2O}$$

succinic anhydride (a cyclic compound)

5. **Oxidation :** On warming oxalic acid with acidified potassium permanganate, it is oxidised to carbon dioxide.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + [O] \longrightarrow 2CO_2 + H_2O$$

Uses :

Oxalic acid is used

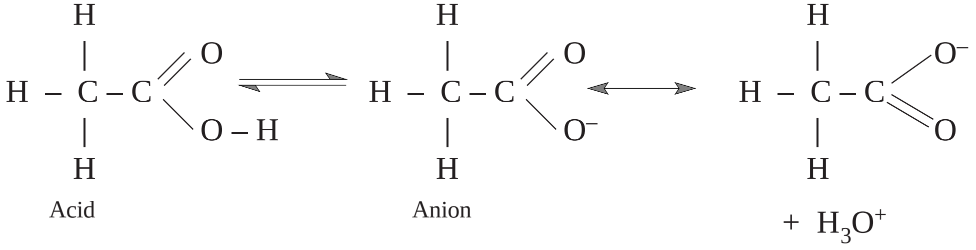
1. for removing ink stains and iron stains.
2. as mordant in dyeing and calico printing.
3. in manufacture of ink and metal polishes.
4. Redox titration

Succinic acid is used :

1. in the manufacture of lacquers and dyes.
2. It is a very important laboratory reagent.

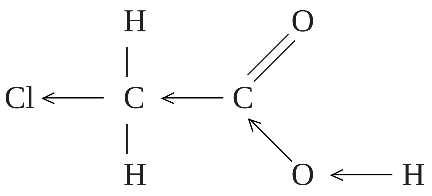
19.5 STRENGTH OF CARBOXYLIC ACIDS

An acid is a proton donor. The base with which a proton can be released determines the strength of an acid. Organic acids are weak acids. **Greater the stability of the anion of the acid, higher is its strength.** Thus, for a carboxylic acid, say acetic acid.

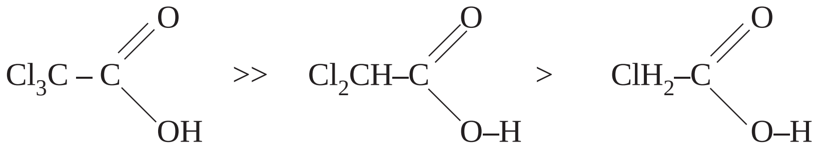


When the bonding pair of electrons between oxygen and hydrogen in –O–H group, is shifted towards oxygen, easier the hydrogen is released as a proton.

Thus when chloroacetic acid is taken, the (–I) effect of chlorine increases its strength.



Thus the strength of the chloro acetic acids varies.



Trichloro acetic acid

Dichloro acetic acid

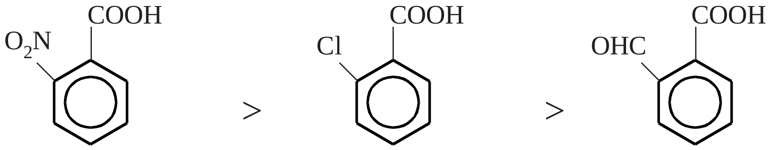
Monochloro acetic acid

On the other hand comparing the strength of carboxylic acids they vary as follows :

$$\underset{\text{propionic acid}}{CH_3CH_2\,COOH} < \underset{\text{acetic acid}}{CH_3COOH} < \underset{\text{formic acid}}{HCOOH}$$

Since alkyl groups are +I groups, they increase the strength of the –O–H bond making the release of hydrogen difficult. (i.e.,) **it becomes a weak acid.**

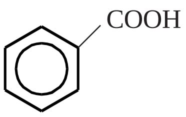
In the case of aromatic acids, presence of chlorine, nitro group, carbonyl group especially at ortho position increases its strength due to –I effect.



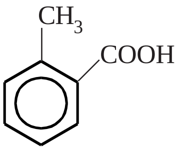
Presence of –OH, Cl^- at para positions **decreases** the strength by resonance effect. (+M effect).

19.6 AROMATIC ACIDS :

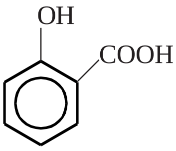
When a carboxylic acid group is **directly linked** to the benzene ring they are called aromatic carboxylic acids.



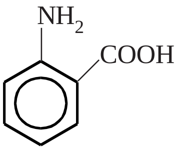
Benzoic acid



o-toluic acid



salicylic acid (o-hydroxy benzoic acid)



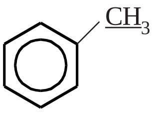
anthranilic acid (o-amino benzoic acid)

Benzoic acid is the simplest of aromatic acids.

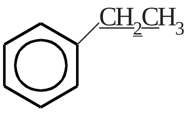
19.6.1 Preparation

By oxidation

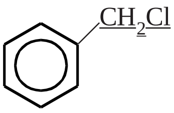
By the oxidation of **'side chain'** of benzene derivatives (side chain - any aliphatic portion linked to benzene ring) The **side chain** oxidation can be carried out by acid dichromate or permanganate or alkaline permanganate etc.



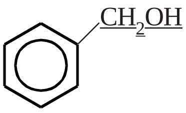
Toluene



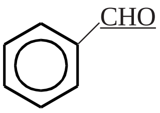
Ethyl benzene



Benzyl chloride



Benzyl alcohol



Benzaldehyde

The underlined portion indicates the side chain.

Toluene is oxidised by acidified $KMnO_4$.

(i) $C_6H_5CH_3 \xrightarrow{H^+/KMnO_4} C_6H_5COOH$ Benzoic acid

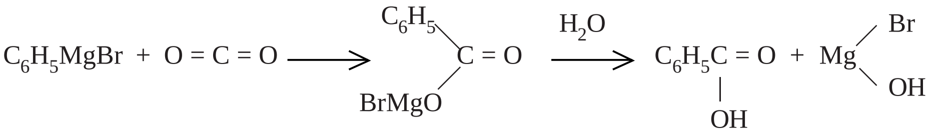
(ii) $C_6H_5CH_2Cl \xrightarrow{NaOH} C_6H_5CH_2OH \xrightarrow[KMnO4]{(O)} C_6H_5COOH$

(iii) $C_6H_5CHO \xrightarrow{H^+/KMnO_4} C_6H_5COOH$

2. Hydrolysis of phenyl cyanide :

$$C_6H_5CN \xrightarrow[H_2O]{H^+} \underset{\text{Benzamide}}{(C_6H_5CONH_2)} \xrightarrow[H_2O]{H^+} C_6H_5COOH$$

3. Carbonation of Grignard reagent followed by hydrolysis.



19.6.2 Properties

Physical properties

White crystalline solid-soluble in hot water, alcohol and ether and slightly soluble in cold water.

Chemical Properties

Reactions of both –COOH group and benzene ring.

1. Acidic properties :

(a) Benzoic acid dissolves in NaOH and NH_4OH forming salts.

$$C_6H_5COOH + NaOH \longrightarrow \underset{\text{(sodium benzoate)}}{C_6H_5COONa} + H_2O$$

$$C_6H_5COOH + NH_4OH \longrightarrow \underset{\text{(Ammonium benzoate)}}{C_6H_5COONH_4} \xrightarrow[\Delta]{-H_2O} C_6H_5CONH_2$$

(b) It forms esters with alcohol in presence of catalytic amount of Con. H_2SO_4.

$$C_6H_5COOH + C_2H_5OH \xrightarrow{H^+} \underset{\text{(ethyl benzoate)}}{C_6H_5COOC_2H_5} + H_2O$$

2. Replacement of OH group.

By the action of phosphorous pentachloride or thionyl chloride, benzoyl chloride is formed.

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl$$

$$C_6H_5COOH + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow C_6H_5COCl + SO_2 + HCl$$

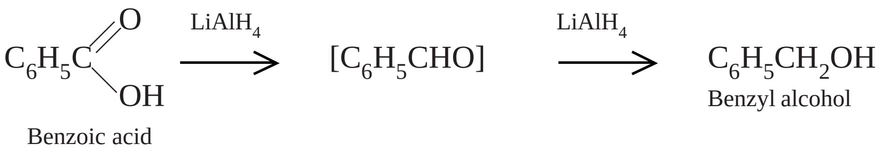
3. Decarboxylation :

Heating with sodalime gives benzene.

$$C_6H_5COOH \xrightarrow[\substack{\text{CaO } \Delta \\ \text{soda lime}}]{\text{NaOH}} C_6H_6 + CO_2$$

4. Reduction :

Lithium Aluminium hydride reduces Benzoic acid to Benzyl alcohol.

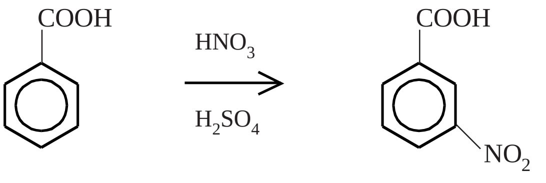


$$\underset{\text{Benzoic acid}}{C_6H_5C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagdown}}} \xrightarrow{LiAlH_4} [C_6H_5CHO] \xrightarrow{LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

5. Reaction of benzene ring :

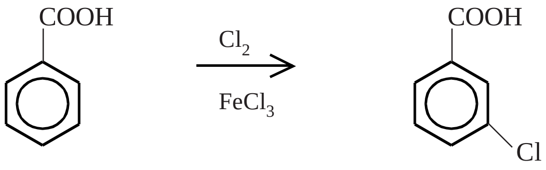
Benzoic acid undergoes electrophilic substitution. The –COOH group decreases the activity of benzene ring with respect to electrophilic substitution and is **meta directing** group.

Nitration :



m-nitro benzoic acid

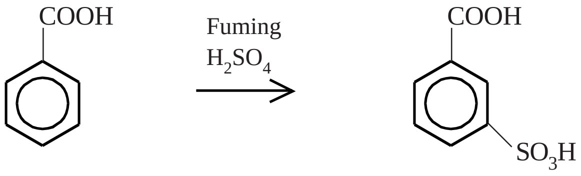
6. Chlorination :



m-chloro benzoic acid

Anhydrous ferric chloride is a Lewis acid - a catalyst in this reaction.

7.Sulphonation :



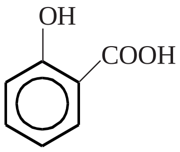
m-sulphonyl benzoic acid

19.6.3 Uses of benzoic acid :

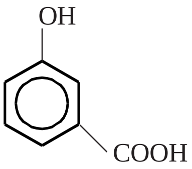
1. Benzoic acid is used as an urinary antiseptic
2. Sodium benzoate is used as food preservative
3. Benzoic acid vapours are used to disinfect bronchial tube.
4. It is used for the manufacture of dyes.

19.7 SALICYLIC ACID

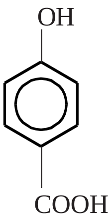
It is o-hydroxy benzoic acid, and isomeric with meta and para hydroxy benzoic acids.



(o-hydroxy benzoic acid)



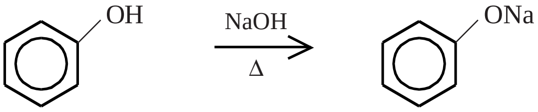
(m-hydroxy benzoic acid)



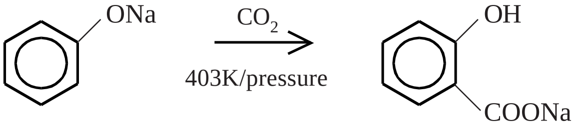
(p-hydroxy benzoic acid)

19.7.1 Preparation :

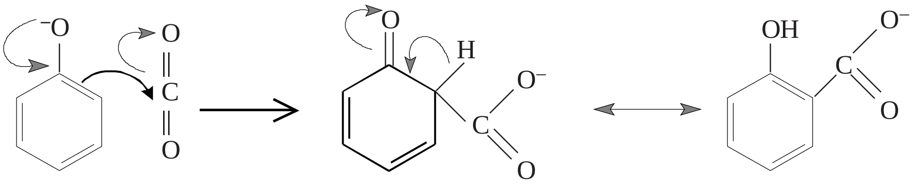
Salicylic acid can be prepared by heating phenol with NaOH to get sodium phenoxide.



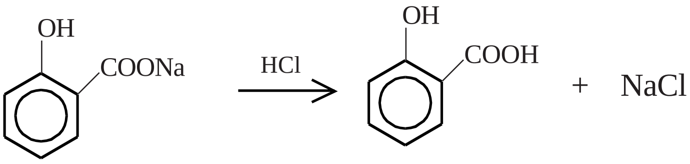
This is heated with carbondioxide at 403K under pressure to form sodium salicylate.



Mechanism :



This reaction is called **'Kolbe's reaction'**. The sodium salt on treatment with dilute hydrochloric acid gives salicylic acid.



(Salicylic acid)

19.7.2 Properties

Physical Properties

It is a white crystalline solid - soluble in hot water, ethanol and ether.

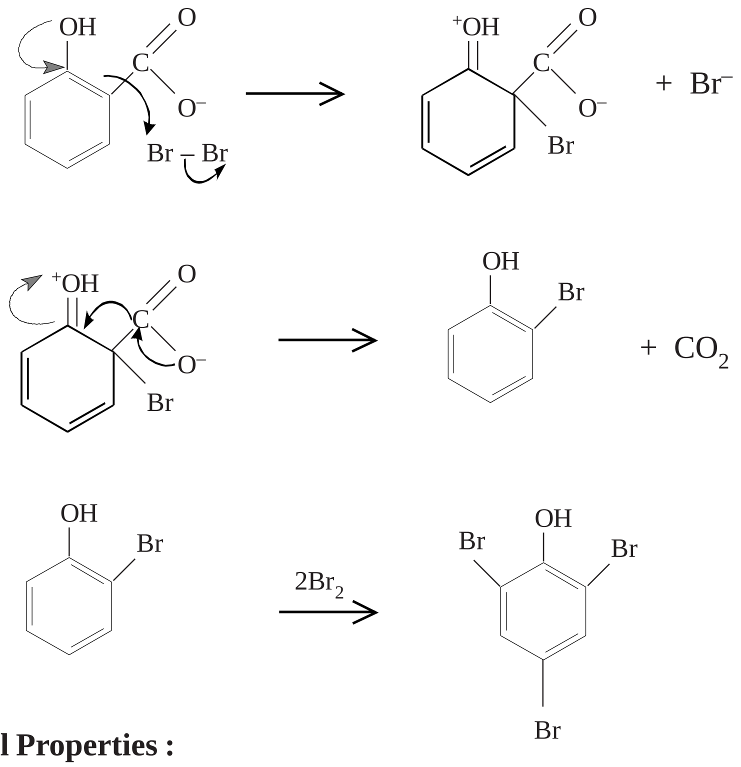
Test for salicylic acid :

1. An aqueous solution of salicylic acid gives violet colour with neutral ferric chloride.
2. It gives effervescence with the sodium bicarbonate.
3. It is soluble in sodium hydroxide and reprecipitated on acidification.

4. With Bromine water the colour is discharged with the formation of white precipitate.

Mechanism :

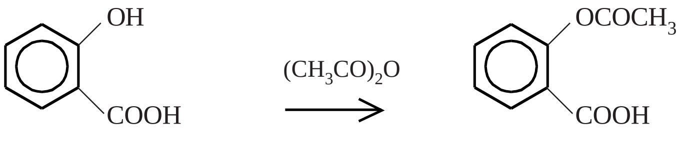
Reaction of bromine with salicylic acid.



Chemical Properties :

Properties of phenolic function.

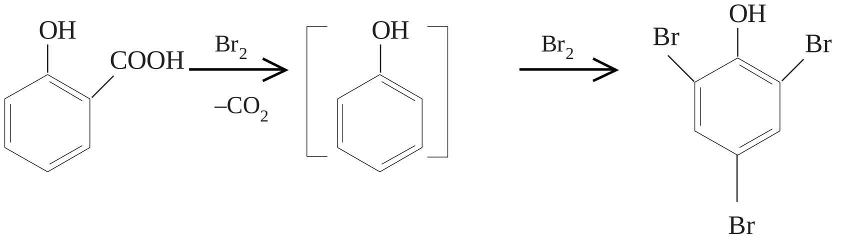
1. Salicylic acid undergoes acetylation by heating with acetic anhydride to form aspirin which is used as an analgesic and antipyretic.



Acetyl salicylic acid or Aspirin

Instead of acetic anhydride, acetyl chloride can also be used.

2. Reaction with bromine water gives a white precipitate of tribromo phenol. This reaction involves bromination with decarboxylation.

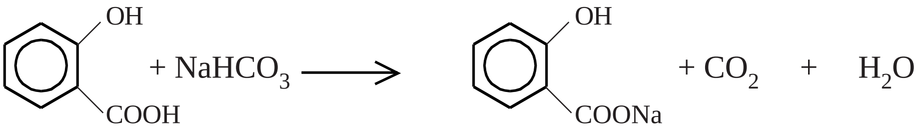


(2,4,6 Tribromo phenol)

Reaction due to –COOH group.

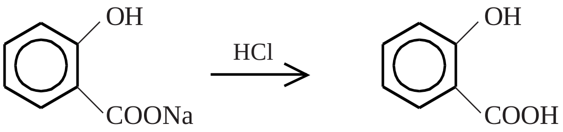
1. With $NaHCO_3$

It gives brisk effervescence with a solution of sodium bicarbonate or sodium carbonate and dissolves forming sodium salicylate.



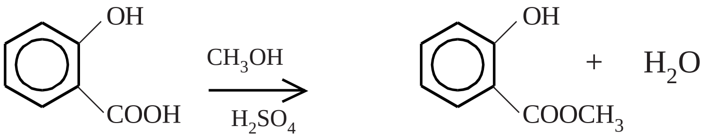
(sodium salicylate)

The solution on treatment with HCl gives salicylic acid.



2. With CH_3OH

On heating with methyl alcohol in presence of con. H_2SO_4 a pleasant smelling liquid-**methyl salicylate is formed.**



(Methyl salicylate)

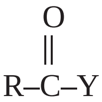
Methyl salicylate is present in the **oil of winter green** and other essential oils.

19.7.3 Uses

Salicylic acid is used (i) It is an antiseptic and disinfectant (ii) as a food preservative (iii) as a medicine for rheumatic pain, (iv) in the manufacture of aspirin, salol, methyl salicylate, (v) in the preparation of azo dyes.

19.8 FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACID :

The general formula is



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Y$$

Y	Functional group	Example	
– OH	Carboxylic acid	CH_3COOH	acetic acid
– halogen	acid halide	CH_3COCl	acetyl chloride
– OCOR	acid anhydride	$CH_3COOCOCH_3$	acetic anhydride
– OR	ester	$CH_3COOC_2H_5$	ethyl acetate
– NH_2	amide	CH_3CONH_2	acetamide

These compounds generally undergo nucleophilic substitution reactions in which a nucleophile replaces the electro negative group (Y) to form carboxyl derivatives. Relative reactivity of carboxylic acid derivatives is as follows.

Acid chloride > acid anhydride > carboxylic acid > ester > amide.

19.8.1 Acetyl chloride : CH_3COCl

Preparation of CH_3COCl

It is prepared easily by the action of PCl_5, PCl_3 or $SOCl_2$ on acetic acid.

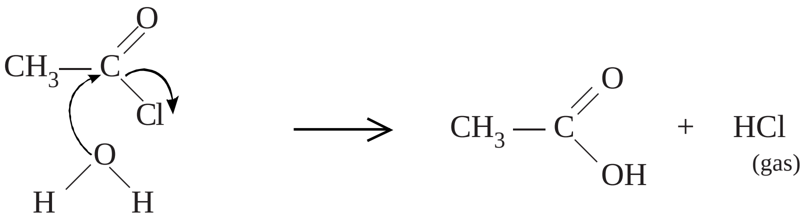
(i) $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

(ii) $3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + \underset{\text{Phosphorus acid}}{H_3PO_3}$

(iii) $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

19.8.2 Physical Properties

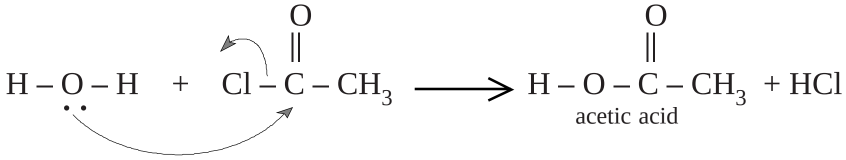
Acetyl chloride is volatile, pungent smelling liquid, this cannot form hydrogen bond. Hence its low boiling point and insolubility in water is explained. It fumes in moist air due to hydrolysis producing hydrogen chloride gas.



Chemical Properties :

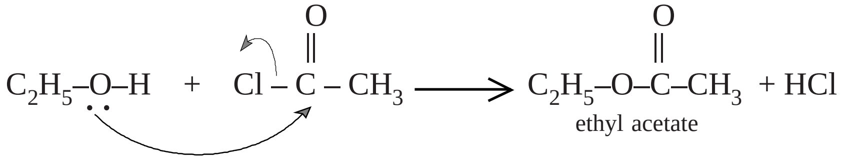
1. It is a powerful acetylating agent, a reagent that introduces CH_3CO - group, especially with compounds containing –OH group or –NH group.

(i)



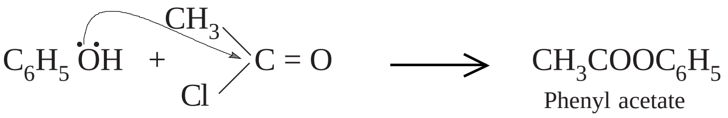
$$\mathrm{H-\ddot{O}-H} \;+\; \mathrm{Cl-\overset{\overset{O}{\|}}{C}-CH_3} \longrightarrow \underset{\text{acetic acid}}{\mathrm{H-O-\overset{\overset{O}{\|}}{C}-CH_3}} + \mathrm{HCl}$$

(ii)



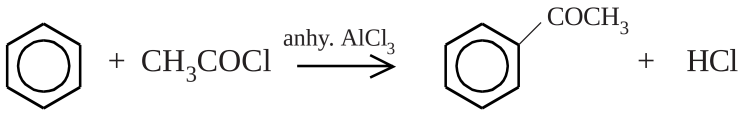
$$\mathrm{C_2H_5{-}\ddot{O}{-}H} \;+\; \mathrm{Cl-\overset{\overset{O}{\|}}{C}-CH_3} \longrightarrow \underset{\text{ethyl acetate}}{\mathrm{C_2H_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3}} + \mathrm{HCl}$$

(iii)



2. Friedel Craft's Acetylation :

In presence of anhydrous Aluminium chloride acetylation of benzene takes place with the formation of acetophenone.



It is an aromatic electrophilic substitution reaction.

