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HIGHER SECONDARY SECOND YEAR

CHEMISTRY

VOLUME - II

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Department of School Education

Untouchability is Inhuman and a Crime

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Key features …

	Scope of Chemistry	Awareness about higher education avenues in the field of Chemistry	
	**Learning objectives**	Describe the specific competency / performance capability acquired by the learner	
	Do you know	Additional information provided to relate the content to day-to-day life / development in the field	
	Example Problems	Model problems worked out for clear-cut comprehension by the learners	
	Evaluate yourself	To help the students to assess their own conceptual understanding	
	Q.R code	Quick access to concepts, videos, animations and tutorials	
	**ICT**	opens up resources for learning; enables the learners to access, extend transform ideas / informations	
	Summary	A glance on the substance of the unit	
	Concept map	Inter relating the concepts for enabling learners to visualize the essence of the unit	
	Evaluation	To assess the level of understanding through multiple choice question,numerical problems etc…	
	Books for Reference	List of relevant books for further reading	
	Key answers	To help the learners confirm the accuracy of the answers arrived and remedy the gaps in learning	
	Glossary	Important terms are enlisted with equivalent Tamil words	

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UNIT 8

IONIC EQUILIBRIUM



Peter Joseph William Debye

Peter Joseph William Debye was Dutch-American physicist greatly contributed to the theory of electrolyte solutions. He also studied the dipole moments of molecules, Debye won the Nobel Prize in Chemistry (1936) for his contributions to the determination of molecular structure through his investigations on dipole moments and X-rays diffraction.

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Learning Objectives

After studying this unit, the students will be able to

- classify the substances into acids and bases based on Arrhenius, Lowry – Bronsted and Lewis concepts.
- define pH scale and establish relationship between pH and pOH
- describe the equilibrium involved in the ionisation of water.
- explain Ostwald's dilution Law and derive a relationship between the dissociation constant and degree of dissociation of a weak electrolyte.
- recognise the concept of common ion effect and explain buffer action.
- apply Henderson equation for the preparation of buffer solution
- calculate solubility product and understand the relation between solubility and solubility product.
- solve numerical problems involving ionic equilibria.

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INTRODUCTION

We have already learnt the chemical equilibrium in XI standard. In this unit, we discuss the ionic equilibria, specifically acid – base equilibria. Some of the important processes in our body involve aqueous equilibria. For example, the carbonic acid – bicarbonate buffer in the blood.

$$H_3O^+(aq)+HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq)+H_2O(l)$$

We have come across many chemical compounds in our daily life among them acids and bases are the most common. For example, milk contains lactic acid, vinegar contains acetic acid, tea contains tannic acid and antacid tablet contains aluminium hydroxide / magnesium hydroxide. Acids and bases have many important industrial applications. For example, sulphuric acid is used in fertilizer industry and sodium hydroxide in soap industry etc… Hence, it is important to understand the properties of acids and bases.

In this unit we shall learn the definitions of acids and bases and study, their ionisation in aqueous solution. We learn the pH scale and also apply the principles of chemical equilibrium to determine the concentration of the species furnished in aqueous solution by acids and bases.

8.1 Acids and bases

The term 'acid' is derived from the latin word *'acidus'* meaning sour. We have already learnt in earlier classes that acid tastes sour, turns blue litmus to red and reacts with metals such as zinc and produces hydrogen gas. Similarly base tastes bitter and turns red litmus to blue.

These classical concepts are not adequate to explain the complete behaviour of acids and bases. So, the scientists developed the acid – base concept based on their behaviour.

Let us, learn the concept developed by scientists Arrhenius, Bronsted and Lowry and Lewis to describe the properties of acids and bases.