The Lewis acid $AlCl_3$ generates the electrophile from acetyl chloride. The electrophile is the acetyl cation $CH_3–C^+ = O$.

19.8.3 Uses of acetylchloride

(a) As an acetylating agent.
(b) An important organic reagent.
(c) In the preparation of acetic anhydride.
(d) In the detection and estimation of alcoholic and amino groups.

19.9 Acetic anhydride : $CH_3COOCOCH_3$

Preparation :

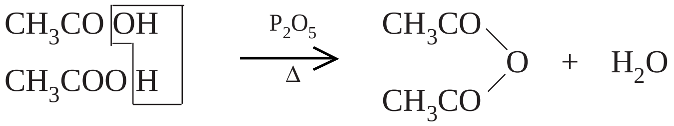
1. From CH_3COCl

By distilling a mixture of anhydrous sodium acetate and acetyl chloride.

$$\underset{\text{(Acetyl chloride)}}{CH_3COCl} + \underset{\text{(Sodium acetate)}}{CH_3COONa} \xrightarrow[\Delta]{} \underset{\text{(Acetic anhydride)}}{CH_3COOCOCH_3} + NaCl$$

2. From acetic acid

By the action of dehydrating agent on acetic acid.



$$\begin{matrix} CH_3CO\,\boxed{OH} \\ CH_3COO\,\boxed{H} \end{matrix} \xrightarrow[\Delta]{P_2O_5} \begin{matrix} CH_3CO \\ \quad\quad O \\ CH_3CO \end{matrix} + H_2O$$

(Acetic anhydride)

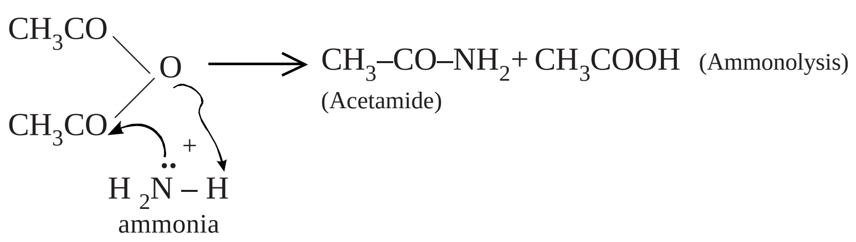
19.9.1 Physical Properties

Acetic anhydride is a colourless, pungent smelling liquid, insoluble in water. It is not as reactive as acetyl chloride and does not fume in moist air.

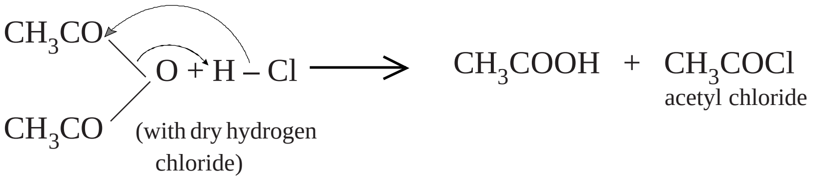
Chemical Properties :

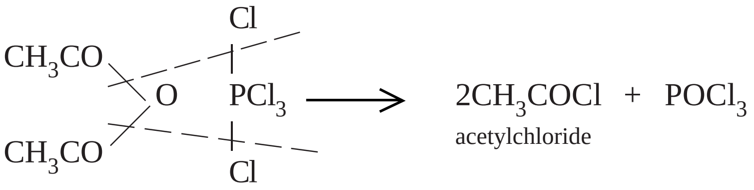
Like acetyl chloride, it reacts with alcohol, phenol and amine, though less reactive, normally acetylation using acetic anhydride is carried out in presence of sodium acetate or concentrated sulphuric acid as catalyst.

1.



2.





19.9.2 Uses of acetic anhydride

1. As an acetylating agent for the manufacture of dyes, cellulose acetate etc.
2. In the manufacture of aspirin and some drugs.

19.10 Methyl acetate

Preparation

1. **By esterification :** When acetic acid is refluxed with methyl alcohol in presence of a small amount of con. H_2SO_4, methyl acetate is formed.

$$CH_3COOH + CH_3OH \xrightarrow{H_2SO_4} \underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O$$

2. By the action of acetyl chloride or acetic anhydride on methyl alcohol, methyl acetate is formed.

$$CH_3COCl + CH_3OH \longrightarrow CH_3COOCH_3 + HCl$$

$$CH_3COOCOCH_3 + CH_3OH \longrightarrow CH_3COOCH_3 + CH_3COOH$$

19.10.1 Physical Properties

It is a pleasant smelling volatile liquid, fairly soluble in water, no hydrogen bonding and less polar than alcohols.

Chemical Properties

1. **Hydrolysis :** Esters are hydrolysed by warming with dil. acids or alkali.

$$CH_3COOCH_3 \xrightarrow{H^+/H_2O} CH_3COOH + CH_3OH$$

$$CH_3COOCH_3 + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + CH_3OH$$

(Saponification)

2. **Alcoholysis :** In presence of a little acid, methyl acetate is cleaved by ethyl alcohol to form ethyl acetate.

$$CH_3COOCH_3 + C_2H_5OH \xrightarrow{H^+} CH_3COOC_2H_5 + CH_3OH$$

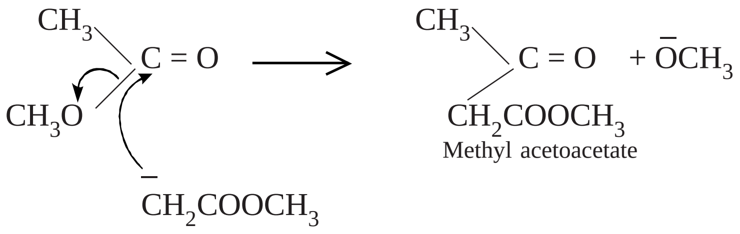
This is called **'trans esterification'.**

3. **Ammonolysis :** Reacts with ammonia on heating to form amide.

$$CH_3COOCH_3 + NH_3 \xrightarrow{\Delta} CH_3CONH_2 + CH_3OH$$

4. **Claisen ester condensation :** In presence of strong bases like sodium ethoxide, it undergoes condensation forming aceto acetic ester.

$$CH_3COOCH_3 \xrightarrow{C_2H_5ONa} \overset{-}{C}H_2COOCH_3 + H^+$$



19.10.2 Uses of methyl acetate

It is a very good laboratory and industrial solvent. Used for the preparation of acetoaceticester a compound of synthetic importance.

19.11 Amides

CH_3CONH_2 Acetamide

Preparation of acetamide

1. By heating ammonium acetate

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

2. Ammonolysis of acetyl chloride, acetic anhydride or esters.

(i) $CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$

(ii) $\underset{\text{Acetic anhydride}}{CH_3COOCOCH_3} + NH_3 \longrightarrow CH_3CONH_2 + CH_3COOH$

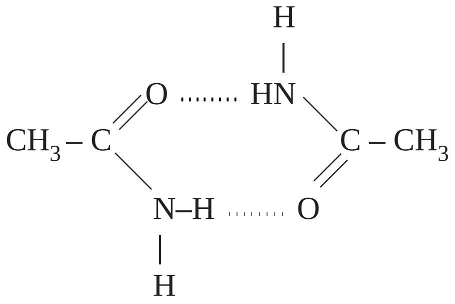
(iii) $\underset{\text{Methyl acetate}}{CH_3COOCH_3} + NH_3 \longrightarrow CH_3CONH_2 + CH_3OH$

3. Partial hydrolysis of methyl cyanide with alkaline hydrogen peroxide.

$$CH_3C{\equiv}N \xrightarrow[NaOH]{H_2O_2} CH_3CONH_2$$

19.11.1 Physical Properties

It exists as a dimer due to hydrogen bonding.



Colourless crystalline solid, soluble in water and alcohol.

It is the least reactive among acid derivative.

19.11.2 Chemical Properties

1. Hydrolysis :

Catalysed by acid or alkali, it is hydrolysed to acid.

(a) $CH_3CONH_2 \xrightarrow[H_2O]{H^+} \underset{\text{(acetic acid)}}{CH_3COOH} + NH_3$

(b) $CH_3CONH_2 \xrightarrow{NaOH} \underset{\text{(Sodium acetate)}}{CH_3COONa} + NH_3$

2. With HCl

It is feebly basic, forms unstable salt with strong inorganic acid.

$$CH_3CONH_2 + HCl \longrightarrow \underset{\text{(amide hydrochloride)}}{CH_3CONH_2 \;.\; HCl}$$

3. **On dehydration** by heating with P_2O_5 it forms methyl cyanide.

$$CH_3CONH_2 \xrightarrow[-\,H_2O]{P_2O_5} CH_3C{\equiv}N$$

4. **It undergoes Hoff mann's reaction** with Br_2/NaOH forming methyl amine.

$$CH_3CONH_2 \xrightarrow[NaOH]{Br_2} CH_3NH_2 + CO_2$$

19.11.3 Uses of acetamide

1. For the preparation of methyl cyanide.
2. In leather tanning.
3. As soldering flux.
4. As a plasticiser in cloth.

SELF EVALUATION

(A) Choose the correct answer :

1. Which of the following is least acidic

(a) C_2H_5OH	(b) CH_3COOH
(c) C_6H_5OH	(d) $ClCH_2COOH$

2. Weakest acid among the following is

(a) Acetic acid	(b) Phenol
(c) Water	(d) Acetylene

3. Ester formation involves the reaction of

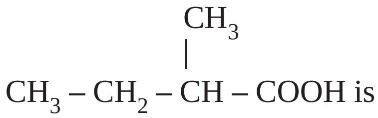
(a) an aldehyde and a ketone
(b) An alcohol with RMgX
(c) Two molecules of an acid with dehydrating agent
(d) An acylhalide with an alcohol

4. Heating a mixture of sodium acetate and soda lime gives

(a) methane	(b) ethane
(c) aceticacid	(d) benzene

5. The acid which reduces Tollen's reagent is

(a) acetic acid	(b) benzoic acid
(c) formicacid	(d) oxalic acid

6. The IUPAC name of  $CH_3-CH_2-\underset{}{\overset{\overset{CH_3}{|}}{CH}}-COOH$ is

(a) α-methyl butric acid	(b) 3-methyl butanoic acid
(c) 2-methyl butanoic acid	(d) Iso pentanoic acid

7. The Isomerism exhibited by CH_3CH_2COOH and CH_3COOCH_3 is

(a) metamerism	(b) position
(c) chain	(d) functional

8. The acid that cannot be prepared by Grignard reagent

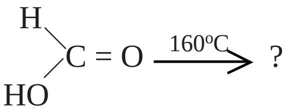
(a) acetic acid	(b) formic acid
(c) butyric acid	(d) benzoic acid

9. Which order of arrangement is correct interms of the strength of the acid

(a) $CH_3–CH_2COOH > CH_3COOH < HCOOH < ClCH_2COOH$
(b) $ClCH_2COOH < HCOOH < CH_3COOH < CH_3CH_2COOH$
(c) $CH_3–CH_2COOH < CH_3COOH < HCOOH < ClCH_2COOH$
(d) $HCOOH > CH_3CH_2COOH < CH_3COOH > ClCH_2COOH$

10. The compound which undergoes intramolecular dehydration with P_2O_5 is

(a) acetic acid	(b) formic acid
(c) propionic acid	(d) Butyric acid

11. 

$H(HO)C = O \xrightarrow{160^oC} ?$ The product is

(a) $CO + H_2O$	(b) $HCOOH$
(c) $H_2 + CO_2$	(d) $HCHO + O_2$

12. When chlorine is passed through acetic acid in presence of red P, it forms.

(a) acetyl chloride	(b) Trichloro acetaldehyde
(c) Trichloro acetic acid	(d) Methyl chloride

13. Which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and CO_2 ?

(a) acetic acid	(b) n-hexanol
(c) phenol	(d) both (a) and (c)

14. When propanoic acid is treated with aqueous sodium - bicarbonatate, CO_2 is liberated. The "C" of CO_2 comes from

(a) methyl group	(b) carboxylic acid group
(c) methylene group	(d) bicarbonate

15. Carboxylic acids are more acidic than phenol and alcohol because of

(a) inter molecular hydrogen bonding
(b) formation of dimers
(c) highly acidic hydrogen
(d) greater resonance stabilisation of their conjugate base

16. Among the following the strongest acid is

(a) $ClCH_2COOH$	(b) Cl_3CCOOH
(c) CH_3COOH	(d) $Cl_2CHCOOH$

17. Which of the following compound is optically active ?

(a) CH_3CH_2COOH (b) $HOOC–CH_2–COOH$

(c) $CH_3CH(OH)COOH$ (d) $Cl_2CHCOOH$

18. $CH_3CH(OH)COOH \xrightarrow[H_2O_2/Fe^{2+}]{}$? The product is

(a) $CH_3COCOOH$ (b) CH_3CH_2COOH

(c) $CH_3CHOHCHO$ (d) $COOHCH_2COOH$

19. The compound found in some stony deposit in kidneys is

(a) potassium oxalate (b) oxalic acid

(c) potassium succinate (d) calcium oxalate

20. Ethylene cyanide on hydrolysis using acid gives

(a) oxalic acid (b) succinic acid

(c) adipic acid (d) propionic acid

(B) Answer in one or two sentences :

1. What are carboxylic acids ?
2. Give the source and trivial names of

   (i) C_3H_7COOH and (ii) $HCOOH$.
3. How is the conversion of acetonitrile to acetic acid effected ?
4. Boling point of carboxylic acids are higher than those of alcohols of same molecular mass - reason out.
5. Formic acid reduces Tollen's reagent, but acetic acid does not-Give reasons.
6. Write two tests of carboxylic acid.
7. Give the resonance structure of carboxylate anion.
8. Mention the inductive effect in monochloro acetic acid.
9. Write a note on esterification reaction with an example.
10. What happens when calcium salt of acetic acid is distilled.
11. Mention the uses of oxalic acid.
12. What is the action of dilute sulphuric acid with lactic acid ?
13. Give the structure of lactyl chloride and lactide.

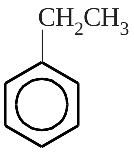
(C) Answer not exceeding sixty words :

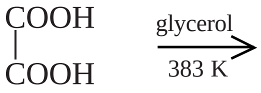
1. How is oxalic acid manufactured from sodium formate ?
2. Explain the isomerism exhibited by carboxylic acids.
3. Write a note on the acidic nature of acetic acid.
4. Give the mechanism involved in the esterification of a carboxylic acid with alcohol.
5. Explain why carboxylic acids behave as acids. Discuss briefly the effect of electron withdrawing and donating substituents on acid strength of carboxylic acids.
6. Account for reducing nature of Formic acid.
7. Explain the following :

   (i) Choloro acetic acid is stronger acid than acetic acid.

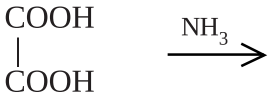
   (ii) Fluoro acetic acid is stronger acid than chloro acetic acid.

   (iii) Formic acid is stronger acid than acetic acid.
8. How is benzoic acid obtained from

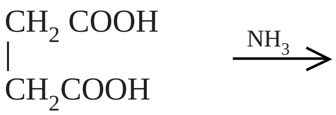
   (a) 
   (b) phenyl cyanide (c) carbon dioxide
9. How do you distinguish formic acid from acetic acid ?
10. Write the products in each of the following.

   (i) 

   $$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow[383\ K]{glycerol}$$

   (ii) 

   $$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow{NH_3}$$

   (iii) 

   $$\begin{array}{l}CH_2\ COOH\\ |\\ CH_2COOH\end{array} \xrightarrow{NH_3}$$

11. How are the follwing conversions carried out ?

(i) Salicylic acid $\longrightarrow$ aspirin

(ii) Salicylic acid $\longrightarrow$ methyl salicylate

(iii) Lactic acid $\longrightarrow$ lactide

12. What happens when lactic acid is

(i) treated with dilute H_2SO_4

(ii) heated alone

(iii) oxidised with alkaline $KMnO_4$

13. Give the uses of (a) oxalic acid and (b) salicylic acid.

14. Outline the mechanism of (a) formation of ethylacetate from acetic acid and ethyl alcohol. (b) Hydrolysis of ethyl cyanide to propionic acid.

15. Explain the order of strength of the following acids.

(a) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(b) p-nitrophenol > m-nitro phenol > phenol > cresol.

SUMMARY :

Aliphatic mono carboxylic acids, hydroxy acids, dicarboxylic acid, aromatic monocarboxylicacid, aromatic hydroxy acid, aromatic dicarboxylic acid - structure and nomenclature - common name and IUPAC names - long chain fatty acid - by the saponification of fats and oils.

General methods of preparation - Oxidation of alcohols aldehydes, hydrolysis of cyanides, esters and using Grignard's reagent.

Properties - Hydrogen bonding - dimeric - higher boiling points - solubility in water.

Acidic property explained by resonance stabilisation of the carboxylate anion - Formation of salt, esters and amide. Esterification, anhydride formation, decarboxylation - α-halogenation - formation of acid chloride.

Formic acid, differ from other carboxylic acid because of the presence of aldyhydic (H – C = O) group. Hence it reduces Fehling's solution, Tollens reagent and alkaline permanganate.

Aromatic acids - Benzoic acid, salicylic acid, phthalicacid - preparation - by oxidation, hydrolysis, Grignard reagent and Kolbe's synthesis. Properties - Formation of salt, esters, acid chlorides, amides and electro philic substitution at benzene ring and uses.

Derivatives of acids - like esters, acid chloride, acid anhydride, amide - structure and nomonclature -preparation and properties - relative reaction - hydrolysis to acids - reduction - uses.

REFERENCES :

1. Text Book of Organic Chemistry - Bahl and Arun Bahl.
2. A guide book to Mechanism in organic chemistry. - Peters Sykes - Pearson Education Ltd.

20. ORGANIC NITROGEN COMPOUNDS

LEARNING OBJECTIVES

- *Nitro alkanes - Structure, isomerism, tautomerism - Nomenclature - primary, secondary and tertiary nitro compounds.*
- *Learning - the methods of preparation, properties, uses of nitroalkanes.*
- *Recognising the presence of α-hydrogen - removed by base to generate carbanion.*
- *Aromatic nitro compounds - structure and nomenclature, preparation - Nitration of benzene - mechanism - properties - reduction under different conditions - Distinction between aromatic and aliphatic nitro compounds.*
- *Aliphatic amines - structure, classification, isomerism, nomenclature - primary, secondary and tertiary amines.*
- *Learning general methods of preparation, properties - Distinction between 1^o, 2^o, 3^o - amines.*
- *Aromatic amines - aralkyl amine - preparation, properties of benzylamine.*
- *Aniline - preparation, properties, - basic strength and resonance - uses.*
- *Distinction between aliphatic amine and aniline, - ethylamine and aniline, benzyl amine and aniline.*
- *Aliphatic nitriles - structure - nomenclature.*
- *Benzene diazonium chloride - preparation - properties related to its synthetic importance.*

20.1 ORGANIC NITROGEN COMPOUNDS

Aliphatic Nitro Compounds

Nitro alkanes are nitro derivatives of paraffins obtained by the replacement of a hydrogen atom by a nitro group.

Nomenclature : $R\text{–}NO_2$

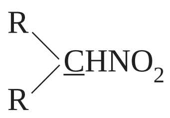
Nitro alkanes are named by prefixing 'nitro' to the name of parent hydrocarbon.

$C_2H_5NO_2$ Nitro ethane $\quad$ $C_3H_7NO_2$ Nitro propane

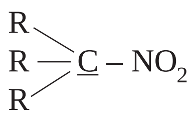
They may be primary, secondary and tertiary depending on whether the nitrogroup is attached to a **primary, secondary** and **tertiary carbon** atom.

$R\underline{C}H_2NO_2$

1°

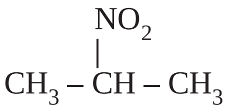


2°



3°

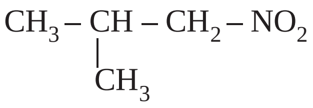
In the IUPAC system the position of the nitrogroup is indicated by number.



$$CH_3-\overset{\overset{\displaystyle NO_2}{|}}{C}H-CH_3$$

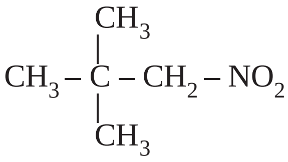
2-nitro propane

$CH_3CH_2CH_2-NO_2$ 1-Nitro propane



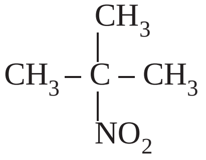
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-NO_2$$

1-Nitro-2-methyl propane



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-NO_2$$

1-Nitro-2,2-dimethyl propane



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-CH_3$$

2-nitro, 2-methyl propane

Isomerism :

Besides chain and position isomerism Nitroalkene shows functional isomerism.

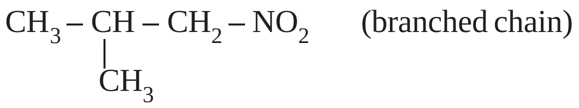
Isomerism :

Nitro compounds exhibit the following three types of isomerism.

1. Chain isomerism arises due to the difference in the arrangement of carbon atoms.

$CH_3 - CH_2 - CH_2 - CH_2 - NO_2$ (linear chain)

1-nitro butane



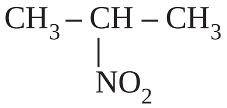
$$\underset{\displaystyle CH_3}{CH_3 - \underset{|}{CH} - CH_2 - NO_2}$$ (branched chain)

1-nitro-2-methyl propane

2. Position isomerism arises due to the difference in the position of nitro group.

$CH_3 - CH_2 - CH_2 - NO_2$

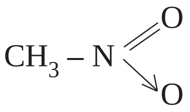
1-nitro propane



$$CH_3 - \underset{\underset{\displaystyle NO_2}{|}}{CH} - CH_3$$

2-nitro propane

3. Functional isomerism is due to the difference in the nature of functional group. Nitro alkanes are functional isomers of alkyl nitrites.

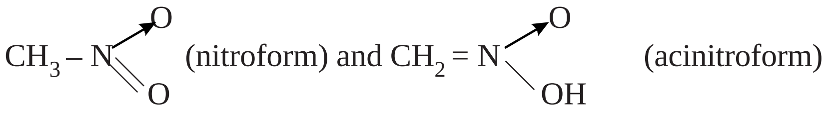


Nitro methane

$CH_3 - O - N = O$

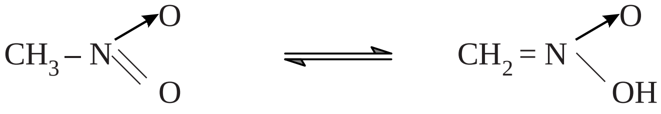
Methyl nitrite

4. Tauto merism : Nitromethane exhibits tautomerism, a special type of isomerism.



(nitroform) and (acinitroform)

These two functional isomers exist in equilibrium.



Nitro Acinitro

This is said to exhibit (''Nitro-acinitro'') tautomerism.

Both primary and secondary nitro compounds exhibit these kinds of tautomerism.

20.1.1 Preparation of nitroalkanes

1. They are prepared by heating an alkyl halide with aqueous ethanolic silver nitrate.

1. $R—X + AgNO_2 \longrightarrow AgX + R — NO_2$

$CH_3CH_2Cl + AgNO_2 \longrightarrow AgCl + CH_3CH_2\,NO_2$

2. **By direct nitration of alkanes :** Hexane and other higher alkanes can be nitrated readily with fuming nitric acid or with oxides of nitrogen. However the lower hydrocarbons can be nitrated only in the vapour phase at higher temperature. (623 – 773 K).

$$C_6H_{14} + HONO_2 \longrightarrow C_6H_{13}NO_2 + H_2O$$

$$\underset{\text{methane}}{CH_4} + \underset{\text{nitric acid}}{HONO_2} \xrightarrow{400^{o}C} \underset{\text{nitro methane}}{CH_3NO_2} + H_2O$$

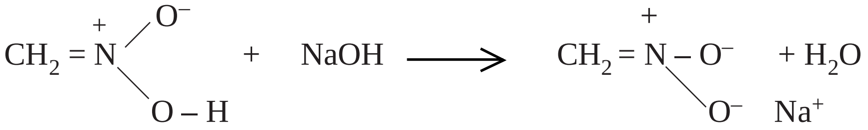
20.1.2 Properties

Nitro alkanes are colourless pleasant smelling liquids. Nitromethane is soluble in water, higher members are sparingly soluble in water but readily soluble in organic solvents.

They are highly polar compounds. Hence they are high boiling than the alkyl halides and alkanes. Nitro methane is slightly acidic.

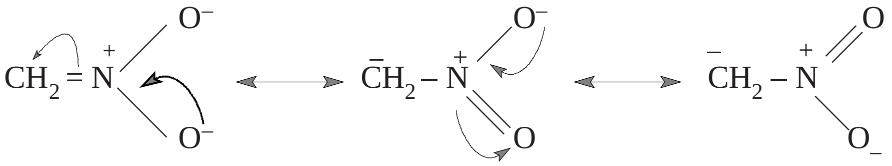
(Nitroform) (Tautomerism) (Aci form)

The aciform contains replaceable hydrogen atom. Hence it dissolves in alkali solution forming salt like compounds.



$$CH_2=\overset{+}{N}(O^-)(O-H) + NaOH \longrightarrow CH_2=\overset{+}{N}(-O^-)(O^-)\;Na^+ + H_2O$$

This anion exhibits resonance.

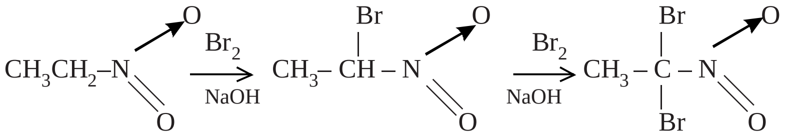


Only primary and secondary nitro compounds behave as acids in presence of strong alkali.

This anion of the nitrolic acid is involved in many of the properties of nitro alkanes. (Nitro methane)

1. Halogenation

Nitro alkanes are readily halogenated in α-position in presence of alkali.



Mono bromo nitro ethane

di bromo nitro ethane

Nitromethane reacts with halogen in presence of alkali to form trihalogen derivative. (e.g.,) with chlorine it forms chloropicrin, CCl_3NO_2 which is used as soil sterilizing agent.

$$CH_3NO_2 + 3Cl_2 \xrightarrow{NaOH} \underset{\text{(trichloro nitro methane)}}{\underset{\text{Chloro picrin}}{CCl_3\,NO_2}} + 3HCl$$

2. Reaction with aldehydes and ketones

Condensation with aldehydes and ketones in presence of alkali solution to give **Nitroalcohols.**

$$HCHO + CH_3NO_2 \xrightarrow{\text{dil. NaOH}} CH_2OH–CH_2NO_2$$
2-nitro ethanol

$$CH_3CHO + CH_3NO_2 \xrightarrow{\text{dil. NaOH}} CH_3CHOH–CH_2NO_2$$
1-nitro-2-propanol

$$CH_3COCH_3 + CH_3NO_2 \xrightarrow{\text{dil. NaOH}} (CH_3)_2COH–CH_2NO_2$$
1-nitro-2-methyl-2-propanol

3. Reduction : (i) Sn/HCl or Fe/HCl or H_2/Raney nickel reduces nitro alkanes to alkyl amines.

$$R – NO_2 \quad + \quad 6\,[H] \xrightarrow{\text{Sn/HCl}} RNH_2 \quad + \quad 2H_2O$$

$$CH_3 – NO_2 \; + \; 6\,[H] \xrightarrow{\text{Sn/HCl}} CH_3NH_2 \quad + \quad 2H_2O$$
Methylamine

(ii) Reduction under neutral conditions using Zn/NH_4Cl or Zn/$CaCl_2$- hydroxyl amines are formed.

$$R–NO_2 \quad + \; 4\,(H) \xrightarrow{Zn/NH_4Cl} RNHOH \; + \; H_2O$$
Hydroxyl amine

$$CH_3 – CH_2NO_2 \quad + \quad 4\,[H] \xrightarrow{Zn/NH_4Cl} CH_3CH_2NHOH \quad + \quad H_2O$$
(Nitro ethane) ethyl hydroxylamine

4. Hydrolysis :

When boiled with mineral acids primary nitro alkane, undergoes disproportionation reaction to form carboxylic acid and hydroxylamine.

$$CH_3CH_2NO_2 \quad + \quad H_2O \xrightarrow{HCl} CH_3COOH \quad + \quad NH_2OH$$
acetic acid hydroxylamine

20.1.3 Uses of nitro alkanes :

1. They are good solvents for a large number of organic compounds including vinyl polymers, cellulose esters, synthetic rubbers, oils, fats, waxes and dyes.

2. Used in organic synthesis.

Account for the following :

(a) Nitro ethane is soluble in NaOH solution.

(b) Nitro ethane reacts with nitrous acid.

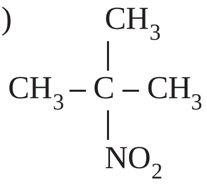
(c) 2-methyl-2-nitro propane is neither soluble in NaOH nor reacts with nitrous acid.

Answers.

(a) exhibits tautomerism of nitroform and aciform. Aciform is acidic and soluble in NaOH.

(b) $CH_3CH_2NO_2$ has **two α-hydrogen** and that reacts with HNO_2.

(c)



$$CH_3-\underset{NO_2}{\overset{CH_3}{C}}-CH_3$$

has no α-hydrogen. Hence it does not have the above properties.

2. Predict the product.

$$CH_3NO_2 + Cl_2 \xrightarrow{NaOH} ?$$

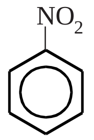
Answer : CCl_3NO_2 (chloro picrin)

3. What happens when nitro ethane is boiled with HCl ?

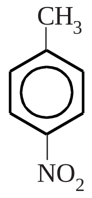
Answer : $CH_3COOH \quad + \quad NH_2OH$

20.2 AROMATIC NITRO COMPOUNDS

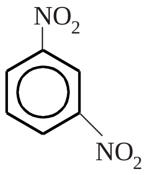
These are the substitution products of aromatic hydrocarbons like benzene. One or more hydrogen atoms of the aromatic ring are replaced by nitro group.



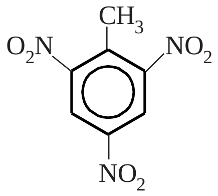
Nitrobenzene



p-nitro toluene

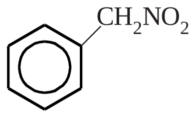


m-dinitro benzene

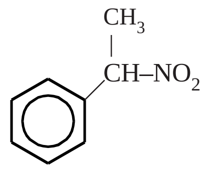


2,4,6-trinitro toluene

There are some aromatic compounds **which do not have nitro group** directly linked to the aromatic nucleus. The Nitro group is present in the side chain.



Phenyl nitro methane

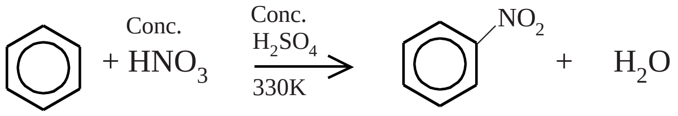


1-nitro,1-phenyl ethane

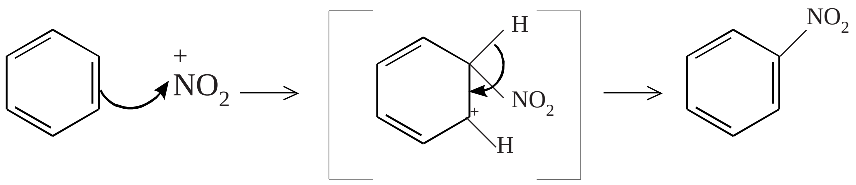
Nitro benzene, the simplest of aromatic nitro compounds, is called **'oil of mirbane'.**

20.2.1 Preparation of nitro benzene

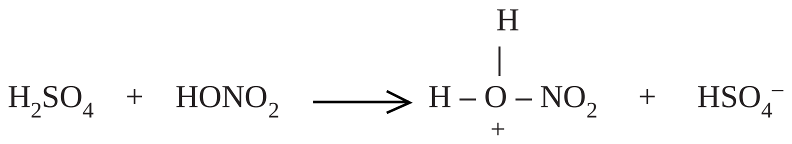
It is prepared by the action of a mixture of con. HNO_3 and con. H_2SO_4 **(nitrating mixture)** on benzene maintaining the temperature below 333 K.



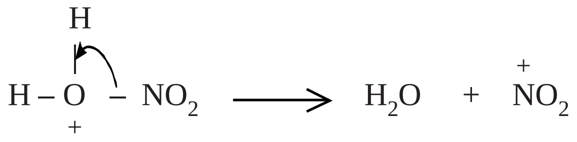
Sulphuric acid generates the electrophile $-NO_2^+$, nitronium ion-from nitric acid. This is an example of aromatic electrophilic substitution reaction.



The generation of nitronium ion.

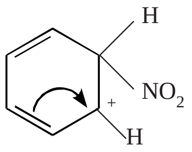


$$H_2SO_4 + HONO_2 \longrightarrow H - \overset{\overset{H}{|}}{\underset{+}{O}} - NO_2 + HSO_4^-$$

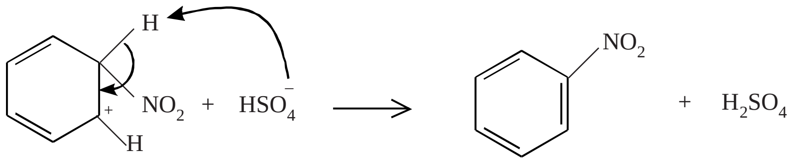


$$H - \overset{\overset{H}{|}}{\underset{+}{O}} - NO_2 \longrightarrow H_2O + \overset{+}{NO_2}$$

To the nitronium ion (being an electron deficient specie) the π bond of benzene, donates a pair of electrons forming a δ-bond. A specie with a + ve charge is formed as an intermediate. This is called **'arenium ion'** and is stabilised by Resonance.



In the last step, the hydrogen atom attached to the carbon carrying the nitro group is pulled out as a proton, by the Lewis base HSO_4^-, so that stable aromatic system is formed.



20.2.2 Physical Properties

Aromatic nitro componds are yellow coloured liquid (nitro benzene) or solids (other members). Nitro benzene has the smell of **'bitter almonds'** and is called **'the oil of Mirbane'.** They are insoluble in water but soluble in organic solvents such as benzene, ethanol and ether. They have high boiling and melting points which is explained by highly polar nature of $-NO_2$ group.

Nitro group contains nitrogen in +3 oxidation state (as nitrogen itself an electronegative element, existing in a +3 oxidation state). Hence reduction of nitro group is the important chemical reaction.

Depending on the nature of the reducing agent and pH of the reducing medium - reduction proceeds to different extents and hence different products are formed.

1. Reduction of nitrobenzene

(a) Strongly acidic medium

When reduced with **tin and hydrochloric acid,** aromatic nitro compounds are converted to aryl amines.

$$\underset{}{C_6H_5NO_2} + 6\,[H] \xrightarrow[\text{or}\ \text{Fe/con.HCl}]{\text{Sn/con.HCl}} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

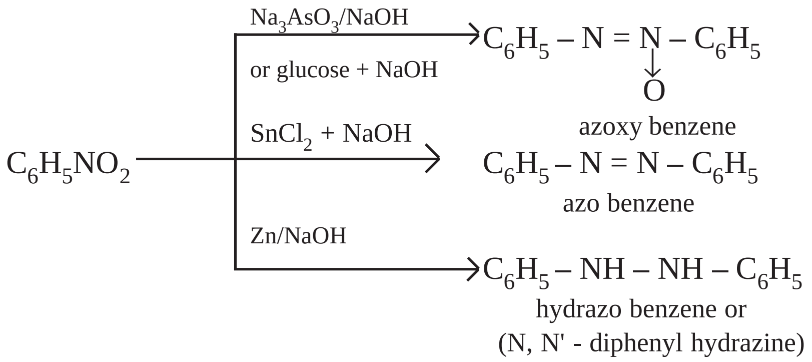
(b) Neutral medium

When reduced **with a neutral,** reducing agents like zinc dust and aqueous ammonium chloride, aromatic nitro compounds form aryl hydroxylamines.

$$C_6H_5NO_2 + 4\,[H] \xrightarrow{\text{Zn/NH}_4\text{Cl}} \underset{\text{Phenyl hydroxylamine}}{C_6H_5NHOH} + H_2O$$

(c) Alkaline medium

In alkaline medium, Nitro benzene on reduction forms the intermediate products nitrosobenzene (C_6H_5NO) and phenyl hydroxylamine (C_6H_5NHOH). These undergo bimolecular condensation reaction. According to the appropriate reducing agent in alkaline medium different products are obtained.



$$C_6H_5NO_2 \xrightarrow[\text{or glucose + NaOH}]{Na_3AsO_3/NaOH} C_6H_5-\underset{\substack{\downarrow\\ O}}{N}=N-C_6H_5$$

azoxy benzene

$$C_6H_5NO_2 \xrightarrow{SnCl_2 + NaOH} C_6H_5-N=N-C_6H_5$$

azo benzene

$$C_6H_5NO_2 \xrightarrow{Zn/NaOH} C_6H_5-NH-NH-C_6H_5$$

hydrazo benzene or
(N, N' - diphenyl hydrazine)

(d) Catalytic reduction

Lithium Aluminium hydride is a powerful hydride ion donor. So it reduces nitro benzene to Aniline. This reduction can also be carried out by H_2/Ni.

$$C_6H_5NO_2 \xrightarrow{LiAlH_4} C_6H_5NH_2 \text{ [Aniline]}$$

$$C_6H_5NO_2 \xrightarrow[\substack{\text{Catalytic}\\ \text{hydrogenation}}]{H_2/Ni} C_6H_5NH_2$$

(e) Electrolytic Reduction :

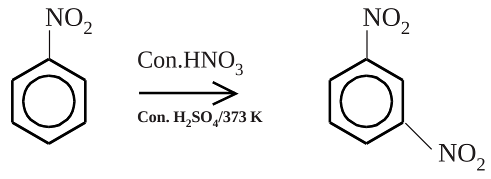
When nitro benzene is reduced electrolytically in presence of concentrated sulphuric acid, phenyl hydroxylamine is first produced which rearranges to give p-amino phenol.

Reactions due to the benzene ring :

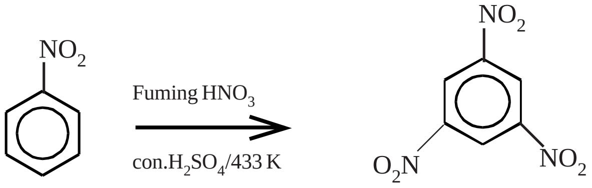
Benzene ring can take part in electrophilic substitution reaction. The presence of nitro group makes the ring less reactive **[deactivate]** towards electrophilic substitution reaction. Nitro group is **metadirecting** group. Hence in these reactions m-substituted products are formed.

1. Nitration

Nitro benzene can be nitrated with the mixture of concentrated nitric acid and sulphuric acid at 100^o C to give m-dinitro benzene. Using fuming nitric acid and con. sulphuric acid and when the temperature is increased to 433 K nitro benzene gives 1,3,5-trinitro benzene.



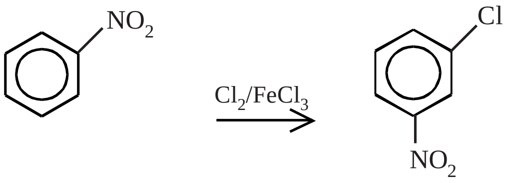
m-dinitrobenzene



1,3,5-Trinitro benzene

2. Chlorination

Chlorine in presence of anhydrous ferric chloride generates positively charged species. Chlorination takes place at meta position.

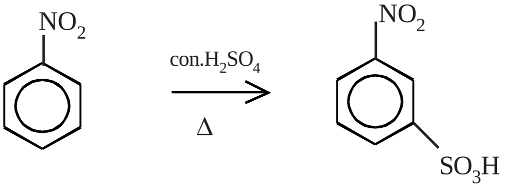


3-chloro nitro benzene

Ferric chloride is the Lewis acid catalyst.

3. Sulphonation

When warmed with con. H_2SO_4, 3-Nitro benzene sulphonic acid is obtained.



m-nitro benzene sulphonic acid

Uses of nitro benzene

1. Aromatic nitro compounds are used to form corresponding amino compounds.

2. They are used to prepare explosives like TNT, 1,3,5-trinitro benzene.

3. Used in making dye stuffs and pharmaceuticals.

SUMMARY OF NITRO COMPOUNDS

Organic nitrogen compounds - structure nomenclature - isomerism - nitro-acinitro tautomerism.

Preparation - direct nitration of hydrocarbons, nucleophilic substitution with alkyl halide.

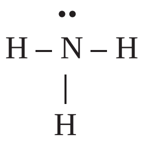
Properties : Polar compounds - high boiling when compared to hydrocarbons or alkyl halides. α-hydrogen can be removed as a proton by a base forming carbanion - This undergoes condensation with aldehydes and ketones - Reduction in acid, neutral medium - Importance of Victor Meyer Test.

Aromatic nitro compound - aromatic electrophilic substitution - nitrating mixture - aromatic nitro compounds - yellow oils or solids - Reduction under various conditions - acidic, neutral, alkaline mediums and electrolytic reduction.

Polynitro compounds - explosives.

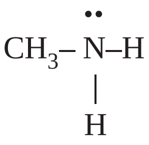
20.3 AMINES

Amines are compounds derived from ammonia by replacing one or more hydrogen atoms by alkyl or aryl group.



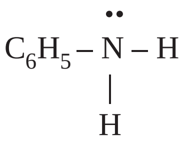
$$H-\overset{\cdot\cdot}{\underset{|\atop H}{N}}-H$$

Ammonia



$$CH_3-\overset{\cdot\cdot}{\underset{|\atop H}{N}}-H$$

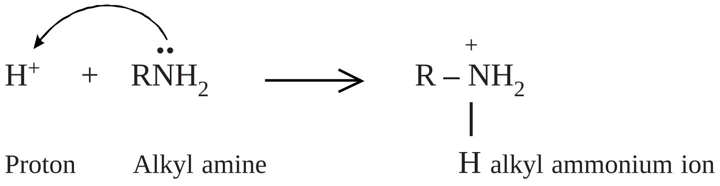
Aliphatic amine



$$C_6H_5-\overset{\cdot\cdot}{\underset{|\atop H}{N}}-H$$

Aromatic amine

Amines are basic in nature. They accept protons forming alkyl or aryl ammonium ions.



$$H^+ + R\ddot{N}H_2 \longrightarrow R-\overset{+}{\underset{|}{N}}H_2$$

20.3.1 Classification of amines

Amines are classified as primary, secondary and tertiary amines. When one of the hydrogen atoms in ammonia is replaced by alkyl or aryl group, it is primary amine.

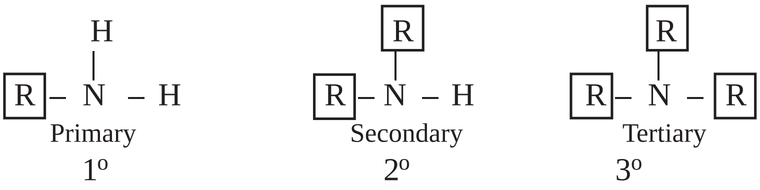
$CH_3CH_2NH_2$	$C_6H_5NH_2$
ethylamine	aniline

If two hydrogen atoms of amino group are replaced by alkyl or aryl groups, it is a secondary amine.

$(CH_3)_2$ NH - dimethyl amine

If three hydrogen atoms are replaced by alkyl or aryl groups, it is tertiary amine.

$(CH_3)_3$ N - Trimethyl amine



Primary amine has ⟶ NH_2 group (two hydrogen atoms bonded to nitrogen)

Secondary amine has ⟶ NH group (only one hydrogen bonded to nitrogen)

Tertiary amine has ⟶ $-\overset{|}{\underset{|}{N}}$ group (No hydrogen atom bonded to nitrogen)

Generally the strength of the base is in the order.

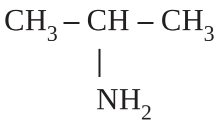
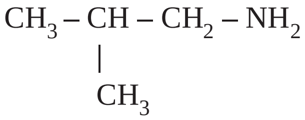
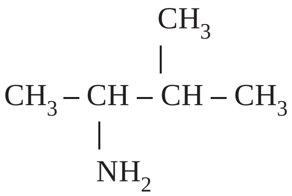
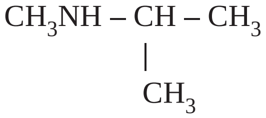
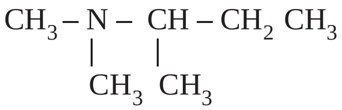
3^o amine > 2^o amine > 1^o amine

But because of steric effect the order of the basic strength is

2^o amine > 1^o amine > 3^o amine

Nomenclature of Aliphatic amines

IUPAC system is similar to that of alkyl halides.