8.1.1 Arrhenius Concept

One of the earliest theories about acids and bases was proposed by swedish chemist Svante Arrhenius. According to him, an acid is a substance that dissociates to give hydrogen ions in water. For example, HCl, H_2SO_4 etc., are acids. Their dissociation in aqueous solution is expressed as

$$HCl(g) \xrightleftharpoons{H_2O} H^+(aq)+Cl^-(aq)$$

The H^+ ion in aqueous solution is highly hydrated and usually represented as H_3O^+, the simplest hydrate of proton $\left[H(H_2O)\right]^+$. We use both $H^+$and H_3O^+ to mean the same.

Similarly a base is a substance that dissociates to give hydroxyl ions in water. For example, substances like NaOH, $Ca(OH)_2$ etc., are bases.

$$Ca(OH)_2 \xrightleftharpoons{H_2O} Ca^{2+}(aq)+2OH^-(aq)$$

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Limitations of Arrhenius concept

i. Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...

ii. This theory does not account for the basic nature of the substances like ammonia (NH_3) which do not possess hydroxyl group.

Evaluate yourself – 1

Classify the following as acid (or) base using Arrhenius concept

i) HNO_3 ii) $Ba(OH)_2$ iii) H_3PO_4 iv) CH_3COOH

8.1.2 Lowry – Bronsted Theory (Proton Theory)

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and H_2O is base. The proton transfer from the acid to base can be represented as

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH_3) acts as a base and H_2O is acid. The reaction is represented as

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

Let us consider the reverse reaction in the following equilibrium

$$\underset{\text{Proton donor (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donor (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

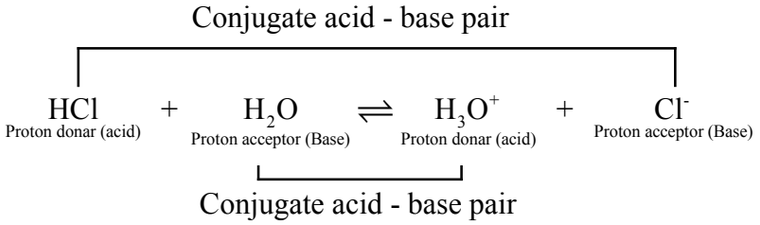
H_3O^+ donates a proton to Cl^- to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

The species that remains after the donation of a proton is a base $(Base_1)$ and is called the conjugate base of the Bronsted acid $(Acid_1)$. In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.

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HCl and Cl^-, H_2O and H_3O^+ are two conjugate acid – base pairs. i.e., Cl^- is the conjugate base of the acid HCl. (or) HCl is conjugate acid of Cl^-. Similarly H_3O^+ is the conjugate acid of H_2O.

Limitations of Lowry – Bronsted theory

i. Substances like BF_3, $AlCl_3$ etc., that do not donate protons are known to behave as acids.

Evaluate yourself – 2

Write a balanced equation for the dissociation of the following in water and identify the conjugate acid –base pairs.

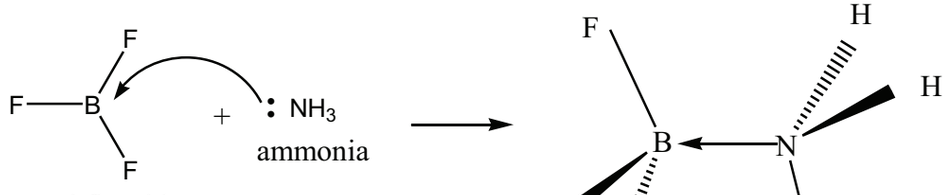
i) NH_4^+ ii) H_2SO_4 iii) CH_3COOH.

8.1.3 Lewis concept

In 1923, Gilbert . N. Lewis proposed a more generalised concept of acids and bases. He considered the electron pair to define a species as an acid (or) a base. According to him, an acid is a species that accepts an electron pair while base is a species that donates an electron pair. We call such species as Lewis acids and bases.

A Lewis acid is a positive ion (or) an electron deficient molecule and a Lewis base is a anion (or) neutral molecule with at least one lone pair of electrons.