Molecular structure	IUPAC name	Common name
CH_3-NH_2	amino methane	methyl amine
 $CH_3-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$	2-amino propane	isopropyl amine
$CH_3CH_2CH_2NH_2$	1-amino propane	n-propyl amine
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-NH_2$	1-amino-2-methyl propane	isobutyl amine
 $CH_3-\underset{NH_2}{\underset{\vert}{CH}}-\overset{CH_3}{\overset{\vert}{CH}}-CH_3$	2-amino-3-methyl butane	isopentyl amine
$CH_3NH\ CH_2\ CH_3$	(N-methyl amino) ethane	ethyl methyl amine
 $CH_3NH-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	2-(N-methyl amino) propane	methyl isopropyl amine
 $CH_3-\underset{CH_3}{\underset{\vert}{N}}-\underset{CH_3}{\underset{\vert}{CH}}-CH_2\ CH_3$	2-(N,N-dimethyl amino) butane	dimethyl sec.butyl amine

20.3.2 General methods of preparation of amines

Reduction of compounds containing carbon-nitrogen bonds.

1. Catalytic or chemical reduction of nitro alkane. Primary amines can be obtained by reduction of nitro alkanes with H_2 / Pt (or Ni) or lithium aluminium hydride.

$$\text{(a)}\quad \underset{\text{Nitro ethane}}{CH_3\,CH_2\,NO_2} \xrightarrow{3H_2/\text{Ni or Pt}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + 2H_2O$$

$$\text{(b)}\quad CH_3\,CH_2\,NO_2 \xrightarrow{\text{Sn (or) Zn/HCl}} CH_3CH_2\,NH_2 + 2H_2O$$

$$\text{(c)}\quad \underset{\text{Nitro methane}}{CH_3NO_2} \xrightarrow{LiAlH_4} \underset{\text{Methyl amine}}{CH_3NH_2}$$

2. Reduction of amides : Amines can be obtained by reduction of amides with lithium aluminium hydride or sodium and alcohol.

$$\text{(a)}\ \underset{\text{(Acetamide)}}{CH_3CONH_2} + 4\,[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

$$\text{(b)}\ \underset{\text{(N-methyl acetamide)}}{CH_3CONHCH_3} \xrightarrow{LiAlH_4} \underset{\substack{\text{(Secondary amine)}\\ \text{methylethylamine}}}{CH_3CH_2NHCH_3}$$

3. Reduction of cyanides :

Primary amines can be prepared by reduction of alkyl cyanides (nitriles) with H_2/Ni or lithium aluminium hydride.

$$\text{(a)}\quad CH_3C \equiv N + 4\,[H] \xrightarrow{Na/C_2H_5OH} CH_3CH_2NH_2$$

$$\text{(b)}\quad CH_3C \equiv N \xrightarrow[\text{Ether}]{LiAlH_4} CH_3CH_2NH_2$$

$$\text{(c)}\quad CH_3C \equiv N \xrightarrow{H_2/Ni} CH_3CH_2NH_2$$

4. Reduction of alkyl isocyanides :

Secondary amine can be prepared by the catalytic reduction or reduction by lithium aluminium hydride of alkyl iso cyanide.

$$\underset{\text{Methyl isocyanide}}{CH_3 - N \equiv C} \xrightarrow{H_2/Pt} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$$

$$CH_3 - N \equiv C \xrightarrow[\text{ether}]{LiAlH_4} CH_3NH\ CH_3$$

5. From amides

By elimination reaction - primary amine is prepared.

Hoffman's hypobromite reaction or Hoffman's bromamide reaction

$$CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2 + CO_2$$

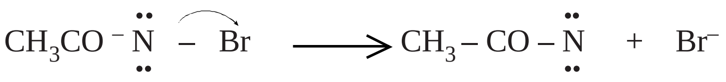
This reaction involves the formation of

(i) Bromamide by substitution of $-NH_2$ hydrogen. $CH_3CONHBr$.

(ii) In presence of KOH [base], salt of bromamide is formed.

$$CH_3CO - \overset{-}{\underset{\cdot\cdot}{N}} - Br + K^+$$

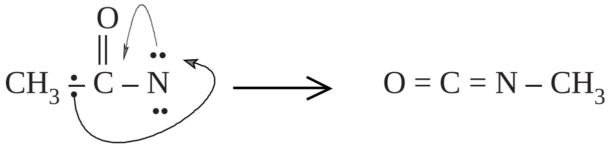
(iii) Bromine leaves as bromide ion forming nitrene.



$$CH_3CO^- \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} - Br \longrightarrow CH_3 - CO - \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} + Br^-$$

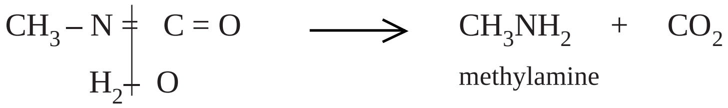
Nitrene - an electron deficient specie.

(iv) Migration of CH_3- to electron deficient nitrogen forms methyl isocyanate.



$$CH_3 - \overset{O}{\overset{\|}{C}} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} \longrightarrow O = C = N - CH_3$$

(v) In aqueous alkaline medium, isocyanate gets cleaved to give primary amine and carbondioxide.



$$\underset{\text{methyl isocyanate}}{CH_3-N=C=O + H_2O} \longrightarrow \underset{\text{methylamine}}{CH_3NH_2} + CO_2$$

6. From ammonia :

By heating an **alkyl halide with alcoholic ammonia** in a sealed tube, a mixture of primary, secondary, tertiary amines and quarternary ammonium salt are obtained.

Nucleophilic substitution of alkyl halide or alcohol by **Ammonolysis.** (Ammonia is the nucleophile in this reaction).

(a) $CH_3Br + NH_3 \longrightarrow CH_3NH_2 + HBr$

$CH_3Br + CH_3NH_2 \longrightarrow (CH_3)_2\ NH + HBr$

$CH_3Br + (CH_3)_2\ NH \longrightarrow (CH_3)_3\ N + HBr$

$CH_3Br + (CH_3)_3\ N \longrightarrow (CH_3)_4\ N^+\ Br^-$

Tetramethyl ammonium bromide (a quarternary ammonium salt)

(b) Amines can be prepared by passing the vapours of alcohol and ammonia over heated alumina at 673 K. A mixture of primary secondary and tertiary amines are produced.

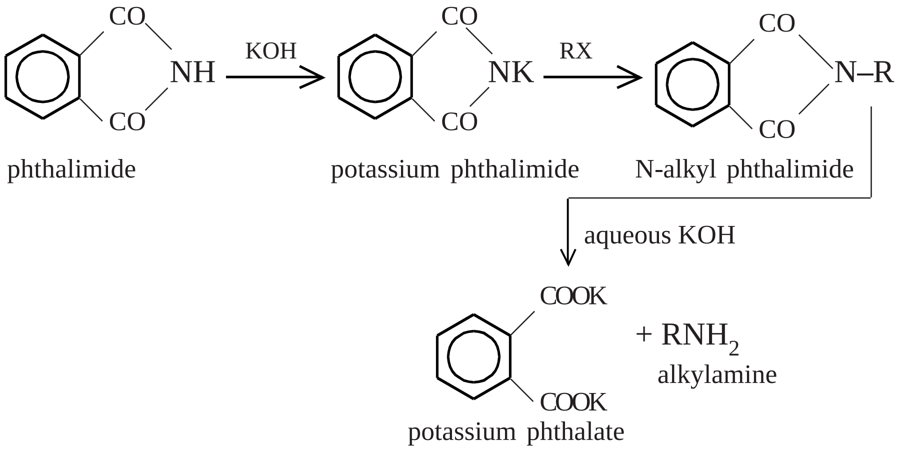
$$CH_3CH_2OH + NH_3 \xrightarrow[723K]{Al_2O_3} \underset{1^o\ \text{amine}}{(CH_3CH_2)\ NH_2} + H_2O$$

$$CH_3CH_2OH + (CH_3CH_2)_2\ NH \xrightarrow{Al_2O_3} \underset{\substack{2^o\text{amine} \\ \text{diethyl amine}}}{(CH_3CH_2)_2NH} + H_2O$$

$$CH_3CH_2OH + (CH_3CH_2)_2NH \xrightarrow{Al_2O_3} \underset{\substack{3^o\ \text{amine} \\ \text{triethylamine}}}{(CH_3CH_2)_3\ N} + H_2O$$

In both of the above methods, pure amines cannot be prepared. Only mixture of amines are obtained.

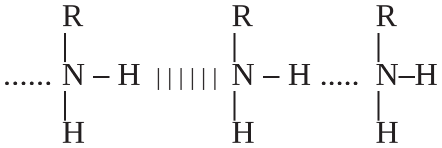
7. **Gabriel's phthalimide synthesis** of primary amine.



This involves the treatment of phthalimide with potassium hydroxide to form potassium salt. The salt is then heated with an alkyl halide to give N-alkyl phthalimide, which in turn reacts with potassium hydroxide to form a potassium phthalate salt and a pure primary amine.

20.3.3 Properties

1. Amines are polar molecules, capable of forming **strong intermolecular hydrogen bonds.**



$$\begin{array}{ccccccc} & R & & R & & R & \\ & | & & | & & | & \\ \ldots\ldots & N-H & |||||| & N-H & \ldots\ldots & N\text{–}H & \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

This explains higher boiling points (compared to hydrocarbons) and solubility in water and alcohol. Higher members are less soluble in water.

2. Generally amines have fishy odour.

3. The strength of hydrogen bonds and hence the boiling points of amines are in the order.

Secondary amine > Primary amine > Tertiary amine

Three alkyl groups hinder the formation of hydrogen bonds or accepting of protons.

Chemical properties :

1. Basic properties :

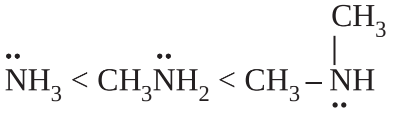
(a) Basic nature of amines

The nitrogen in amines possess **an unshared pair of electrons** (lone pair). The lone pair of electrons is available for the formation of a new bond with a proton or Lewis acids. Thus amines are basic in nature and they react with acids to form salts.

Amines are weak bases and they produce small amount of ions in aqueous solutions. The extent of ion formation is described by an equilibrium constant K_b. This basicity constant explains the relative strength of a weak base. Stronger bases will have higher numerical values of (K_b) this constant.

Relative basic strength

The greater is the number of electron releasing alkyl groups, the greater the availability of nitrogen's lone pair and stronger the base.



$$\ddot{N}H_3 < CH_3\ddot{N}H_2 < CH_3-\underset{\cdot\cdot}{\overset{\overset{CH_3}{|}}{N}}H$$

But in trimethyl amine bonding by proton is relatively difficult **due to steric crowding** of methyl groups.

Amines react with water forming alkyl ammonium hydroxide.

$$CH_3-\ddot{N}H_2 + H_2O \longrightarrow \underset{\text{methyl ammonium hydroxide}}{CH_3\overset{+}{N}H_3\ OH^-}$$

(b) Salt formation :

Amines are basic compounds. They react with acids to form alkyl ammonium salts.

$$CH_3\ddot{N}H_2 + HCl \longrightarrow \underset{\text{methyl ammonium chloride}}{CH_3NH_3^+\ Cl^-}$$

2. Alkylation of amine :

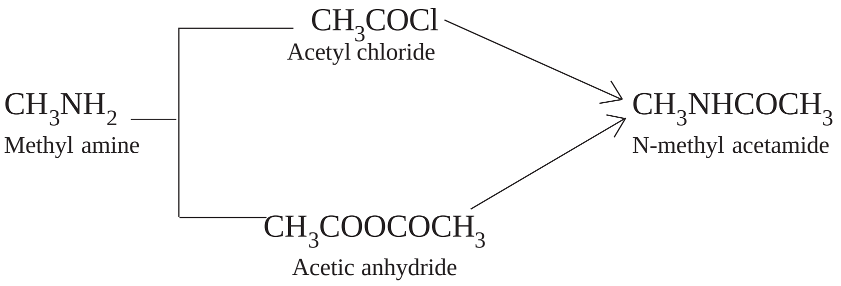
When an amine is treated with alkyl halide, hydrogen atoms attached to the nitrogen atom are successively replaced by alkyl groups. In the final step, the tertiary amine adds one molecule of the alkyl halide to yield a **quaternary ammonium salt.**

$$\underset{1^o\ \text{amine}}{CH_3NH_2} \xrightarrow{CH_3Br} \underset{2^o\ \text{amine}}{CH_3NHCH_3} \xrightarrow{CH_3Br} \underset{3^o\ \text{amine}}{(CH_3)_2\ NCH_3} \xrightarrow{CH_3Br} \underset{\text{Quarternary salts}}{(CH_3)_4\ N^+Br^-}$$

These reactions involve S_N2 mechanism.

3. Acylation of amine :

On treatment with acetyl chloride or on heating with acetic anhydride, N-alkyl acetamide is formed.



Both the above reactions involve nucleophilic substitution reaction - the nucleophile being alkyl amine and the leaving group the halide ion or acetate ion.

4. Reaction with Nitrous acid :

(a) Primary amines react with nitrous acid to form alcohols and nitrogen gas.

$$\underset{\text{primary amine}}{CH_3NH_2} + O = N - OH \longrightarrow \underset{\text{unstable}}{[CH_3{-}N{=}N - OH]} \longrightarrow CH_3OH + N_2$$

Aliphatic diazonium compound is unstable because of absence of resonance stabilisation.

(b) **Secondary amines** react with nitrous acid to form N-nitroso amines which are water insoluble yellow oils.

$$(CH_3)_2\,NH + HO-N=O \longrightarrow (CH_3)_2\,N-N=O$$

Secondary amine   N-nitroso dimethyl amine - yellow oil (insoluble in water)

(c) Tertiary amines react with nitrous acid to form trialkyl ammonium nitrite salts which are soluble in water.

$$(CH_3)_3\,N + HONO \longrightarrow (CH_3)_3\,NH^+\,NO_2^-$$

Tertiary amine   trimethyl ammonium nitrite (salt soluble in water)

5. Carbylamine reaction :

Primary amines on heating with chloroform and alcoholic potash forms a foul smelling substance called carbylamine or alkyl isocyanide.

$$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$$

Chloroform   Methyl isocyanide

This reaction is characteristic of primary amines. Secondary and tertiary amines do not undergo this reaction.

6. Mustard oil reaction :

This is also a reaction characteristic of primary amine. When primary amines are warmed with carbondisulphide and mercuric chloride, alkyl isothiocyanate, having a pungent **mustard like odour** is obtained.

$$CH_3NH_2 + S=C=S \longrightarrow CH_3-N=C=S + H_2S$$

Carbondisulphide   methyl isothiocyanate

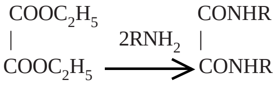
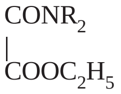
7. Formation of Schiff's base

Primary amines condense with aromatic aldehydes forming **Schiff's bases.**

$$C_6H_5CHO + H_2N\,CH_3 \longrightarrow C_6H_5CH=NCH_3$$

Schiff's base
(benzal-N-methyl amine)

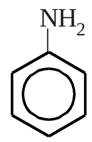
20.3.4 Distinction between primary, secondary and tertiary amines

Primary amine **RNH_2**	**Secondary amine** **R_2NH**	**Tertiary amine** **R_3N**
1. With HNO_2 forms alcohol.	forms N-nitroso amine.	forms salt.
2. With $CHCl_3$/KOH forms carbylamine	No reaction.	No reaction
3. With acetyl chloride forms N-alkyl acetamide.	form N,N-dialkyl acetamide.	No reaction
4. With CS_2 and $HgCl_2$ alkyl isothiocyanate is formed.	No reaction	No reaction
5. With Diethyl oxalate  $\begin{array}{l}COOC_2H_5\\ \vert\\ COOC_2H_5\end{array} \xrightarrow{2RNH_2} \begin{array}{l}CONHR\\ \vert\\ CONHR\end{array}$ dialkyl oxamide, a solid at room temperature is formed.	Forms N,N-dialkyl oxamic ester, a liquid.  $\begin{array}{l}CONR_2\\ \vert\\ COOC_2H_5\end{array}$	No reaction
6. With three molar proportion of alkyl halide, quarternary ammonium salt-crystalline compound is formed. $3RX + RNH_2 \longrightarrow R_4N^+X^-$	With two molar proportion of alkyl halide, quaternary ammonium salt is formed. $R_2NH + 2RH \longrightarrow R_4N^+ X^-$	With only one molar proportion of alkyl halide quarternary ammonium salt is formed. $R_3N + RX \longrightarrow R_4N^+ X^-$

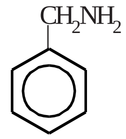
20.4 Aromatic amines

Amines containing phenyl group are known as aromatic amines. These aromatic amines are of two types.

(i) Amines in which the amino group is directly attached to the benzene ring.



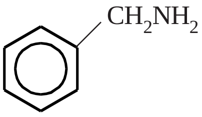
(ii) Amines in which the amino group is attached to the side chain of benzene ring.



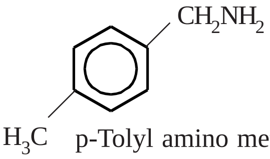
benzyl amine

Aralkyl amines :

These are amines having aromatic system such as benzene ring but the amino group is present in the side chain.



Benzyl amine



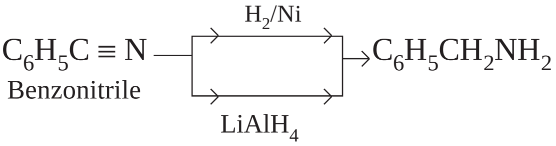
p-Tolyl amino methane

[IUPAC : phenyl amino methane]

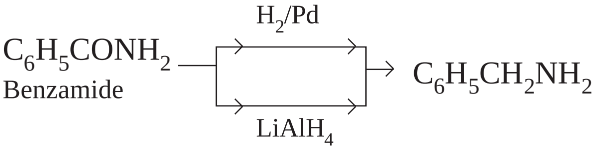
20.4.1 Preparation of benzyl amine

1. Reduction of benzonitriles or benzamides

By the reduction of benzonitrile or benzamide catalytically or with Lithium Aluminium Hydride.



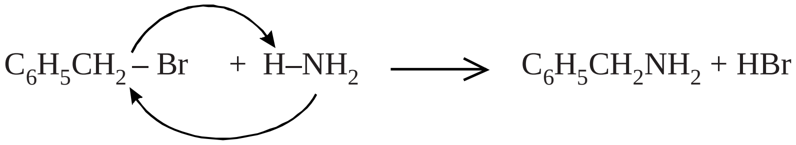
$$\underset{\text{Benzonitrile}}{C_6H_5C \equiv N} \xrightarrow[LiAlH_4]{H_2/Ni} C_6H_5CH_2NH_2$$



$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[LiAlH_4]{H_2/Pd} C_6H_5CH_2NH_2$$

2. From benzylbromide

By the action of alcoholic ammonia on benzyl bromide.



$$C_6H_5CH_2-Br \quad + \quad H\text{–}NH_2 \longrightarrow C_6H_5CH_2NH_2 + HBr$$

20.4.2 Physical Properties

Colourless liquid, sparingly soluble in water. It is a weaker base than methylamine.

Chemical Properties

1. Basic properties :

It reacts with acids to form salt.

$$\underset{\text{benzylamine}}{C_6H_5CH_2NH_2} \quad + \quad HCl \longrightarrow \underset{\text{benzyl ammonium chloride}}{C_6H_5CH_2\overset{+}{N}H_3 \;\; Cl^-}$$

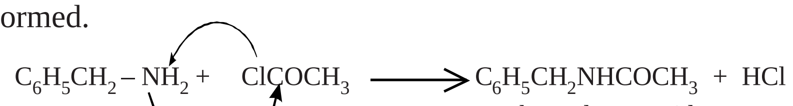
2. Substitution at Nitrogen

N-alkylation : With alkyl halide it forms secondary amine, tertiary amine and finally quaternary ammonium salt.

$$\begin{tikzcd} C_6H_5CH_2NH_2 \arrow[r, "CH_3Br"] & C_6H_5CH_2NHCH_3 \arrow[r, "CH_3Br"] & C_6H_5CH_2\,N\,(CH_3)_2 \arrow[d] \\ & C_6H_5CH_2\,\overset{+}{N}\,(CH_3)_3\;Br^- & \arrow[l, "CH_3Br"'] \end{tikzcd}$$

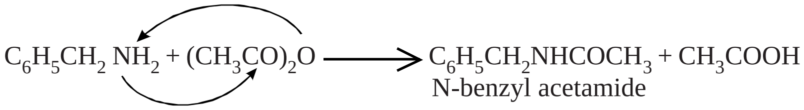
N-Acetylation :

With acetyl chloride or heating with acetic anhydride N-benzyl acetamide is formed.



$$C_6H_5CH_2-NH_2 + \quad ClCOCH_3 \longrightarrow C_6H_5CH_2NHCOCH_3 \;+\; HCl$$

N-benzyl acetamide



$$C_6H_5CH_2\;NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5CH_2NHCOCH_3 + CH_3COOH$$

N-benzyl acetamide

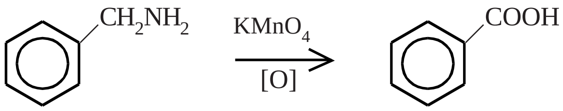
3. With nitrous acid

With nitrous acid it forms benzyl alcohol.

$$C_6H_5CH_2NH_2 \quad + \quad O = N - OH \longrightarrow C_6H_5CH_2OH \quad + \quad N_2$$

4. Oxidation

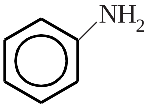
On oxidation with permanganate the side chain with the amino group is oxidised to give benzoic acid.



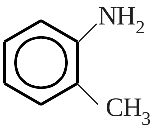
Benzylamine Benzoic acid

20.4.3 Aromatic amines :

These are compounds in which amino group is directly bonded to a carbon atom forming the benzene or any aromatic ring.



Aniline



o-Toluidine

Aniline or amino benzene, O-Toluidine or orthoamino toluene. These are also called **nuclear substituted amines.**

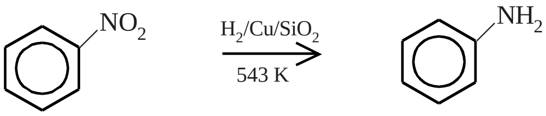
20.4.4 Aniline

Preparation :

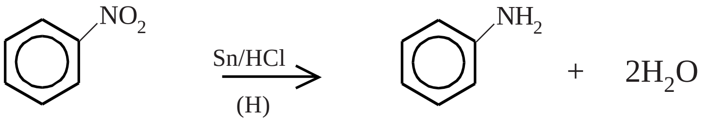
Manufacture :

1. By the catalytic reduction of nitro benzene.

Vapourised nitro benzene with hydrogen is passed over copper supported on silica at 543 K and aniline is obtained.



2. By the chemical reduction of nitrobenzene under strongly acidic condition such as Sn/HCl or with Hydride donors like $LiAlH_4$.