Les us consider the reaction between Boron tri fluoride and ammonia



electron deficient - electron pair donar - adduct

(Lewis acid) - (Lewis base)

Here, boron has a vacant 2p orbital to accept the lone pair of electrons donated by ammonia to form a new coordinate covalent bond. We have already learnt that in coordination compounds, the Ligands act as a Lewis base and the central metal atom or ion that accepts a pair of electrons from the ligand behaves as a Lewis acid.

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Lewis acids	Lewis bases
Electron deficient molecules such as $BF_3, AlCl_3, BeF_2$ etc...	Molecules with one (or) more lone pairs of electrons. NH_3, H_2O, R-O-H, R-O-R, R - NH_2
All metal ions Examples: $Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}$ etc...	All anions $F^-, Cl^-, CN^-, SCN^-, SO_4^{2-}$ etc...
Molecules that contain a polar double bond Examples : SO_2, CO_2, SO_3 etc...	Molecules that contain carbon – carbon multiple bond Examples: $CH_2 = CH_2$, $CH \equiv CH$ etc...
Molecules in which the central atom can expand its octet due to the availability of empty d – orbitals Example: $SiF_4, SF_4, FeCl_3$ etc..	All metal oxides CaO, MgO, Na_2O etc...
Carbonium ion $(CH_3)_3 C^+$	Carbanion CH_3^-

Example

Identify the Lewis acid and the Lewis base in the following reactions.

$Cr^{3+} + 6\ H_2O \rightarrow [Cr(H_2O)_6]^{3+}$

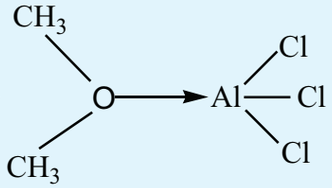
In the hydration of ion, each of six water molecules donates a pair of electron to Cr^{3+} to from the hydrated cation, hexaaquachromium (III) ion, thus, the Lewis acid is Cr^{3+} and the Lewis base H_2O.

Evaluate yourself – 3

Identify the Lewis acid and the Lewis base in the following reactions.

i. $CaO + CO_2 \rightarrow CaCO_3$

ii. $CH_3 - O - CH_3 + AlCl_3 \longrightarrow$



Evaluate yourself – 4

H_3BO_3 accepts hydroxide ion from water as shown below

$H_3BO_3(aq)+H_2O(l) \rightleftharpoons B(OH)_4^- + H^+$

Predict the nature of H_3BO_3 using Lewis concept

8.2 Strength of Acids and Bases

The strength of acids and bases can be determined by the concentration of H_3O^+ (or) OH^- produced per mole of the substance dissolved in H_2O. Generally we classify the acids / bases either as strong or weak. A strong acid is the one that is almost completely dissociated in water while a weak acid is only partially dissociated in water.

Let us quantitatively define the strength of an acid (HA) by considering the following general equilibrium.

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{A^-}$$

The equilibrium constant for the above ionisation is given by the following expression

$$K=\frac{[H_3O^+][A^-]}{[HA][H_2O]} \qquad .....(8.1)$$

We can omit the concentration of H_2O in the above expression since it is present in large excess and essentially unchanged.

$$K_a=\frac{[H_3O^+][A^-]}{[HA]} \qquad .....(8.2)$$

Here, K_a is called the ionisation constant or dissociation constant of the acid. It measures the strength of an acid. Acids such as HCl, HNO_3 etc... are almost completely ionised and hence they have high K_a value (K_a for HCl at 25°C is 2×10^6) Acids such as formic acid ($K_a=1.8\times10^{-4}$ at 25°C), acetic acid (1.8×10^{-5} at 25°C) etc.. are partially ionised in solution and in such cases, there is an equilibrium between the unionised acid molecules and their dissociated ions. Generally, acids with K_a value greater than ten are considered as strong acids and less than one are considered as weak acids.

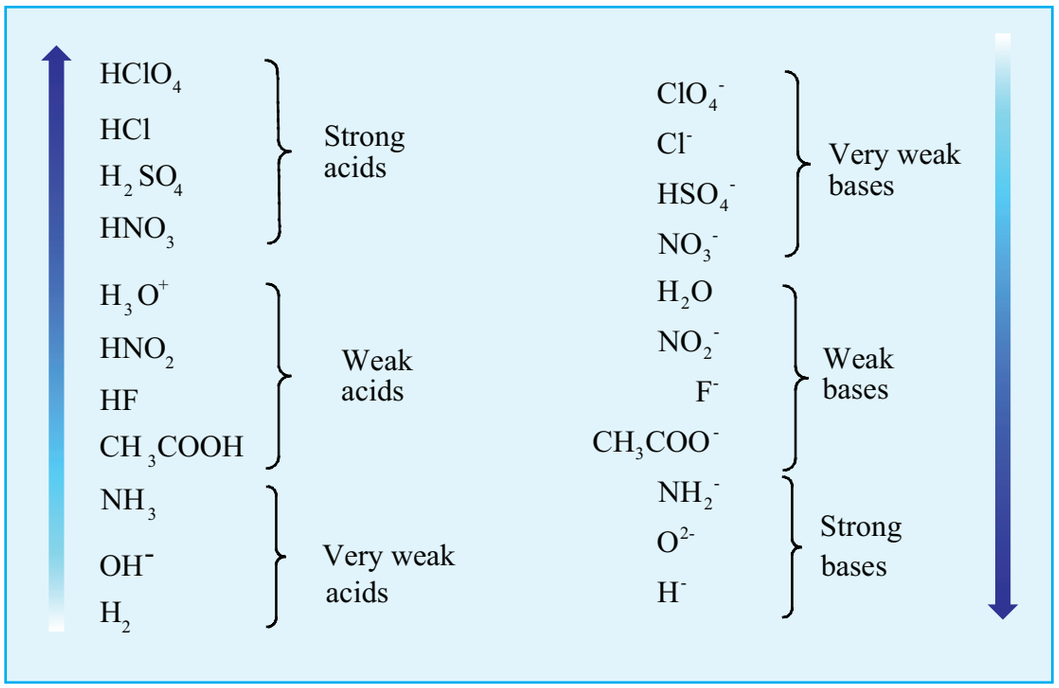
Let us consider the dissociation of HCl in aqueous solution,

$$\underset{\text{acid 1}}{HCl} + \underset{\text{base 2}}{H - OH} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-}$$

As discussed earlier, due to the complete dissociation, the equilibrium lies almost 100% to the right. i.e., the Cl^- ion has only a negligible tendency to accept a proton form H_3O^+ . It means that the conjugate base of a strong acid is a weak base and vice versa.

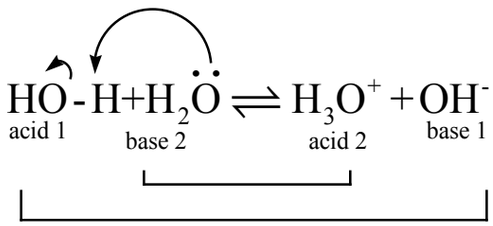
The following table illustrates the relative strength of conjugate acid – base pairs.

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8.3 Ionisation of water

We have learnt that when an acidic or a basic substance is dissolved in water, depending upon its nature, it can either donate (or) accept a proton. In addition to that the pure water itself has a little tendency to dissociate. i.e, one water molecule donates a proton to an another water molecule. This is known as auto ionisation of water and it is represented as below.



Conjugate acid - base pairs

In the above ionisation, one water molecule acts as an acid while the another water molecule acts as a base.