Reduction with Fe/con. HCl is used for the large scale preparation of aniline.

3. By the ammonolysis of chloro benzene at high temperature and pressure in presence of copper salts, aniline is prepared.

$$C_6H_5Cl + 2NH_3 \xrightarrow{CuCl_2} C_6H_5NH_2 + \underset{\text{ammonium chloride}}{NH_4Cl}$$

4. Hoffmann reaction : Using benzamide.

When an amide is treated with bromine and alkali, the amide is converted into primary amine containing one carbon less than that of amide.

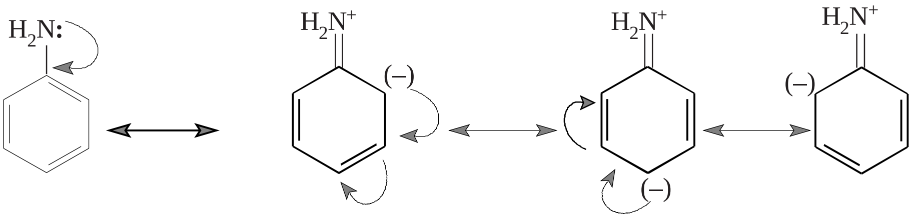
$$C_6H_5CONH_2 \xrightarrow[KOH]{Br_2} C_6H_5NH_2 + CO_2$$

20.4.5 Properties

A colourless oily liquid sparingly soluble in water. Soluble in organic solvent. It has higher boiling point than benzene, **because of intermolecular hydrogen bonding.** This liquid turns brown on exposure to air due to oxidation.

Basic nature of Aromatic amines :

Aniline is less basic than aliphatic amines. This is because, the lone pair of electrons on the nitrogen atom is involved in resonance and is not easily available for donation to protons. Because of positive charge on nitrogen **protonation becomes difficult.**



Consequence of the resonance shown above :

1. Weaker base than aliphatic amine.

2. The electron density is increased in the benzene ring and hence the benzene ring is activated towards electrophilic substitution reaction.

3. Ortho and para positions are more electron dense hence electrophilic substitution takes place **at ortho** and **para positions.**

4. Nitrogen is strongly bound to the nucleus hence is not easily removed. (partial C-N double bond character)

1. Basic property :

These form crystalline salts with strong mineral acids such as HCl or H_2SO_4.

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3\ Cl^-$$

aniline hydrochloride or phenyl ammonium chloride

2. Substitution of nitrogen :

(a) Alkylation with alkyl halides it forms 2^o, 3^o amines and finally quaternary ammonium salt.

$$C_6H_5NH_2 + CH_3I \longrightarrow \underset{\text{(N-methyl aniline)}}{\underset{2^o \text{ amine}}{C_6H_5NHCH_3}} \xrightarrow{CH_3I} \underset{\text{(N, N-dimethyl aniline)}}{\underset{3^o \text{ amine}}{C_6H_5N\,(CH_3)_2}}$$

$$C_6H_5N\,(CH_3)_2 \xrightarrow{CH_3I} C_6H_5\overset{+}{N}\,(CH_3)_3\ I^-$$

Phenyl trimethyl ammonium iodide

(b) Aniline reacts with acetyl chloride and acetic anhydride to form corresponding amides called **anilides.**

$$C_6H_5NH_2 + \underset{\text{Acetyl chloride}}{ClCOCH_3} \longrightarrow \underset{\text{N-phenyl acetamide}}{C_6H_5NHCOCH_3} + HCl$$

$$C_6H_5NH_2 + \underset{\text{Acetic anhydride}}{CH_3COOCOCH_3} \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHCOCH_3} + CH_3COOH$$

(c) With Benzoyl chloride. In presence of sodium hydroxide, benzanilide is formed.

$$C_6H_5NH_2 + \underset{\text{benzoyl chloride}}{ClCOC_6H_5} \xrightarrow{NaOH} \underset{\text{benzanilide}}{C_6H_5NHCOC_6H_5}$$

This reaction is an example of **Schotten-Baumann reaction.**

3. Formation of Schiffs base

Aniline is Primary aromatic amine. It reacts with aldehydes to form aldimines or Schiff's base.

$$C_6H_5NH_2 \quad + \quad O = CHR \longrightarrow C_6H_5N = CHR$$

(Aldimine or Schiff's base)

In all the above reactions the initial stage is the **nucleophilic attack**. The nucleophile is the amine and the site of attack is either halogen carrying carbon or carbonyl carbon. This is an addition - elimination reaction.

4. Reaction with nitrous acid :

3. A cold solution of sodium nitrite reacts with aniline dissolved in hydrochloric acid, a clear solution is obtained. This solution contains **'benzene diazonium chloride'**. This reaction is known as **'diazotisation'.**

$$C_6H_5N\boxed{H_2 \ + \ O}=N\text{–}OH \xrightarrow{HCl} C_6H_5 - N = N - Cl$$

(Benzene diazonium chloride)

5. Carbylamine reaction :

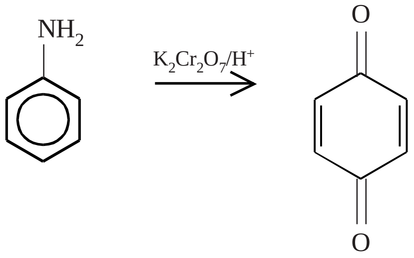
Aniline reacts with chloroform and alcoholic KOH to give an offensive smelling liquid, phenyl isocyanide.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5NC \quad + \quad 3KCl \quad + \quad 3H_2O$$

(phenyl isocyanide)

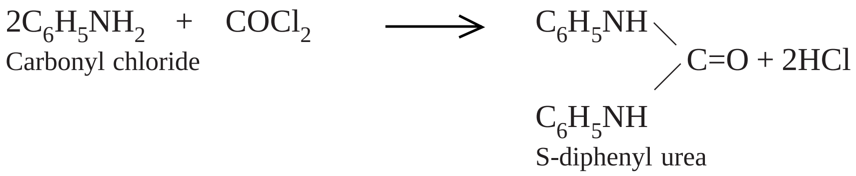
6. Oxidation :

Aromatic amines are readily oxidised by dichromate and sulphuric acid to p-benzoquinone.



7. Reaction with carbonyl chloride :

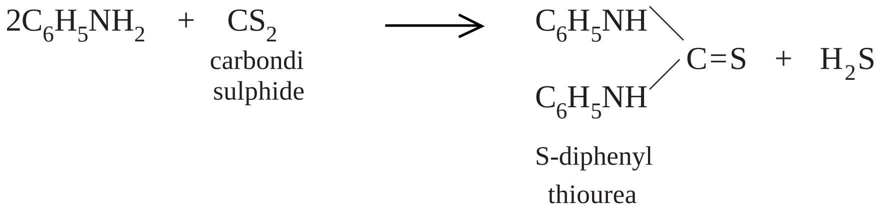
Carbonyl chloride form S-diphenyl urea with aniline. In the first step phenyl isocyanate is formed. ($C_6H_5N = C = O$).



$$\underset{\text{Carbonyl chloride}}{2C_6H_5NH_2 + COCl_2} \longrightarrow \underset{\text{S-diphenyl urea}}{\begin{matrix} C_6H_5NH \diagdown \\ C{=}O \\ C_6H_5NH \diagup \end{matrix}} + 2HCl$$

('S' stands for symmetric)

8. With carbondisulphide, S-diphenyl thiourea is formed. Phenyl isothiocyanate is formed in the first step. ($C_6H_5\text{–}N{=}C{=}S$)



$$2C_6H_5NH_2 + \underset{\substack{\text{carbondi}\\\text{sulphide}}}{CS_2} \longrightarrow \underset{\substack{\text{S-diphenyl}\\\text{thiourea}}}{\begin{matrix} C_6H_5NH \diagdown \\ C{=}S \\ C_6H_5NH \diagup \end{matrix}} + H_2S$$

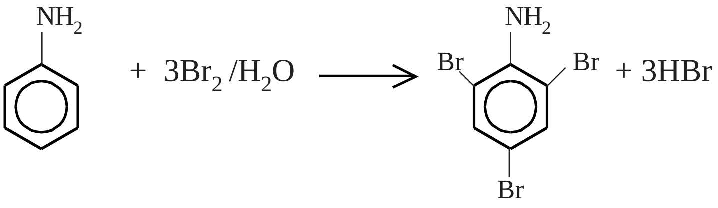
('S' stands for symmetric)

9. Electrophilic substitution reaction

Because of the presence of - activated benzene ring in aniline, electrophilic substitution reaction proceed under milder conditions.

(a) Halogenation :

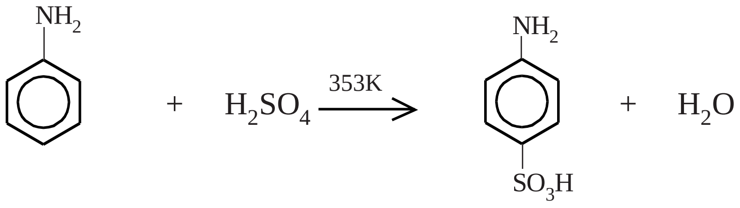
Aniline decolourises bromine water with the formation of white precipitate, which is 2,4,6-tribromoaniline.



2,4,6-nitro bromoaniline

(b) Sulphonation :

Heating with fuming sulphuric acid, p-amino benzene sulphonic acid is formed.

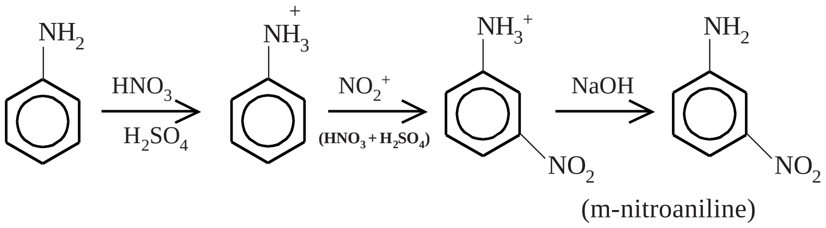


Ortho amino benzene sulphonic acid is sterically less favoured.

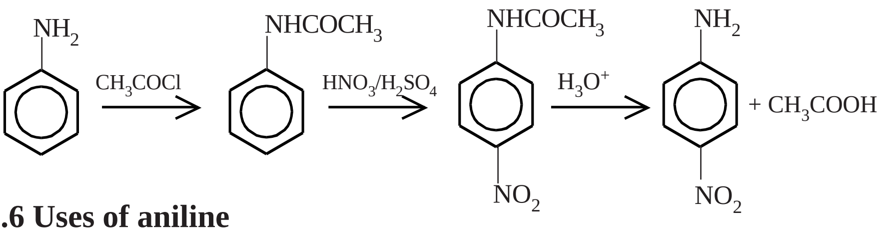
(c) Nitration : Nitration is accompanied by oxidation

But a mixture of con.HNO_3 and con. H_2SO_4 gives m-nitroaniline also. This can be explained as follows.

Nitric acid is a strong acid. It protonates aniline forming aniliniun ion. $C_6H_5NH_3^+$. Because of positive charge on nitrogen it is meta directing.



p-nitro aniline is prepared in the following three stages.



20.4.6 Uses of aniline

1. For preparing dyes and dye intermediates.

2. For the manufacture of anti oxidants in Rubber industry.

3. For preparing drugs (e.g.,) sulpha drugs.

4. For making isocyanates required for polyurethane plastics.

SUMMARY

AMINO COMPOUNDS

Structure, nomenclature, classification and isomerism including metamerism - of aliphatic amines.

Preparation - Reduction of nitro compounds, amides, cyanides - phthalimide synthesis - nucleophilic substitution - Ammonolysis.

Properties - hydrogen bonding and polar - higher boiling points - basic and nucleophilic character.

Classification - primary, secondary and tertiary amine - Basic strength of amines - N-alkylation, N-acylation, carbylamine reaction - quaternary ammonium salt.

Uses - Distinction between primary, secondary and tertiary amines.

Aralkyl amine - Benzyl amine - preparation - reduction of amides, cyanides - properties. Weaker a base than aliphatic amines - gives reactions of aliphatic primary amine - oxidation of side chain to give benzoic acid.

Aromatic amines - aniline and toluidines - structure, nomenclature and isomerism - preparation - reduction of nitro benzene - chemical and catalytic - chloro benzene and ammonia, Hoffmann reaction.

Properties - inter molecular hydrogen bonding - higher boiling point - less basic than aliphatic amines - resonance in aniline - N-alkylation, N-acylation, formation of Schiff's base, carbylamine reaction, reaction with phosgene, carbondisulphide - Formation of phenol - diazotisation and formation of azo dyes - electrophilic substitution in the benzene ring - bromination, sulphonation and nitration - uses.

20.5 ALIPHATIC NITRILES

Alkyl cyanides :

These are compounds in which one hydrogen atom is replaced from a hydrocarbon by a 'cyanide' group.

$$\text{HCN} \longrightarrow \text{R – CN} \longleftarrow \text{R – H}$$

They can also be considered as being derived from hydrocyanic acid.

Nomenclature :

Common system : By addng ‘cyanide’ to the name of the alkyl group.

$CH_3 - CN$
Methyl cyanide

‘Acid nitrile’ system :

In this system, they are named on the basis of the acid they produce on hydrolysis.

$$CH_3 - C \equiv N - \text{Hydrolysis} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

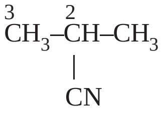
Hence it is called ‘Acetonitrile’.

$$C_6H_5 - C \equiv N - \text{Hydrolysis} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

Hence it is called ‘benzonitrile’.

IUPAC system :

They are named by suffixing ‘nitrile’ to the name of the parent hydrocarbon.

Formula	As cyanide	As acid nitrile	IUPAC name
HCN	Hydrogen cyanide	Formonitrile	Methane nitrile
CH_3CN	Methyl cyanide	Acetonitrile	Ethane nitrile
CH_3CH_2CN	Ethyl cyanide	Propionitrile (or) propiononitrile	Propane nitrile
 $\overset{3}{C}H_3-\underset{\displaystyle CN}{\overset{2}{C}H}-CH_3$	isopropyl cyanide	isobutyronitrile	2-methyl-propane nitrile (or) 2-cyano propane (as a substituent)

20.5.1 Uses of Nitriles

It is an important synthetic reagent to prepare, aldehydes, acids, amides, esters, amines alcohols etc.

Acrylo nitrile ($CH_2=CH–CN$) is used in the manufacture of synthetic polymers like PAN.

Acetonitrile (CH_3CN) is used as a solvent for extraction, crystallisation and as reaction medium.

20.6 Benzene Diazonium Chloride : $C_6H_5N_2^+Cl^-$

Aryl diazonium salts form an important class of compounds, characterised by the presence of the functional group $–N^+ \equiv N$ (diazonium ion) directly bonded to an aryl group –Ar.

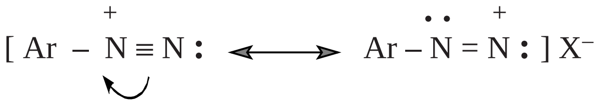
The aryl diazonium ion $Ar\text{-}N^+ \equiv N$ forms salts with anions such as Cl^-, Br^-, NO_2^-, HSO_4^-, BF_4^- etc., These are collectively called aryl diazonium salts.

Nomenclature :

By adding ‘diazonium’ to the name of the parent aromatic compound followed by the name of the anion.

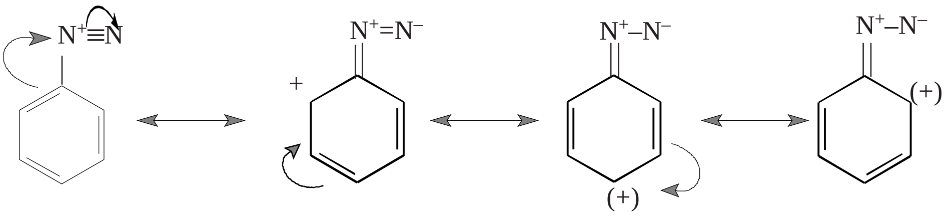
Thus, $C_6H_5N_2^+\ Cl^-$ is called benzene diazonium chloride.

Structure : The electronic structure



$$[\ Ar - \overset{+}{N} \equiv N : \longleftrightarrow Ar - \overset{\cdot\cdot}{N} = \overset{+}{N} :\ ]\ X^-$$

Resonance stabilised diazonium ion is further stabilised by the involvement of the benzene ring, in benzene diazonium ion.



C–N bond in aryl diazonium salt is stronger than that in aliphatic diazonium salt.

20.6.1 Preparation

Benzene diazonium chloride is prepared by the action of nitrous acid on aniline at 273 – 278 K. Nitrous acid is formed by mixing aqueous solutions of sodium nitrite and mineral acid like HCl or H_2SO_4.

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

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273 - 278\ K} C_6H_5N_2^+Cl^- + 2H_2O$$

This is stable only under ice cold condition. In the dry condition it is quite unstable and decomposes violently.

20.6.2 Properties

Colourless crystalline solids turning brown on exposure to air. Only diazonium $[ArN_2^+\ BF_4^-]$ fluro borate can be dried without decomposition, soluble in water and alcohol and insoluble in ether.

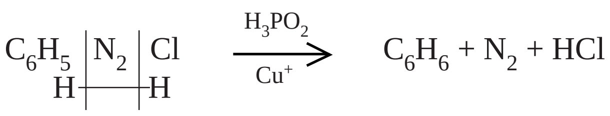
Chemical properties :

They are highly reactive compounds. They undergo reaction in which (1) $-N_2$ group is retained or (2) eliminated. In both cases useful compounds can be prepared. They are as useful as Grignard reagent for synthesis.

1. Reactions in which $-N_2^+\ X^-$ is replaced.

(a) Reduction to arenes :

Benzene diazonium chloride with Hypophosphorous acid, is reduced to benzene.

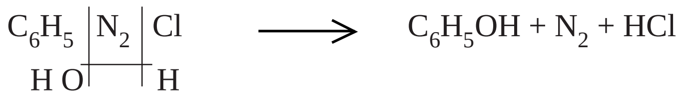


$$C_6H_5\,|\,N_2\,|\,Cl \; (H\ \ H) \xrightarrow[Cu^+]{H_3PO_2} C_6H_6 + N_2 + HCl$$

Cuprous salts catalyse this reaction.

(b) Replacement by –OH

When the aqueous solution is boiled, phenol is obtained.



$$\begin{array}{lll} C_6H_5 & N_2 & Cl \\ HO & & H \end{array} \longrightarrow C_6H_5OH + N_2 + HCl$$

This is an example of S_N1 reaction in which $C_6H_5N_2Cl$ initially gives $C_6H_5^+$ and water is the nucleophile.

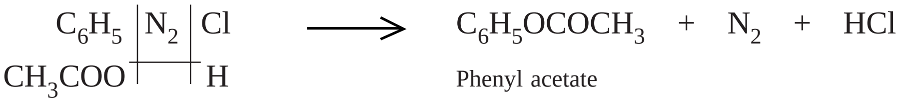
(c) Replacement of RO– (or) RCOO⁻ groups :

Similarly $-N_2Cl$ can be replaced by alkoxy group by warming with alcohol or by acyloxy group by boiling with carboxylic acids.

$$\begin{array}{lll} C_6H_5 & N_2 & Cl \\ CH_3O & & H \end{array} \longrightarrow C_6H_5OCH_3 + N_2 + HCl$$

[Alcohol is the nucleophile]

Aromatic ethers (anisole)



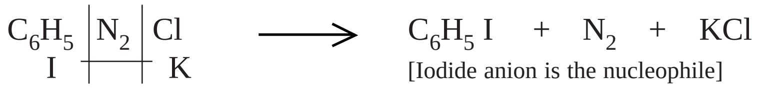
$$\begin{array}{lll} C_6H_5 & N_2 & Cl \\ CH_3COO & & H \end{array} \longrightarrow C_6H_5OCOCH_3 + N_2 + HCl$$

[Carboxylate ion is the nucleophile]

Phenyl acetate (ester)

(d) Replacement by Iodine :

Aqueous solution of diazonium salt reacts with potassium iodide solution to form Iodobenzene.



$$\begin{array}{lll} C_6H_5 & N_2 & Cl \\ I & & K \end{array} \longrightarrow C_6H_5I + N_2 + KCl$$

[Iodide anion is the nucleophile]

(e) Replacement by Nitro group :

Diazonium salt when treated with sodium nitrite in the presence of cuprous ion as a catalyst forms Nitro compounds.

$$C_6H_5N_2Cl \xrightarrow[Cu^+]{NaNO_2} C_6H_5NO_2$$

2. Replacement by chlorine or bromine :

(a) Sand Meyer Reaction :

When aqueous solution of diazonium chloride is warmed with Cu_2Cl_2 or Cu_2Br_2 in halogen acid, halogenated benzene is formed.

$$C_6H_5N_2Cl \xrightarrow[Cu_2Cl_2]{HCl} C_6H_5 - Cl \quad + \quad N_2$$

$$C_6H_5N_2Cl \xrightarrow[Cu_2Br_2]{HBr} C_6H_5Br \quad + \quad N_2$$

(b) Gattermann reaction :

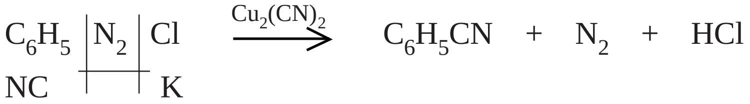
When the diazonium chloride solution is warmed with copper powder and the hydrogen halide, the corresponding halobenzene is obtained. Iodo benzene cannot be prepared by this procedure.

$$C_6H_5N_2Cl \xrightarrow[HCl]{Cu} C_6H_5Cl + N_2$$

$$C_6H_5N_2Cl \xrightarrow[HBr]{Cu} C_6H_5Br + N_2$$

3. Replacement by cyanide group :

The diazonium salt solution when treated with cuprous cyanide / potassium cyanide mixture, phenyl cyanide is formed.



$$\begin{array}{lll} C_6H_5 & \boxed{N_2} & Cl \\ NC & & K \end{array} \xrightarrow{Cu_2(CN)_2} C_6H_5CN \quad + \quad N_2 \quad + \quad HCl$$

Treatment of diazonium chloride with KCN solution in presence of copper, also gives phenyl cyanide.

$$C_6H_5N_2Cl \quad + \quad KCN \xrightarrow{Cu} C_6H_5CN \quad + \quad N_2 \quad + \quad KCl$$

4. Replacement by an aryl group : (Gomberg Bachmann Reaction)

Decomposition of diazonium salts in presence of sodium hydroxide and benzene, results in the formation of Biphenyl.

$$C_6H_5N_2Cl \quad + \quad C_6H_6 \xrightarrow{NaOH} \underset{\text{Biphenyl}}{C_6H_5 - C_6H_5} \quad + \; N_2 \quad + \quad HCl$$

This reaction is known as **'Gomberg'** or **'Gomberg Bachmann'** reaction.