The dissociation constant for the above ionisation is given by the following expression

$$K=\frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad .....(8.3)$$

The concentration of pure liquid water is one. i.e, $[H_2O]^2 = 1$

$$\because\ K_w=[H_3O^+][OH^-] \qquad .....(8.4)$$

Here, K_w represents the ionic product (ionic product constant) of water

It was experimentally found that the concentration of H_3O^+ in pure water is 1×10^{-7} at 25°C. Since the dissociation of water produces equal number of H_3O^+ and OH^-, the concentration of OH^- is also equal to 1×10^{-7} at 25°C.

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Therefore, the ionic product of water at 25°C is

$$K_W=[H_3O]^+[OH^-].....(8.4)$$

$$K_W=(1\times10^{-7})(1\times10^{-7})$$

$$=1\times10^{-14}.$$

Like all equilibrium constants, K_w is also a constant at a particular temperature. The dissociation of water is an endothermic reaction. With the increase in temperature, the concentration of H_3O^+ and OH^- also increases, and hence the ionic product also increases.

K_w values at different temperatures are given in the following below

Temperature (°C)	K_w
0	1.14×10^{-15}
10	2.95×10^{-15}
25	1.00×10^{-14}
40	2.71×10^{-14}
50	5.30×10^{-14}

In neutral aqueous solution like NaCl solution, the concentration of H_3O^+ is always equal to the concentration of OH^- whereas in case of an aqueous solution of a substance which may behave as an acid (or) a base, the concentration of H_3O^+ will not be equal to $[OH^-]$.

We can understand this by considering the aqueous HCl as an example. In addition to the auto ionisation of water, the following equilibrium due to the dissociation of HCl can also exist.

$$HCl+H_2O \rightleftharpoons H_3O^+ + Cl^-$$

In this case, in addition to the auto ionisation of water, HCl molecules also produces H_3O^+ ion by donating a proton to water and hence $[H_3O^+]>[OH^-]$. It means that the aqueous HCl solution is acidic. Similarly, in basic solution such as aqueous NH_3, NaOH etc….. $[OH^-]>[H_3O^+]$.

Example 8.1

Calculate the concentration of OH^- in a fruit juice which contains 2×10^{-3} M, H_3O^+ ion. Identify the nature of the solution.

Given that $H_3O^+=2\times10^{-3}M$

$$K_w=[H_3O^+][OH^-]$$

$$\therefore [OH^-]=\frac{K_w}{[H_3O^+]}=\frac{1\times10^{-14}}{2\times10^{-3}}=5\times10^{-12}M$$

$$2\times10^{-3} >> 5\times10^{-12}$$

i.e., $[H_3O^+]>>[OH^-]$, hence the juice is acidic in nature

Evaluate yourself - 5

At a particular temperature, the K_w of a neutral solution was equal to 4×10^{-14}. Calculate the concentration of $[H_3O^+]$ and $[OH^-]$.

8.4 The pH scale

We usually deal with acid / base solution in the concentration range 10^{-1} to 10^{-7}M. To express the strength of such low concentrations, Sorensen introduced a logarithmic scale known as the pH scale. The term pH is derived from the French word *'Purissance de hydrogene'* meaning, the power of hydrogen. pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = - \log_{10}[H_3O^+] \qquad .....(8.5)$$

The concentration of H_3O^+ in a solution of known pH can be calculated using the following expression.

$$[H_3O^+]=10^{-pH} \text{ (or) } [H_3O^+]= \text{antilog of (-pH)} \qquad .....(8.6)$$

Similarly, pOH can also be defined as follows

$$pOH = - \log_{10}[OH^-] \qquad .....(8.7)$$

As discussed earlier, in neutral solutions, the concentration of $[H_3O^+]$ as well as $[OH^+]$ is equal to 1×10^{-7}M at 25°C. The pH of a neutral solution can be calculated by substituting this H_3O^+concentration in the expression (8.5)

$$pH = - \log_{10}[H_3O^+]$$

$$= - \log_{10} 10^{-7}$$

$$=(-7)(-1)\log_{10}10= +7\ (1)= 7 \qquad [\because \log_{10}10=1]$$

Similary, we can calculate the pOH of a neutral solution using the expression (8.7), it is also equal to 7.

The negative sign in the expression (8.5) indicates that when the concentration of $[H_3O^+]$ increases the pH value decreases. For example, if the $[H_3O^+]$ increases from to 10^{-7}to10^{-5}M, the pH value of the solution decreases from 7 to 5. We know that in acidic solution, $[H_3O^+] > [OH^-]$, i.e., $[H_3O^+] > 10^{-7}$. Similarly in basic solution $[H_3O^+] < 10^{-7}$. So, we can conclude that acidic solution should have pH value less than 7 and basic solution should have pH value greater than 7.

8.4.1 Relation between pH and pOH

A relation between pH and pOH can be established using their following definitions

$$pH=-\log_{10}[H_3O^+] \qquad .....(8.5)$$

$$pOH = - \log_{10}[OH^-] \qquad .....(8.7)$$

Adding equation (8.5) and (8.7)

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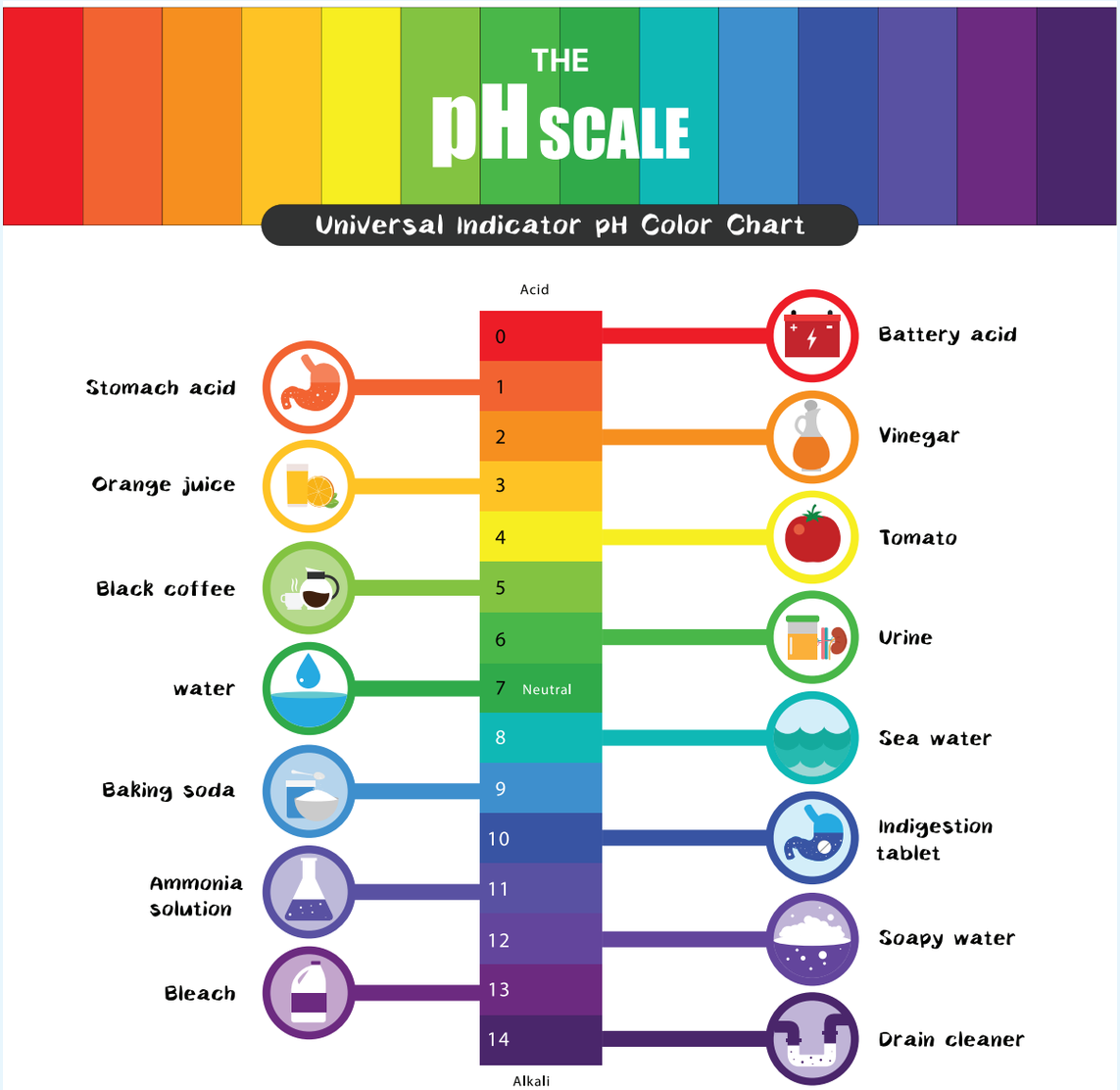