The above reactions do not follow strictly S_N mechanism. Instead free radicals are formed as intermediates.

5. Reduction :

Diazonium chloride is reduced to phenyl hydrazine on treatment with $SnCl_2$/HCl or Zn/HCl or $NaHSO_3$.

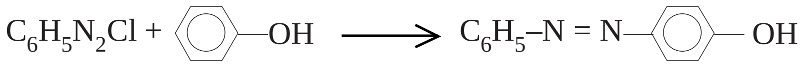
$$C_6H_5N_2Cl \xrightarrow{4[H]} C_6H_5NHNH_2 \quad + \quad HCl$$

6. Diazonium coupling reaction :

Diazonium salt reacts with aromatic amine and phenols to give azo compounds of the general formula.

$$Ar - N = N - Ar'$$

This reaction is known as Coupling reaction since all these compounds are intensely coloured and used as dyes, thousands of azo dyes have been synthesised by this procedure.



[p-hydroxy azo benzene]

Red dye

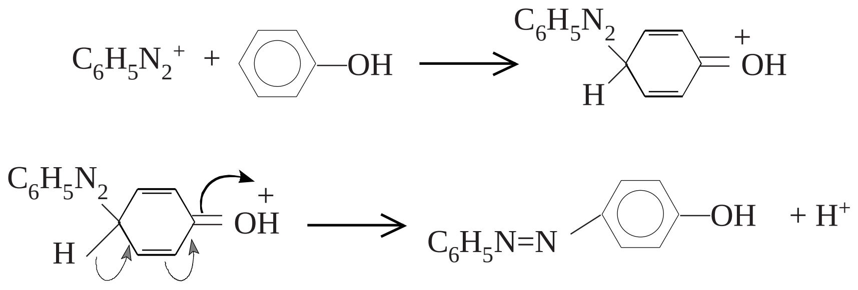
The aromatic compound with which it couples should have any one of the groups like –OH, $–NH_2$, –OR, –NHR, $–NR_2$ etc. coupling usually occurs at para position.

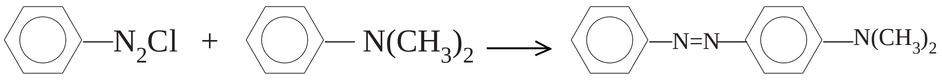
ALL THE COUPLING REACTIONS INVOLVE

I. Formation of diazonium ion $C_6H_5N_2^+$ (an electrophile)

II. Electrophilic substitution on electron rich aromatic compounds like phenols, amines etc., at para-position.

III. Diazo coupling reaction takes place in ice cold condition.



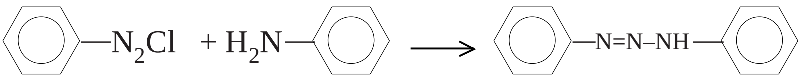


N, N - dimethyl aniline

p-dimethyl amino azo benzene

Reaction with primary amine takes place in a different way :

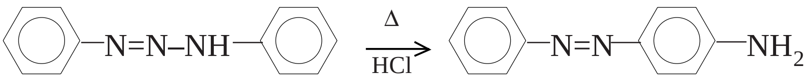
(I)



Diazoaminobenzene

(Substitution at Nitrogen)

(II)



[Rearrangement]

p-amino azo benzene
(Substitution at carbon)

Uses of diazonium salts :

It is a very valuable intermediate in the preparation of many class of compounds like phenols, halides, cyanides etc.

Valuable laboratory reagents like phenyl hydrazine can be prepared.

Very useful in the manufacture of azo dyes.

SUMMARY

Benzene Diazonium chloride - structure - diazotisation of aniline - properties - stable at low temperature - hydrogenolysis to benzene, hydrolysis to phenol, formation of halo benzene, cyano benzene, nitrobenzene, anisole - reduction to phenyl hydrazine - diazo coupling with aromatic amines and phenols - formation of dyes.

Name reactions

1. Sandmeyer reaction 2. Gattermann reaction

3. Gomberg reaction 4. Diazo coupling reaction

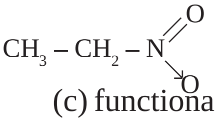
Alkyl cyanides - nomenclature as Nitriles.

SELF EVALUATION

(A) Choose the correct answer :

1. Bromo ethane reacts with silver nitrite to give

(a) $C_2H_5NO_2$ (b) $C_2H_5–O–NO$
(c) $C_2H_5Ag + NaBr$ (d) C_2H_5NC

2. The isomerism exhibited by 
$CH_3 – CH_2 – N\overset{\nearrow O}{\underset{\searrow O}{}}$ and $CH_3\,CH_2 – O – N = O$ is

(a) position (b) chain (c) functional (d) tautomerism

3. In nitro alkanes $–NO_2$ group is converted to $–NH_2$ group by the reaction with

(a) Sn/HCl (b) Zn dust (c) Zn/NH_4Cl (d) Zn/NaOH

4. When nitromethane is reduced with Zn dust + NH_4Cl in neutral medium, we get

(a) CH_3NH_2 (b) $C_2H_5NH_2$ (c) CH_3NHOH (d) C_2H_5COOH

5. The compound that is most reactive towards electrophilic nitration is

(a) Toluene (b) benzene (c) benzoic acid (d) nitrobenzene

6. Nitromethane condenses with acetaldehyde to give

(a) nitro propane (b) 1-nitro-2-propanol
(c) 2-nitro-1-propanol (d) 3-nitro propanol

7. Which of the following compounds has the smell of bitter almonds ?

(a) aniline (b) nitro methane
(c) benzene sulphonic acid (d) nitrobenzene

8. Nitration of nitrobenzene results in

(a) o-dinitro benzene (b) 1,3,5-trinitro benzene
(c) p-dinitro benzene (d) m-dinitro benzene

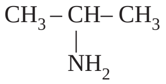
9. Nitrobenzene on electrolytic reduction in con. sulphuric acid, the intermediate formed is

(a) $C_6H_5NH - NHC_6H_5$ (b) $C_6H_5 - NHOH$
(c) $C_6H_5 - N = N - C_6H_5$ (d) $C_6H_5.HSO_4$

10. Electrophile used in the nitration of benzene is

(a) hydronium ion (b) sulphonic acid
(c) nitronium ion (d) bromide ion

11. The reduction of $CH_3 - CH_2 - C \equiv N$ with sodium and alcohol results in the formation of

(a) 
$CH_3 - \underset{\underset{NH_2}{|}}{CH} - CH_3$

(b) $CH_3 - CH_2 - CH_2 - OH + N_2$
(c) $CH_3 - CH_2 - CH_2 - NH_2$ (d) $CH_3 - CH_2 - NH_2$

12. The basic character of amines is due to the

(a) tetrahedral structure (b) presence of nitrogen atom
(c) lone pair of electrons on nitrogen atom
(d) high electronegativity of nitrogen

13. The organic compound that undergoes carbylamine reaction is

(a) $(C_2H_5)_2NH$ (b) $C_2H_5NH_2$ (c) $(C_2H_5)_3N$ (d) $(C_2H_5)_4 N^+ I^-$

14. Primary amine acts as

(a) Electrophile (b) Lewis base (c) Lewis acid (d) Free radical

15. Oxidation of aniline with acidified potassium dichromate gives

(a) p-benzo quinone (b) benzoic acid
(c) benzaldehyde (d) benzyl alcohol

16. Which one of the following is a secondary amine ?

(a) aniline (b) diphenyl amine (c) sec.butylamine (d) tert.butylamine

17. $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} X$. Identify X.

(a) C_6H_5Cl (b) C_6H_5NHOH
(c) $C_6H_5N_2Cl$ (d) C_6H_5OH

18. Which of the following will not undergo diazotisation ?

(a) m-toluidine	(b) aniline
(c) p-amino phenol	(d) benzyl amine

19. Aniline differs from ethylamine by the reaction with

(a) metallic sodium	(b) an alkyl halide
(c) chloroform and caustic potash	(d) nitrous acid

20. When aqueous solution of benzene diazonium chloride is boiled the product formed is

(a) benzyl alcohol	(b) benzene + N_2
(c) phenol	(d) phenyl hydroxylamine

(B) Answer in one or two sentences :

1. How are nitro alkanes prepared ?
2. Write about the functional isomerism of nitro methane ?
3. Give the reduction of nitromethane in (a) acid medium, (b) neutral medium.
4. Mention the uses of nitromethane.
5. How will you convert benzene to m-dinitro benzene ?
6. Explain the electrolytic reduction of nitro benzene ?
7. What are amines ? How are they classified ?
8. Give the structural formula of (i) 2-amino-2-methyl propane.
   (ii) 2-(N, N-dimethyl) amino butane
9. What happens when acetonitrile is hydrolysed ?
10. Write the name and structure of four isomeric amines having the molecular formula C_3H_9N.
11. How will you distinguish between ethylamine and diethylamine ?
12. Write a note on the basicity of amines ?
13. Explain why ethylamine is stronger than ammonia ?
14. What is Gabriel phthalimide synthesis ?
15. How is nitrobenzene converted to aniline ?
16. What happens when aniline is treated with bromine ?
17. What happens when aniline is treated with phosgene ?
18. How will you distinguish between aniline and ethylamine ?

19. Explain why aniline is less basic than methylamine ?

20. How is benzene diazonium chloride prepared ?

21. Write a note on Sandmeyer reaction.

22. How will you synthesise, benzylamine from aniline ?

Ans : Aniline $\xrightarrow[\text{HCl, } 0^{\circ}\text{C}]{NaNO_2}$ Benzene diazonium chloride $\xrightarrow{CuCN}$ cyano benzene $\xrightarrow{LiAlH_4}$ Benzyl amine

23. What are the reagents that would convert the following into Ethyl amines ?

(a) CH_3CONH_2 (b) CH_3CN (c) $CH_3CH_2NO_2$ (d) $CH_3CH = NOH$

24. Account for the following :

(a) $(CH_3)_2NH$ is a stronger base than NH_3

(b) $CH_3CH_2NH_2$ is more basic than CH_3CONH_2

(c) Aniline is less basic than Ethyl amine

(d) On sulphonation of aniline, p-amino benzene sulphonic acid is formed.

25. What is the action of $NaNO_2/HCl$ (aq) at ice cold temperature on

(a) $C_2H_5NH_2$ (b) $C_6H_5NH_2$ (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

26. What happens when ethylamine is treated with

(a) $CHCl_3/NaOH$ (b) CS_2 (c) $COCl_2$ (d) C_6H_5CHO

27. Justify :

(a) Diazo coupling reaction is an example of aromatic electrophilic substitution reaction

(b) Formation of acetanilide from aniline and acetic anhydride is a nucleophilic attack by aniline

(c) Formation of methylamine by ammonolysis of methyl iodide is an example of S_N^2 reaction

(d) Addition of bromine water to aniline, gives a white precipitate.

This is an example of aromatic electrophilic substitution.

28. What is the action of

(a) Diethyl oxalate on Ethylamine
(b) Diethyl oxalate on Diethyl amine
(c) Nitrous acid on Diethyl amine
(d) Nitrous acid on Triethyl amine

29. Account for

(a) Reduction of CH_3CN gives $CH_3CH_2NH_2$ while CH_3NC gives $(CH_3)_2NH$

(b) $(CH_3)_2NH$ requires two molar proportion of CH_3I to give the same crystalline product formed by $(CH_3)_3N$ with one mole of CH_3I

(c) Nitration of aniline with con.HNO_3 may end up with same meta nitro product

(d) p-toluidine is a stronger base than p-nitroaniline.

30. Account for the following :

(a) Nitroethane is soluble in NaOH

(b) Nitro ethane reacts with nitrous acid

(c) 2-methyl-2-nitro propane has neither of the properties.

31. What happens when

(a) nitro ethane is boiled with HCl

(b) nitro benzene is treated with Lithium Aluminium Hydride

(c) When Toluene is treated with fuming nitric acid and sulphuric acid.

32. Account for

(a) Nitration of benzene is easier than nitration of nitrobenzene

(b) Benzaldehyde undergoes condensation with nitro methane in presence of KOH

(c) Nitromethane gives trichloro nitro methane on treatment with chlorine/NaOH while nitro ethane gives only dichloro ethane

33. How can the following conversions be effected ?

(a) Nitro benzene $\longrightarrow$ Nitrosobenzene

(b) Nitro benzene $\longrightarrow$ azoxy benzene

(c) Nitrobenzene $\longrightarrow$ Hydrazobenzene

34. Distinguish between

(a) Nitroethane and ethyl nitrite
(b) Nitro benzene and nitro phenol
(c) Nitro toluene and phenyl, nitromethane

(C) Answer not exceeding sixty words :

1. Write the methods of preparation of nitro methane ?
2. Explain the reduction of nitro methane in different medium.
3. Write a note on the ‘reduction of nitro benzene under different conditions.
4. Explain the mechanism of nitration of nitro benzene.
5. Write the differences between nitro methane and nitro benzene.
6. Give three methods of preparing ethylamine from aceto nitrile ?
7. Distinguish between primary, secondary and tertiary amines.
8. Write the mechanism of ‘Hoffmann’s bromamide reaction’.
9. How do primary, secondary and tertiary amines react with nitrous acid ?
10. Write any three methods of preparing benzylamine ?
11. Comment on the ‘basic nature’ of aniline.
12. Write a note on

    (i) Carbylamine reaction, (ii) Mustard oil reaction, (iii) Acetylation of benzylamine, (iv) Formation of Schiff’s base, (v) Diazotisation reaction.
13. Distinguish between benzylamine and aniline.
14. How are the following compounds obtained from benzene diazonium chloride ?

    (i) phenol, (ii) ester, (iii) p-hydroxy azo benzene.

(D) Solve the problems :

1. Nitrobenzene does not undergo Friedel-Crafts alkylation. Give reasons.

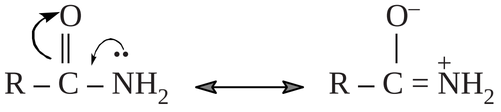
Ans. Due to powerful electron withdrawing effect of the $-NO_2$ group, the benzene ring in $C_6H_5NO_2$ is deactivated towards Friedel Craft’s alkylation and hence it is used as a solvent in many Fridel-Craft’s reaction.

2. Boiling points of nitroalkanes are much higher than those of hydrocarbons of comparable mass - give reasons.

Ans. Nitroalkanes are polar in nature ($\mu = 3 - 4D$) and thus have greater dipolar attraction than hydrocarbons. This results in higher values of b.p. (μ = Dipole moment)

3. Explain why amines are more basic than amides.

Ans. In simple amines the lone pair of electrons is on nitrogen and hence available for protonation. In amides, on the other hand, the electron pair on nitrogen is delocalized to the carbonyl oxygen through resonance.



$$R-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H_2$$

amide

4. An organic compound (A) with molecular formula C_6H_7N gives (B) with HNO_2/HCl at 273 K. The aqueous solution of (B) on heating gives compound (C) which gives violet colour with neutral $FeCl_3$. Identify the compounds A, B and C and write the equations.

   Ans. (A) $C_6H_5NH_2$ - aniline, (B) $C_6H_5N_2Cl$ - benzene diazonium chloride, (C) Phenol

5. Outline the mechanism of

   (a) Nitration of aniline
   (b) Acetylation of aniline to form acetanilide

6. Outline the preparation of

   (a) para nitroaniline from aniline
   (b) tri bromo benzene from tribromo aniline

7. Indicate the mechanism of

   (a) the formation of N-methyl aniline from aniline
   (b) the formation of p–hydroxy azobenene from benzene diazonium chloride

8. Explain the following order of strength of bases.

   (a) $(CH_3)_2\,NH > CH_3NH_2 > NH_3$

   (b) p-toluidine > Aniline > p-nitro aniline

Diazonium chloride

1. How are the following conversions effected ?

   (a) $C_6H_5NH_2 \longrightarrow C_6H_6$
   (b) $C_6H_5NO_2 \longrightarrow C_6H_5OH$

(c) $C_6H_5NH_2 \longrightarrow C_6H_5I$

(d) $C_6H_5NH_2 \longrightarrow C_6H_5NO_2$

2. Starting from aniline how can the following be prepared ?

(a) Chloro benzene	(b) p-hydroxy azobenzene
(c) Benzonitrile	(d) p-amino azo benzene

3. How can the following conversion be effected ?
   (a) Nitrobenzene to anisole
   (b) Chloro benzene to phenyl hydrazine
   (c) Aniline to benzoic acid
   (d) Benzene diazonium chloride to Ethyl benzene
4. Identify the electrophile and nucleophile in the following reactions :

(a) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + KCl$

(b) $C_6H_5N_2Cl + C_6H_5OH \longrightarrow C_6H_5N{=}N{-}C_6H_4OH$

(c) $C_6H_5N_2Cl + CH_3OH \longrightarrow C_6H_5OCH_3$

(d) $C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH$

KEY

1. (a) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{H_3PO_2} C_6H_6$

(b) $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow{HNO_2} C_6H_5N_2Cl \xrightarrow{H_2O} C_6H_5OH$

(c) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{KI} C_6H_5I$

(d) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{NaNO_2} C_6H_5NO_2$

2. (a) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow[Cu_2Cl_2]{HCl} C_6H_5Cl$

(b) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_5H_5N_2Cl \xrightarrow{\text{Phenol}} C_6H_5\text{–}N = N\text{–}C_6H_4\text{–}OH$

(c) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow[Cu_2(CN)_2]{KCN} C_6H_5CN$

(d) $C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{\text{Aniline}} C_6H_5N{=}N\ C_6H_4NH_2$

3. $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{CH_3OH} C_6H_5OCH_3$

$C_6H_5Cl \xrightarrow[HCl]{NH_3} C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow{Sn/HCl} C_6H_5NHNH_2$

$C_6H_5NH_2 \xrightarrow[HCl]{HNO_2} C_6H_5N_2Cl \xrightarrow[Cu_2(CN)_2]{KCN} C_6H_5CN \xrightarrow{H_3O^+} C_6H_5COOH$

$C_6H_5N_2Cl \xrightarrow[Cu_2Br_2]{HBr} C_6H_5Br \xrightarrow[\substack{C_2H_5Br \\ \text{dry ether}}]{Na} C_6H_5\text{–}C_2H_5$

4. (a) I^- - nucleophile
   (b) $C_6H_5N_2^+$ - electrophile
   (c) CH_3OH - nucleophile
   (d) H_2O - nucleophile

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2. A guide book to Mechanism in organic chemistry. - Peters Sykes - Pearson Education Ltd.

21. BIOMOLECULES

LEARNING OBJECTIVES

- *Recognises the importance of carbohydrates, proteins, amino acids and lipids.*
- *Classification of carbohydrates.*
- *Structural elucidation of simple carbohydrates.*
- *Proteins and amino acids.*
- *Classification, structure and functions of lipids in biosystems.*

A living organism is a collection of organic molecules which interact with each other and with their environment in a very unique way. All living organisms are made of one or more cells which are considered as the smallest units of life. Cells are essentially packets of chemicals necessary for life. The compounds present in cells are composed of carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur. Nearly all the carbon compounds found in living cells can be placed into one or another of the following four classes.

(i) Carbohydrates, (ii) Amino acids and proteins, (iii) Nucleic acids and (iv) Lipids.

21.1 CARBOHYDRATES

Carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones. They are naturally occuring organic substances. They are present in both plants and animals. Carbohydrates are formed in the plants by photosynthesis from carbon dioxide and water in sunlight.

Classification :

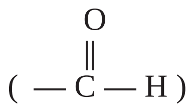
Carbohydrates may be **classified into two broad** groups.

1. Sugars and 2. Non-sugars or polysaccharides.

1. Sugars : Sugars are sweet crystalline substances and soluble in water.

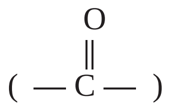
(i) Monosaccharides : The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be hydrolysed into simpler sugars. They may again be classified according to the nature of carbonyl group.

(a) Aldoses, which contain an aldehyde group



$$\left(-\overset{\displaystyle O}{\overset{\|}{C}}-H \right)$$

(b) Ketoses, which contain a keto group

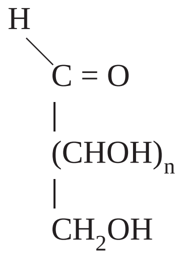


$$\left(-\overset{\displaystyle O}{\overset{\|}{C}}- \right)$$

The aldoses and ketoses are further divided into sub-groups on the basis of the number of carbon atoms in their molecules, as trioses, tetroses, pentoses, hexoses etc.

Thus monosaccharides are generally referred to as aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses etc.

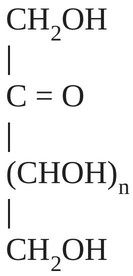
The aldoses and ketoses may be represented by the following general formulae.



$$\begin{array}{l} H \\ \quad\diagdown \\ \quad C=O \\ \quad | \\ \quad (CHOH)_n \\ \quad | \\ \quad CH_2OH \end{array}$$

aldoses

(n = 1, 2, 3, 4, 5)



$$\begin{array}{l} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_n \\ | \\ CH_2OH \end{array}$$

ketoses

(n = 0, 1, 2, 3, 4)

(ii) Oligosaccharides :

Oligosaccharides are sugars that yield two to ten monosaccharide molecules on hydrolysis and are thus again classified into various groups depending upon the number of monosaccharide units formed on hydrolysis.

(a) **Disaccharides :** The disaccharides are sugars which on hydrolysis give **two molecules** of the same or different monosaccharides.

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

(b) **Trisaccharides :** These give **three molecules** of monosaccharides on hydrolysis.

$$\underset{\text{Raffinose}}{C_{18}H_{32}O_{16}} + 2H_2O \longrightarrow \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

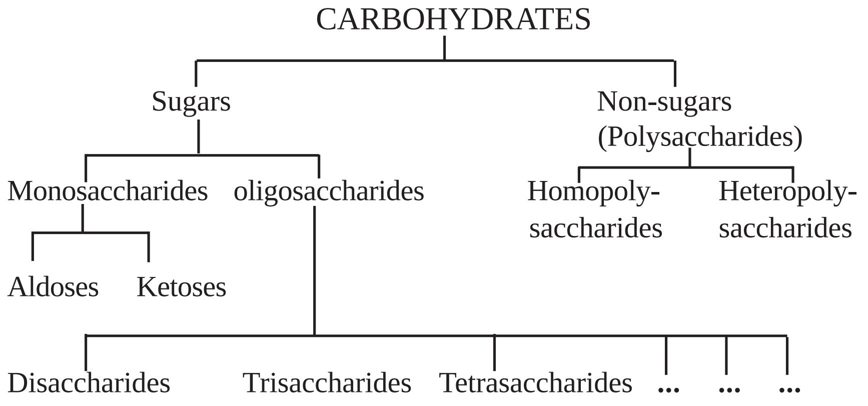
2. Non-sugars (or) Polysaccharides

These are carbohydrates which involve a large number of monosaccharide units linked to each other by **oxide bridges.** These linkages are called glycosidic linkages. The common and widely distributed polysaccharides correspond to the general formula $(C_6H_{10}O_5)_n$. They get hydrolysed to give monosaccharides.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

Thus chemically, polysaccharides are long chain polymers of monosaccharides. Starch, Cellulose and inulin are examples of polysaccharides.