Figure 8.1 The pH scale

$$pH + pOH = -\log_{10}[H_3O^+] - \log_{10}[OH^-]$$

$$= -\left(\log_{10}[H_3O^+] + \log_{10}[OH^-]\right)$$

$$pH+pOH = -\log_{10}[H_3O^+][OH^-] \qquad [\because \log a + \log b = \log ab]$$

We know that $[H_3O^+][OH^-] = K_W$

$$\Rightarrow pH+pOH = -\log_{10} K_W$$

$$\Rightarrow pH+pOH = pK_W \qquad [\because pK_W = -\log_{10} K_w] \qquad .....(8.8)$$

at 25°C, the ionic product of water, $K_W = 1\times10^{-14}$

$$pK_W = -\log_{10} 10^{-14} = 14\log_{10} 10$$

$$= 14$$

$\therefore$ (8.7) $\Rightarrow$ $\therefore$ At 25°C, pH + pOH = 14

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Example 8.2

Calculate the pH of 0.001M HCl solution

$$\underset{0.001\ M}{HCl} \xrightleftharpoons{H_2O} \underset{0.001\ M}{H_3O^+} + \underset{0.001M}{Cl^-}$$

H_3O^+ from the auto ionisation of H_2O $(10^{-7}M)$ is negligible when compared to the H_3O^+ from 10^{-3}M HCl.

Hence $[H_3O^+] = 0.001$ mol dm^{-3}

$$pH = -\log_{10}[H_3O^+]$$
$$= -\log_{10}(0.001)$$
$$= -\log_{10}(10^{-3}) = 3$$

Note: If the concentration of the acid or base is less than 10^{-6} M, the concentration of H_3O^+ produced due to the auto ionisation of water cannot be negleted and in such cases

$[H_3O^+] = 10^{-7}$ (from water) + $[H_3O^+]$ (from the acid)

similarly, $[OH^-] = 10^{-7}$M (from water) + $[OH^-]$ (from the base)

Example 8.3

Calculate pH of 10^{-7} M HCl

If we do not consider $[H_3O^+]$ from the ionisation of H_2O,

then $[H_3O^+] = [HCl] = 10^{-7}$M

i.e., pH = 7, which is a pH of a neutral solution. We know that HCl solution is acidic whatever may be the concentration of HCl i.e, the pH value should be less than 7. In this case the concentration of the acid is very low $(10^{-7}M)$ Hence, the H_3O^+ $(10^{-7}M)$ formed due to the auto ionisation of water cannot be neglected.

so, in this case we should consider $[H_3O^+]$ from ionisation of H_2O

$$[H_3O^+] = 10^{-7} \text{ (from HCl)} + 10^{-7} \text{ (from water)}$$
$$= 10^{-7}\ (1+1) \quad = 2\times10^{-7}$$
$$pH = -\log_{10}[H_3O^+]$$
$$= -\log_{10}(2\times10^{-7}) = -\left[\log 2 + \log 10^{-7}\right]$$
$$= -\log 2 - (-7).\log_{10} 10$$
$$= 7 - \log 2$$
$$= 7 - 0.3010 = 6.6990$$
$$= 6.70$$