Thus whole of the classification of the carbohydrates may be summarised as below.



21.2 Preparation, structure and uses of Glucose and Fructose

Glucose : Glucose is a monosaccharide and belongs to aldohexose. Glucose is known as **dextrose** because it occurs in nature as the optically active dextro-rotatory isomer. It is also called **grape sugar** as it is found in most sweet fruits especially grapes. It is present in honey also.

Preparation : It is prepared in laboratory by acid hydrolysis of cane sugar in presence of alcohol.

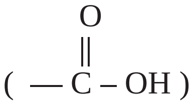
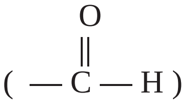
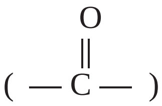
$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Structure of Glucose :

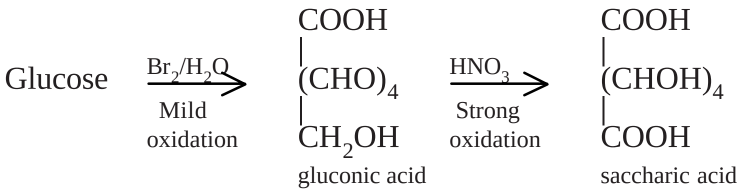
The structure of glucose has been derived from the following facts.

1. Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$.
2. Complete reduction of glucose with concentrated hydriodic acid in the presence of red phosphorous produces n-hexane as the major product. This indicates that the six carbon atoms in the glucose molecule form an unbranched chain of six carbon atoms.

$$\text{Glucose} \xrightarrow[\text{Reduction}]{\text{HI/P}} \underset{\text{n-hexane}}{CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3}$$

3. Glucose readily dissolves in water to give a neutral solution. This indicates that the glucose molecule does not contain a carboxyl  $(- \overset{O}{\overset{\|}{C}} - OH)$ group.
4. Glucose reacts with hydroxylamine to form a monoxime or adds only one mole of HCN to give a cyanohydrin. This reaction indicates the **presence of either an aldehyde**  $(- \overset{O}{\overset{\|}{C}} - H)$ **or a ketone**  $(- \overset{O}{\overset{\|}{C}} -)$ group.

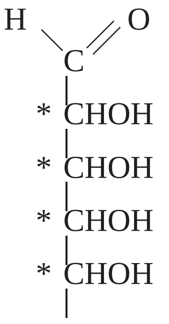
5. Mild oxidation of glucose with bromine water gives gluconic acid. This indicates the **presence of an aldehyde group** since only the aldehyde group can be oxidised to an acid, containing same number of carbon atoms. Since the six carbon atoms in glucose form a consecutive unbranched chain, the aldehyde group, must occupy one end of this chain.
6. Further oxidation of gluconic acid with nitric acid gives saccharic acid. This indicates the **presence of a primary alcoholic group.**



$$\text{Glucose} \xrightarrow[\text{Mild oxidation}]{Br_2/H_2O} \underset{\text{gluconic acid}}{\begin{array}{l} COOH \\ | \\ (CHO)_4 \\ | \\ CH_2OH \end{array}} \xrightarrow[\text{Strong oxidation}]{HNO_3} \underset{\text{saccharic acid}}{\begin{array}{l} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}}$$

7. Glucose **reduces** an ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver or a basic solution of cupric ion (Fehling's solution) to red cuprous oxide. These reactions further confirm the **presence** of a **aldehyde group.**
8. Glucose reacts with acetic anhydride in the presence of pyridine to form a penta acetate. This reaction indicates the **presence of five hydroxyl groups** in a glucose molecule.

From the above evidences we conclude that glucose is a penta hydroxy hexanal (an aldohexose) and can be represented by the following structure.



*C = asymmetric carbon atom

Glucose

(2,3,4,5,6 penta hydroxy hexanal)

FRUCTOSE :

Fructose is present in abundance in fruits and hence it is called as fruit sugar. It is also present in cane sugar and honey alongwith glucose in combined form. Since naturally occuring fructose is laevorotatory, it is also known as laevolose. It is a **ketohexose.**

Preparation :

Fructose is obtained by hydrolysis, of cane sugar with sulphuric acid, along with glucose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{dil.}H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The solution having equal molecules of D (+) glucose and D (–) fructose is termed as **invert sugar** and the process is known as **inversion of sucrose.**

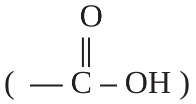
Structure :

The structure of fructose has been derived from the following facts.

1. Elemental analysis and molecular weight determination show that the molecular formula of fructose is $C_6H_{12}O_6$.
2. Complete reduction of fructose with concentrated hydriodic acid in the presence of red phosphorous gives n-hexane as the major product. This **indicates that the six carbon atoms** in the fructose molecule form a **consecutive unbranched chain.**

$$\text{Fructose} \xrightarrow[\text{Reduction}]{\text{HI/P}} \underset{\text{n-hexane}}{CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3}$$

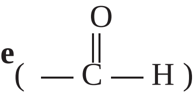
3. Fructose readily dissolves in water to give a neutral solution. This indicates that the fructose molecule **does not contain** a carboxyl group.



$$(-\overset{\overset{\displaystyle O}{\|}}{C} - OH)$$

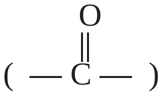
4. Fructose reacts with acetic anhydride in the presence of pyridine to form a penta acetate. This reaction indicates **the presence of five hydroxyl groups** in a fructose molecule.

5. Fructose reacts with hydroxylamine to form a monoxime, or adds only one mole of HCN to give a cyanohydrin. This reaction indicate the **presence of either an aldehyde**



$$(-\overset{\overset{\displaystyle O}{\|}}{C}- H)$$

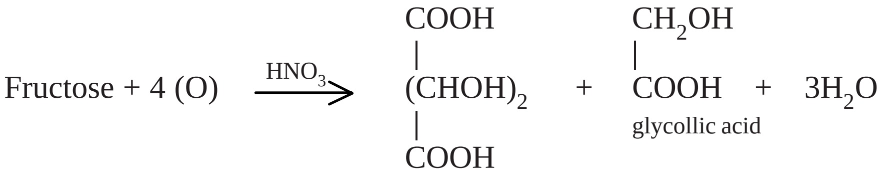
or a ketonic group.



$$(-\overset{\overset{\displaystyle O}{\|}}{C}-)$$

6. Fructose is not oxidised by Bromine water indicating the absence of aldehydic group.

   Oxidation of fructose with concentrated nitric acid yields a mixture of glycollic acid and tartaric acid. Since this oxidation occurs with the rupture of the carbon chain, the **carbonyl group must be present as a ketone group.**



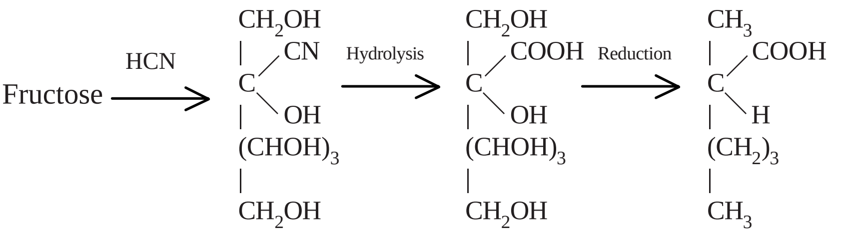
$$\text{Fructose} + 4\,(O) \xrightarrow{HNO_3} \begin{matrix} COOH \\ | \\ (CHOH)_2 \\ | \\ COOH \end{matrix} + \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix} + 3H_2O$$

tartaric acid

glycollic acid

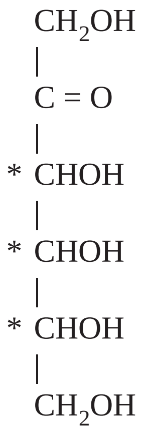
7. Partial reduction of fructose with sodium amalgam and water produces a mixture of two epimeric alcohols, sorbitol and mannitol, **because a new asymmetric centre** is being created at C–2. This confirms the **presence of a ketonic group.**

8. When fructose is treated with HCN, it forms an addition product which upon hydrolysis and subsequent reduction with hydriodic acid and red phosphorous gives 2-methyl-hexanoic acid. This indicates that the ketone group is **adjacent to one of the terminal carbon** atoms.



2-methyl hexanoic acid

From the above evidences we conclude that fructose is a **pentahydroxyhexanone** (a ketohexose) and can be represented by the following structure.



$$\begin{array}{rl} & CH_2OH \\ & | \\ & C = O \\ & | \\ * & CHOH \\ & | \\ * & CHOH \\ & | \\ * & CHOH \\ & | \\ & CH_2OH \end{array}$$

* C = asymmetric carbon atom

fructose

(1, 3, 4, 5, 6, pentahydroxy-2-hexanone)

21.3 DISACCHARIDES

Disaccharides are sweet tasting, crystalline, water-soluble substances, easily hydrolysed by enzymes and dilute mineral acids to two monosaccharide units.

$$\underset{\text{disaccharide}}{C_{12}H_{22}O_{11}} + H_2O \rightleftharpoons \underset{\text{monosaccharide}}{C_6H_{12}O_6} + \underset{\text{monosaccharide}}{C_6H_{12}O_6}$$

The hydrolysis involves a cleavage of glycosidic linkage (i.e.,) in the formation of disaccharide molecule atleast one monosaccharide unit is linked to the other through the carbonyl carbon (C_1 in glucose and C_2 in fructose).

1. Disaccharides linked through the glycosidic carbon atoms of each component (C_1 of glucose to C_2 of fructose) are non-reducing disaccharides. (e.g.,) Sucrose.
2. Disaccharides linked through C_1 of the first to C_4 or C_6 of the second component. (Reducing disaccharides) (e.g.,) Lactose.

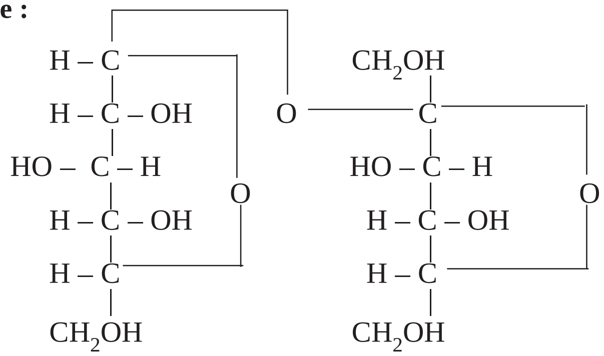
Sucrose : Sucrose is the commonest sugar known. The most important sources are sugar cane and sugar beets.

It is a colourless, odourless crystalline compound. It is soluble in water. It is dextrorotatory. It is a **non-reducing sugar** as it does not reduce Tollen's or Fehling's reagent. Sucrose, on heating slowly and carefully, melts and when allowed to cool, **it solidifies to pale yellow** glassy mass called **'Barley Sugar'.**

When heated to 200^{o}C, it loses water to form **brown amorphous mass called caramel.** On strong heating, it chars to almost pure carbon giving the **smell of burnt sugar.**

It is composed of α-D-glucose unit and β-D-fructose unit. These units are joined by a-β-glycosidic linkage between C-1 of the glucose unit C-2 of the fructose unit.

Structure :



Polysaccharides

Polysaccharides are polymers of monosaccharides. The most important polysaccharides are starch and cellulose. They have a general formula $(C_6H_{10}O_5)_n$.

Starch : Starch is a white amorphous substance with no taste or smell. Starch is present in wheat, corn, barley, rice, potatoes, nuts, etc.

When heated to a temperature between 200–250°C, it changes into dextrin. At higher temperature charring occurs. When boiled with dilute acid, starch ultimately yields glucose.

$$\begin{tikzcd}
\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \arrow[r] & \underset{\text{Dextrin}}{(C_6H_{10}O_5)_n} \arrow[r] & \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \arrow[d] \\
 & & \underset{\text{Glucose}}{C_6H_{12}O_6}
\end{tikzcd}$$

When treated with enzyme, diastase, it yields maltose.

$$2\ (C_6H_{10}O_5)_n + nH_2O \longrightarrow \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Starch solution gives a blue colour with a drop of iodine. The exact chemical nature of starch varies from source to source. Even the starch obtained from same source consists of two fractions (i) amylose and (ii) amylopectin.

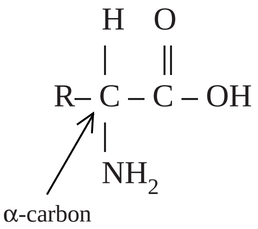
Cellulose : Cellulose is found in all plants and so is the most abundant of all carbohydrates. It is the material used to form cell walls and other structural features of the plants.

Cellulose is insoluble in water and in most of the organic solvents. When it is boiled with dilute H_2SO_4, it is completely hydrolysed into D-glucose.

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

21.4 AMINO ACIDS

An amino acid is bifunctional organic molecule that contains **both a carboxyl group, –COOH as well as an amine group, –NH_2.** Amino acids derived from proteins have the amino group on the alpha (α) carbon, that is, the carbon atom next to the carboxyl group. These α-amino acids may be represented by the following general formula.

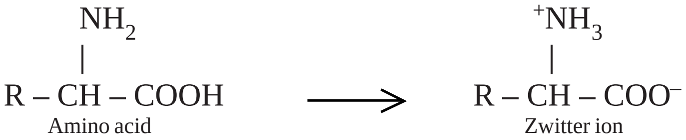


$$R-\underset{\displaystyle NH_2}{\overset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

The **aminoacids** differ in the nature of R-group bonded to α-carbon atom. The nature of R-group determines the properties of proteins.

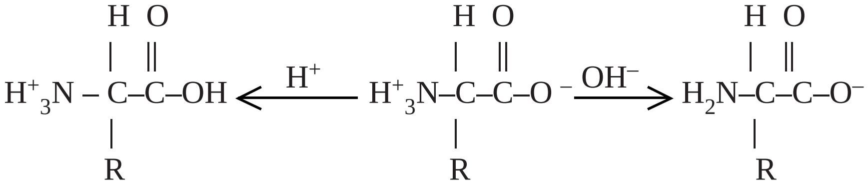
Nearly twenty five amino acids have been obtained from the hydrolysis of proteins. The human body can synthesise some of the amino acids that it needs for maintaining good health. Those amino acids that cannot be synthesised by the body and must be supplied in the diet are called **Essential Amino acids.** The amino acids that can be synthesised from other compounds by the tissues of the body are called **Non - essential Amino acids.**

Except Glycine ($NH_2 - CH_2 - COOH$), all the α-amino acids have an asymmetric carbon atom. Hence, each of these amino acids can exist as optical isomers. Due to the presence of an acidic and a basic group in the same molecule, amino acids exist in an ionic form called a **Zwitter ion** where the proton of –COOH group is transferred to the $-NH_2$ group.



$$\underset{\text{Amino acid}}{R-\overset{\displaystyle NH_2}{\overset{|}{C}H}-COOH} \longrightarrow \underset{\text{Zwitter ion}}{R-\overset{\displaystyle {}^{+}NH_3}{\overset{|}{C}H}-COO^-}$$

Depending on the pH of the solution, the amino acid can donate or accept a proton.



$$H^+{}_3N-\underset{\displaystyle R}{\overset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH \xleftarrow{H^+} H^+{}_3N-\underset{\displaystyle R}{\overset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^- \xrightarrow{OH^-} H_2N-\underset{\displaystyle R}{\overset{\displaystyle H}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

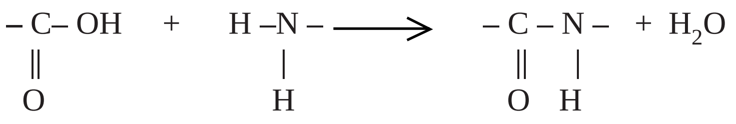
+Low pH cation (Acidic solution) (II)

Zwitter ion (I)

High pH Anion (Basic solution) (III)

When an ionised form of amino acid is placed in an electric field, it will migrate towards the opposite electrode. In acidic solution (low pH), the cation (II) move towards cathode. In basic solution (high pH), the anion (III) move towards anode. The zwitter ion does not move towards any of the electrodes. **The pH at which the amino acid shows no tendency to migrate when placed in an electric field is known as isoelectric point.** This is characteristic of a given amino acid.

Proteins are formed by joining the carboxyl group of one amino acid to the α-amino group of another amino acid. **The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond.**



$$-\underset{\underset{\textstyle O}{\|}}{C}-OH \quad + \quad H-\underset{\underset{\textstyle H}{|}}{N}- \longrightarrow -\underset{\underset{\textstyle O}{\|}}{C}-\underset{\underset{\textstyle H}{|}}{N}- \quad + \quad H_2O$$

Carboxyl group of one amino acid

Amine group of other amino acid

Peptide bond

The product formed by linking amino acid molecules through peptide linkages, – CO – NH –, is called a **peptide.** Peptides are further designated as di, tri, tetra or penta peptides accordingly as they contain two, three, four or five amino acid molecules, same or different, joined together.

In peptide formation the two different amino acid molecules may react in one of the two ways.

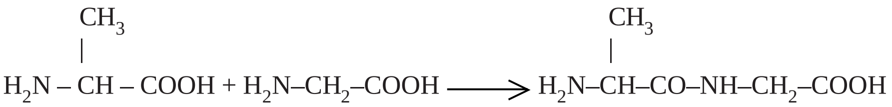
(i) 

$$NH_2-CH_2-COOH + H_2N-\overset{\overset{\textstyle CH_3}{|}}{CH}-COOH \longrightarrow H_2N-CH_2-CO-NH-\overset{\overset{\textstyle CH_3}{|}}{CH}-COOH$$

Glycine

Alanine

Glycylalanine (a dipeptide)

(ii) 

$$H_2N-\overset{\overset{\textstyle CH_3}{|}}{CH}-COOH + H_2N-CH_2-COOH \longrightarrow H_2N-\overset{\overset{\textstyle CH_3}{|}}{CH}-CO-NH-CH_2-COOH$$

Alanine

Glycine

Alanyl glycine (a dipeptide)

21.5 LIPIDS

Lipids form a group of organic compounds which are widely distributed in living system. Lipids are mainly divided into three types, namely simple, compound and derived, depending on the basis of the nature of products obtained on hydrolysis.

Functions of lipids in biosystems :

Fats and oils act as storage of energy in plants and animals. In the animal body, fats are stored in fatty tissues, which are almost pure fat,. Fat give about 2¼ times as much energy as carbohydrates or proteins. Thus, as far as weight is concerned, storage of fat is the most economical way for the body to maintain a reserve energy supply. Fat is a poor conductor of heat. Hence, fat layer under skin serves to prevent losses of heat from the body.

Wax acts as a **protective** agent on the surfaces of animals and plants. Waxy coating on the surface of plants and fruits protects them from excessive loss of moisture and becoming infected with fungi and bacteria.

Phospholipids like lecithins, and cephalins play a greater role in biosystem. The lecithins are required for normal transport and utilisation of other lipids, especially in the liver. lecithin aids in the organisation of the cell structure. Cephalins are found in the brain. **Cephalins** have been implicated in the process of blood coagulation.

Galactolipids occur in considerable amount in the white matter of the brain and of all nervous tissue. The presence of galactose in the glycolipids suggests the importance of milk sugar in the diet of infants and children during the development of the brain and nervous system.

SELF EVALUATION

(A) Choose the correct answer :

1. Which is a mono saccharide among the following :

(a) Sucrose (b) Cellulose (c) Maltose (d) Glucose

2. Identify the reducing sugar.

(a) Sucrose (b) Cellulose (c) Starch (d) Glucose

3. Sucrose is not

(a) a di saccharide (b) a non-reducing sugar.
(c) hydrolysed to only glucose (d) hydrolysed to glucose & fructose

4. Sucrose contains glucose and fructose linked by

(a) $C_1 - C_1$ (b) $C_1 - C_2$ (c) $C_1 - C_4$ (d) $C_1 - C_6$

5. Glucose is not oxidised to gluconic acid by

(a) Br_2/H_2O (b) Fehling solutions
(c) Tollen's reagent (d) Conc. HNO_3

6. Inversion of sucrose refers to

(a) oxidation of sucrose (b) reduction of sucrose
(c) hydrolysis of sucrose to glucose and fructose
(d) polymerisation of sucrose.

7. Glucose forms____________ with acetic anhydride and sodium acetate.

(a) di acetate (b) tetra acetate
(c) penta acetate (d) hexa acetate

8. The amino acid without chiral carbon is

(a) Glysine (b) Alanine (c) Proline (d) Thyrosine

9. The building block of proteins are

(a) α-hydroxy acids (b) α-amino acids
(c) β-hydroxy acids (d) β-amino acids

10. Which is not true of amino acid ?

(a) amino acid forms Zwitter ion
(b) has isoelectric point
(c) dual behaviours
(d) amino acid is insoluble in NaOH solution

11. Two amino acids say A, B- react to give
(a) two dipeptides (b) three dipeptides
(c) four dipeptides (d) only one

12. A di peptide does not have
(a) two peptide units (b) portions of two amino acids
(c) an amido group (d) salt like structure

13. Proteins are not sensitive to
(a) acids (b) bases
(c) elevated temperature (d) water

14. Denaturation does not involve
(a) breaking up of H– bonding in proteins
(b) the loss of biological action of enzyme
(c) the loss of secondary structure
(d) loss of primary structure of proteins

15. Specificity of enzyme is due to
(a) the sequence of amino acids
(b) secondary structure
(c) tertiary structure
(d) all of the above

16. Ultimate products of hydrolysis of proteins is
(a) aniline (b) aliphatic acid
(c) amino acid (d) aromatic acid

17. Proteins are
(a) polypeptides (b) poly acids
(c) poly phenols (d) poly esters

18. Which of the following contains a lipid ?
(a) starch (b) mineral oil
(c) edible oil (d) peptide

19. Which among the following contains triglyceride ?
(a) Wax (b) Cooking oil
(c) Essential oil (d) Albumin

20. Which contains a long chain ester ?
(a) wax (b) cooking oil
(c) turpentine oil (d) cellulose

21. An example of a fatty acid obtained from a cooking oil is

(a) acetic acid	(b) stearic acid
(c) benzoic acid	(d) oxalic acid

22. Which is not a saturated fatty acid ?

(a) Palmitic acid	(b) Stearic acid
(c) Oleic acid	(d) Glyceric acid

23. Alkaline hydrolysis of cooking oil gives

(a) soap	(b) glycerol
(c) fatty acid	(d) both (a) and (b)

24. Hair and nail contains

(a) cellulose	(b) fat
(c) keratin	(d) lipid

25. Important constituent of cell wall is

(a) lipid	(b) cellulose
(c) protein	(d) vitamin

(B) Answer in one or two sentences :

1. What are carbohydrates ? Give two examples
2. Give the structure of sucrose.
3. What is starch ? What are the ultimate hydrolysis products ?
4. What is the action of con. HI on glucose ?
5. What is Saponification ?

(C) Answer not exceeding sixty words :

1. Outline the classification of carbohydrates giving example for each.
2. How can a reducing sugar differ from non-reducing sugar.
3. Distinguish glucose from fructose.
4. Show the formation of a peptide bond with an equation.
5. Mention the biological importance of lipids.
6. Write about the preparation and properties of glucose.
7. How is the structure of fructose determined ?
8. Write short notes on the manufacture of Soap and Wax ?

SUMMARY :

The molecules, which form the basis of our life, are complex molecules called biomolecules which in turn combine and form the living beings, carbohydrates, proteins, nucleic acids and lipids are biomolecules.

Carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones. They are naturally occuring organic substances.

Proteins are complex polyamides formed from amino acids. They are essential for proper growth and maintenance of body. They contain many peptide –CO–NH– bonds. Therefore, proteins are long polymers of amino acids linked by peptide bonds.

Amino acids are the compounds which contain carboxylic acid group and amino group. Amino acids form proteins. Except glycine all the α-amino acids are optically active. The dipolar form of aminoacid is called **Zwitter ion.** The pH at which the amino acid shows no tendency to migrate when placed in an electric field is known as isolectric point.

REFERENCES :

1. Organic Chemistry by Morrison and Boyd.
2. Chemistry of natural products by O.P. Agarwal Vol. I and II.

22. CHEMISTRY IN ACTION

LEARNING OBJECTIVES

- *To know the applications of chemistry for overcoming numerous problems faced by the mankind in various fields.*
- *To learn the uses of chemical compounds in the field of medicine as anesthetics, analgesics, antipyretics, antiseptics and antimalarials, etc.*
- *To study the nature of Dyes and their applications.*
- *To know the applications of chemical compounds as food preservatives, artificial sweetening agents, antioxidants.*
- *To know about rocket propellants.*
- *To learn about the modern chemical industry's chief product - polymers. A detailed account of types, preparation and uses of polymers are given.*

We find ourselves associated with hundreds of things which are either chemical in nature themselves or have their origin in chemistry. Thus, the proverb, ''*Chemistry is not for chemists alone*'' is true in its absolute term. It has helped in overcoming a large number of problems faced by the mankind in recent past, in the fields of food, shelter and disease.

To a common man, however, this contribution of chemistry remains unknown though not unnoticed. Here, in this unit, a brief account of ''*chemistry in action*'' is presented.

22.1 MEDICINAL CHEMISTRY

The chemical compounds which exert, various physiological effects of therapeutic value are called **drugs**. Drugs fall into two general categories :

(i) The drugs that are used in the treatment and cure of any specific disease.

(ii) The drugs that have some characteristic effect on the animal organism, but do not have any remedial effect for a particular disease. This class includes, morphine, cocaine etc.

The effects of the drugs belonging to the first category are described by the term **chemotherapy.**

Treatment of certain diseases by destroying the *invading organism* without damaging the cells of the host, by the use of certain organic compounds in known as chemotherapy.

1. Anaesthetics

The drugs which produce loss of sensation are called anaesthetics. They are classified into two types. (i) **General anaesthetics** are the agent, which bring about loss of all modalities of sensation, particularly pain along with 'reversible' loss of conciousness. (ii) **Local anaesthetics** prevent the pain sensation in localised areas without affecting the degree of conciousness.

(i) Nitrous oxide N_2O : It is a colourless, inoragnic non-irritating gas. It is the safest of the anaesthetic agents. This is used after mixing general anaesthetics like ether.

(ii) Chloroform $CHCl_3$: Volatile liquid. It has pleasent smell and sweet taste. With oxygen it forms a toxic carbonyl chloride. Hence it is not used now.

(iii) Ether : The present form of $C_2H_5–O–C_2H_5$ is a volatile liquid. This is mixed with stabilizer 0.002% propyl halide. After absorption by tissues it attacks the central nervous system and makes unconcious.

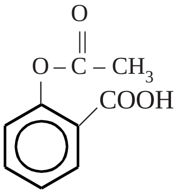
2. Analgesics

Analgesics are the compounds which relieve all sorts of pains without the loss of consciousness. These are also called as *pain killer*, or *pain relievers*. These are effective in headaches, myalgia and arthalgia.

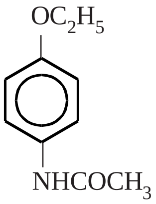
Examples : Aspirin, Novalgin are commonly used analgesics. Aspirin acts both as antipyretic as well as analgesic. Certain narcotics (which produce sleep and unconsciousness) are also used as analgesics.

3. Antipyretics

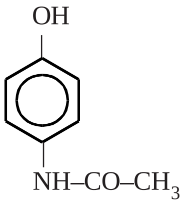
Antipyretics are the compounds which are used for the purpose of reducing fever (lowering the body temperature to the normal). The most common antipyretics are, aspirin, antipyrine, phenacetin, and paracetamol. Their administration (taking these drugs) often leads to perspiration.



acetyl salicylic acid
(aspirin)



phenacetin



p-acetamidophenol
(paracetamol)

4. Antiseptic :

Antiseptic is a substance that rendors micro organisms innocuous by killing them or preventing their growth. This term is used particularly for preparations applied to living tissues.

(i) Iodoform, CHI_3 is used as an antiseptic and its 1% solution is a disinfectant.

(ii) 0.2 percent solution of phenol acts as an antiseptic and its 1% solution is a disinfectant.

5. Antiprotozoals (Antimalarial)

Malaria causes shivering and fever. The body temperature rises to 103-106^{o}F. It causes physical weakness with the side-effects in lever and also causes aneamia.

Extracts of certain plants, specially the roots and stems, are extensively used as antimalarial. Cinchona bark which gives rise to quinine acts as antimalarial. The last antimalarial discovered in 1961 is pyrimethamine. However, quinine, primaquine and chloroquine are some of the best antimalarials.

Chloroquine is used specially to control malarial parasite of the ovale vivax etc. It is not used in curing the disease. It is used as a mixture with other antimalarials.

6. Antibiotics

Many microorganisms (bacteria, fungi and moulds) produce certain chemicals which inhibit the growth or metabolism of some other microorganism. Such chemical compounds are known as *antibiotics.* These need be present only in low concentration to be effective in their antibiotic action. The first antibiotic, discovered by Alexander Fleming in1929, from mould Penicillium notatum, was penicillin.

There are three main sources of antibiotics.

(i) Bacteria (ii) Fungi and (iii) Actinomycetes

Penicillins

Penicillins is the name given to the mixture of natural compounds having the molecular formula $C_9H_{11}N_2O_4$ S - R, and differing only in the nature of R. Depending upon the nature of R, there are at least six natural penicillins.

Uses. Penicillin is extensively used for rheumatic fever, **narrowing of heart wall,** bronchitis, and pneumonia etc.

7. Antacids

Quite often, after eating oily and spicy food, one may feel uncomfortable due to some burning sensation in stomach/food pipe. This is due to the imbalance in the acidity in the stomach.

Certain drug formulations provide relief from such burning sensation. These are known as **antacids.**

Antacids are available in tablet as well as gel/syrup forms. These antacids contain magnesium and aluminium hydroxides, in addition to flavouring agents and colour.

8. Antispasmodics

There are a group of medicines that include natural bellodona alkaloids (atropine, bellodona).

These medicines are used to relieve cramps, spasms of the stomach, intestines and bladder. Some are used with antacid, or other medicine in the treatment of peptic ulcer. These medicine prevent nausea, vomiting and motion sickness. In certain surgical and emergency procedure, these are used to help relax stomach and intestine for certain types of examination or diagnosis.

Example : Anisotropine, Atropine, Dicyclomine, Cindinium cap

22.2 DYES

Since time immemorial, human beings have been fascinated by colour. In the beginning, the colour materials were extracted from vegetable sources. Now a days, such substances are synthesized in factories through simple chemical reactions.

Dyes are coloured compounds used in imparting colour to textiles, food stuffs etc. A dye should have the following characteristics.

(i) It should have a suitable colour.

(ii) It should be able to fix itself or be capable of being fixed to the fabric.

(iii) It should be fast to light.

(iv) It should be resistant to the action of water, dilute acids and alkalies (all detergents and washing soaps are alkaline in nature).

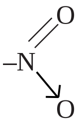
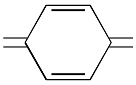
Many natural dyes have been known for a long time. These were obtained from vegetable sources. Now a days, practically all the dyes are synthetic, and are prepared from aromatic compounds obtained from coal tar. Therefore, such dyes are sometimes called as *coal tar dyes*.

22.3 Colour and Structure of Dyes

The relationship between the colour of a substance and its structure was explained by a German scientist Otto Witt (1876) through the **chromophore and auxochrome** theory. According to this theory,

(i) An organic compound appears coloured due to the presence of certain *unsaturated groups* (the groups with multiple bonds) in it. Such groups with multiple bonds are called **chromophores**.

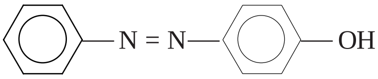
Some typical chromophores are,

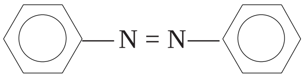
Nitro	 $-N(=O)\rightarrow O$	Azoxy	$-\,N = \overset{\vert}{N} \longrightarrow O$	Carbonyl	$> C = O$
Azo	$-N = N-$	Quininoid		Polyene	$-(HC{=}CH)_n-$

(ii) The compounds containing the chromophore group is called **chromogen.** The colour intensity increases with the number of chromophores or the degree of conjugation. For example, ethene ($CH_2 = CH_2$) is colourless, but the compound $CH_3 - (CH = CH)_6 - CH_3$ is yellow in colour.

(iii) The presence of certain groups which are not chromophores themselves, but deepen the colour of the chromogen. Such supporting groups are called **auxochromes.** Auxochromes may be acidic (phenolic) or basic. Some important auxochromes are –OH, $-NH_2$, –NHR, NR_2.

The presence of an auxochrome in the chromogen molecule is essential to make it a dye. However, if an *auxochrome* is present in the meta position to the chromophore, it does not affect the colour. For example, in the compound p-hydroxyazobenzene (a bright red dye),



(a) azobenzene,  is the chromogen

(b) diazo group, – N = N – is the chromophore

(c) hydroxyl group, –OH is auxochrome

22.4 CHEMICALS IN FOOD

Foods can also be preserved by using certain chemical substances which can kill the food spoiling microorganisms. These chemical substances either directly kill such organisms, or produce some other chemical substance in the preserved food which then kills the food spoiling microorganisms. This method of food preservation is called **chemical preservation.**

A chemical substance which prevents the spoilage of food material by destroying the food-spoiling microorganisms in it is called a **food preservative.**

Sodium benzoate, and potassium metabisulphite are used for food preservation.

Sodium benzoate is used to preserve fruit juices and squash as sodium benzoate is soluble in water. It kills the food spoiling microorganisms.

Potassium meta-bisulphite is used for preserving the colourless fruits like apple, litchi, mango chutney and lemon squashes etc. Potassium metabisulphite reacts with the acid of fruit/juice and produces SO_2, which kills the microorganisms.

22.4.1 Artificial Sweetening Agents

Mono and disaccharides are sweet in taste. Sweetness is commonly associated with sugars. However, certain organic compounds which have been synthesized in laboratories are known to be many times sweeter than canesugar. Such compounds are called **artificial sweetening agents** or **artificial sweetners.**

Some commonly used artificial sweetners are, (i) Saccharin, (ii) Dulcin, (iii) Cyclamate, (iv) Nectarin and (v) Sucralose

22.4.2 Antioxidants

The substances that act against oxidants are called **antioxidants.** Antioxidants thus minimise the damage caused by oxidants. Antioxidants protect us against cardiovascular disease, cancer and cataract and they slow down the effect of ageing. The most important antioxidants are vitamin C, vitamin E and β-carotene.

Antioxidants act as radical inhibitors. These antioxidants can be used as food preservatives. Vitamin E is a naturally occurring preservative found in vegetable oil.

22.5 ROCKET PROPELLANTS

Rockets have been in use since early fifty's. Russians used powerful rockets to put their space vehicles in space. United States of America used Saturn rockets for their Apollo space missions. India has recently launched its satellite launch vehicle SLV-3 from Sriharikota.

Rocket motors are used both in space vehicles and in offensive weapons such as missiles. The *propulsion system* in most space vehicles consists of rocket engines powered by chemical propellants. These also called *rocket propellants*.

Propellants are combustible compounds which on ignition undergo rapid combustion to release large quantities of hot gases. A propellant is a combination of an *oxidiser* and a *fuel*.

Working of a propellant. When a propellant is ignited, it burns to produce a large quantity of hot gases. These gases then come out through the nozzle of the rocket motor. The passage of gases through the nozzle of the rocket motor, provides the necessary thrust for the rocket to move forward according to the Newton's Third law of Motion (to every action, there is an equal and opposite reaction).

Some of the examples for propellents are Hydrazine, Liquid hydrogen, Polyurethane, etc.

22.6 POLYMERS :

A polymer is a giant molecule obtained by intermolecular combination of a large number of small molecules of the same or different type.

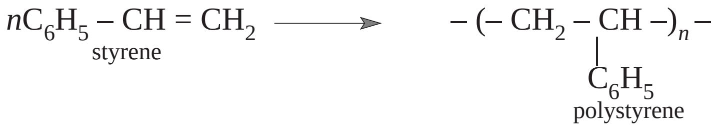
22.6.1 Polyalkenes

Polyalkenes are the polymers which are derived from unsaturated hydrocarbons containing double bond. Important polymers of this class are :

(a) **Polyethylene, (polyethene).** It is obtained from ethylene (ethene). Ethene polymerizes under high pressure and high temperature to give polyethene (also called polyethylene). This polymerization is catalysed by traces of oxygen or organic peroxides.

$$\underset{\text{ethene}}{nCH_2 = CH_2} \xrightarrow[\text{high pressure}]{\text{peroxide, high temp.}} \underset{\text{polyethene}}{-(-CH_2-CH_2-)_n}$$

(b) **Polystyrene.** This polymer is obtained from the monomer styrene ($C_6H_5-CH=CH_2$). The mechanism of polymerization is similar to that for other alkene polymers.



$$\underset{\text{styrene}}{nC_6H_5-CH=CH_2} \longrightarrow \underset{\text{polystyrene}}{-(-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-)_n-}$$

Properties and Uses : Polystyrene is good transparent polymer. It is used for hot-drink cups, toys, household articles, etc.

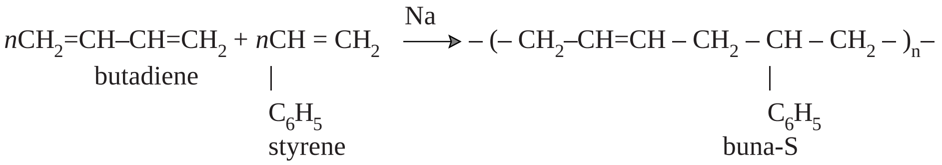
(c) **Synthetic rubbers.** Synthetic rubbers obtained from butadiene are :

(i) Buna rubbers (ii) Butyl rubbers

Buna rubbers

Buna rubbers are obtained as a result of polymerisation / copolymerisation of butadiene with acrylonitrile or styrene. There are two types of Buna-rubbers.

Buna-S. It is obtained by the polymerization of butadiene and styrene in presence of sodium metal.



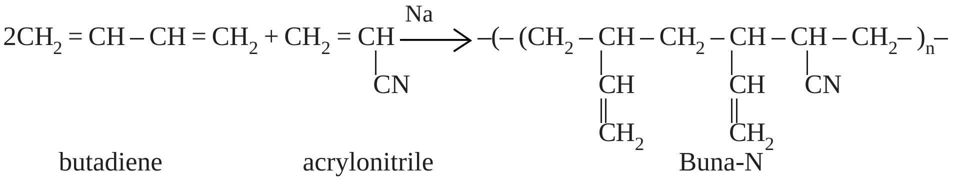
$$\underset{\text{butadiene}}{nCH_2=CH-CH=CH_2} + \underset{\text{styrene}}{n\underset{C_6H_5}{\underset{|}{CH}}=CH_2} \xrightarrow{\text{Na}} \underset{\text{buna-S}}{-(-CH_2-CH=CH-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-)_n-}$$

In the name Buna-S, *Bu* stands for butadiene, *na* for sodium (acting as polymerization initiator), and S- for styrene.

Buna-S is also called General Purpose Rubber Styrene (GRS). In actual practice, it is obtained as a result of copolymerisation of three parts of butadiene with one part of styrene.

Properties and Uses : Neoprene and Buna-S are extremely resistant towards wear and tear and used for the manufacture of tyres, rubber tubes and other mechanical rubber goods.

Buna-N. It is obtained as a result of copolymerisation of two parts of butadiene with one part of acrylonitrile in the presence of sodium metal. The reaction is,



$$2CH_2 = CH - CH = CH_2 + CH_2 = \underset{\substack{|\\ CN}}{CH} \xrightarrow{Na} -(-(CH_2 - \underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH} - CH_2 - \underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH} - \underset{\substack{|\\ CN}}{CH} - CH_2 -)_n-$$

Properties and Uses : Buna-N rubber is hard and extremely resistant to the swelling action of oils (petrol), solvents, heat etc. Therefore, it is used for the manufacture of storage tanks for the solvents.

22.6.2 CONDENSATION POLYMERS

Some important condensation polymers of commercial/industrial interest are described below.

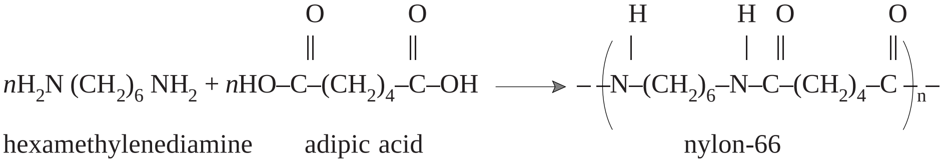
(i) Polyesters

The polymers having ester linkage are known as *polyesters*. Some important polyesters are : Terylene (dacron) and glyptal.

(ii) Polyamides

The polymers having an amide linkage between their monomers are called polyamides. Typical polyamide polymers are described below.

(a) Nylon-66. It is obtained by condensing adipic acid with hexamethylenediamine with the elimination of water molecule. The chain length depends upon the temperature and time for which the process is carried out.



$$nH_2N\,(CH_2)_6\,NH_2 + nHO-\overset{\substack{O\\ \|}}{C}-(CH_2)_4-\overset{\substack{O\\ \|}}{C}-OH \longrightarrow -\left(\overset{\substack{H\\ |}}{N}-(CH_2)_6-\overset{\substack{H\\ |}}{N}-\overset{\substack{O\\ \|}}{C}-(CH_2)_4-\overset{\substack{O\\ \|}}{C}\right)_n-$$

The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore, the product is described as nylon-66.

Properties and Uses : Nylon-66 is a linear polymer, and has very high tensile strength. It shows good resistance to abrasion. Nylon-66 is usually fabricated into sheets, bristles for brushes and in textile. Crinkled nylon fibres are used for making elastic hosiery.

22.6.3 Formaldehyde Resins

Formaldehyde resins are typical thermosetting plastics. This class of plastics include phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins. On heating, these resins become highly cross-linked thereby forming infusible and insoluble product.

SELF EVALUATION

(A) Choose the correct answer :

1. The substance capable of absorbing blue light from the visible radiation would appear
   (a) yellow (b) yellow-green (c) red (d) blue
2. The unsaturated group(s) present in an organic compound is/are called
   (a) chromogens (b) auxochromes
   (c) no specific name (d) chromophores
3. If an auxochrome does not affect the colour of the chromogen, it should be present in the .... position relative to chromophore.
   (a) para- (b) meta- (c) ortho- (d) same-
4. In the compound, $O_2N–C_6H_4–N=N–C_6H_4–N(CH_3)_2$, the chromophore is
   (a) $–NO_2$ (b) – N = N – (c) – NO_2 and –N = N – (d) $–N(CH_3)_2$
5. Diazonium salts give coupling reactions with
   (a) alcohol (b) aromatic amines (c) all amines (d) amines and phenols
6. Substances which bring the body temperature down to normal temperature are known as
   (a) antipyretics (b) analgesics (c) antibiotics (d) none
7. The compound which acts both as antipyretic as well as analgesic is
   (a) phenacetin (b) sulpha drugs (c) paracetamol (d) aspirin

8. A 1% solution of phenol is a
   (a) antiseptic (b) disinfectant (c) antimalarial drug (d) antihistamine
9. The medicine used for curing rabies is called
   (a) antibacterial (b) antiviral (c) antifungal (d) antibiotics
10. The substance that function as a moisture barrier between the skin and the atmosphere is called
   (a) preservative (b) emulsifier (c) anticaking agent (d) moisturizer

(B) Answer in one or two sentences :

1. Define chemotherapy.
2. What are anaesthetics ? Give one example.
3. In what way antipyretics are important.
4. Why Iodoform and phenolic solutions are called antiseptic ?
5. Give two examples of antimalarials.
6. What are antibiotics ?
7. In what way antacids are important ?
8. What are antipasmodics ?
9. Give any two characteristics of Dye.
10. What are chromophores ? Give two examples.
11. What are artificial sweetening agents ? Give two examples.
12. What is Buna-S ?

(C) Answer not exceeding sixty words :

1. Write briefly on antibiotics ? In what way antipasmodics are helpful ?
2. Explain briefly on characteristics of rocket propellants.

SUMMARY :

The chemicals which can cure several diseases are called drugs. Medicinal chemistry deals with action of various chemical compounds which are used as drug. Each drug is unique in character. Anaesthetics, analgesics, antipyretics, antimalarials, antacids, antispasmodics are very important. The nature of dyes and the relation between colour and structure of dyes. Chemicals used in food, are also dealt with. Rocket propellants are discussed briefly. A detailed account on polymers like, addition, condensation polymers, discussed.

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