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Evaluate yourself - 6

a) Calculate pH of 10^{-8}M H_2SO_4

B) Calculate the concentration of hydrogen ion in moles per litre of a solution whose pH is 5.4

c) Calculate the pH of an aqueous solution obtained by mixing 50ml of 0.2 M HCl with 50ml 0.1 M NaOH

8.5 Ionisation of weak acids

We have already learnt that weak acids are partially dissociated in water and there is an equilibrium between the undissociated acid and its dissociated ions.

Consider the ionisation of a weak monobasic acid HA in water.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Applying law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad .....(8.9)$$

The square brackets, as usual, represent the concentrations of the respective species in moles per litre.

In dilute solutions, water is present in large excess and hence, its concentration may be taken as constant say K. Further H_3O^+ indicates that hydrogen ion is hydrated, for simplicity it may be replaced by H^+. The above equation may then be written as,

$$K_C = \frac{[H^+][A^-]}{[HA] \times K} \quad .....(8.10)$$

The product of the two constants K_C and K gives another constant. Let it be K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad .....(8.11)$$

The constant K_a is called dissociation constant of the acid. Like other equilibrium constants, K_a also varies only with temperature.

Similarly, for a weak base, the dissociation constant can be written as below.

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad ....(8.12)$$

8.5.1 Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c). Degree of dissociation (α) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic acid (CH_3COOH). The dissociation of acetic acid can be represented as

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

The dissociation constant of acetic acid is,

$$k_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad .....(8.13)$$

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation of CH_3COOH	α	-	-
Number of moles at equilibrium	$1-\alpha$	α	α
Equilibrium concentration	$(1-\alpha)\,C$	$\alpha\,C$	$\alpha\,C$

Substituting the equilibrium concentration in equation (8.13)

$$K_a = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$K_a = \frac{\alpha^2 C}{1-\alpha} \qquad .....(8.14)$$

We know that weak acid dissociates only to a very small extent. Compared to one, α is so small and hence in the denominator $(1-\alpha) \simeq 1$. The above expression (8.14) now becomes,

$$K_a = \alpha^2 C$$

$$\Rightarrow \alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}} \qquad .....(8.15)$$

Let us consider an acid with K_a value 4×10^{-4} and calculate the degree of dissociation of that acid at two different concentration 1×10^{-2}M and 1×10^{-4}M using the above expression (8.15)

For 1×10^{-2}M,

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$$\alpha = \sqrt{\frac{4 \times 10^{-4}}{10^{-2}}}$$
$$= \sqrt{4 \times 10^{-2}}$$
$$= 2 \times 10^{-1}$$
$$= 0.2$$

For 1×10^{-4}M acid,

$$\alpha = \sqrt{\frac{4 \times 10^{-4}}{10^{-4}}}$$
$$= 2$$

i.e, When the dilution increases by 100 times, (Concentration decreases from 1×10^{-2}M to 1×10^{-4}M), the dissociation increases by 10 times.

Thus, we can conclude that, when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.

The concentration of $H^+(H_3O^+)$ can be calculated using the K_a value as below.

$[H^+] = \alpha C$ (Refer table) .....(8.16)

Equilibrium molar concentration of $[H^+]$ is equal to αC

$$\therefore [H^+] = \left(\sqrt{\frac{K_a}{C}}\right) C \qquad [\because \text{ equation (8.15)}]$$
$$= \sqrt{\frac{K_a C^2}{C}}$$
$$[H^+] = \sqrt{K_a C} \qquad .....(8.17)$$

Similarly, for a weak base

$$K_b = \alpha^2 C \quad \text{and} \quad \alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \alpha C$$

(or)

$$[OH^-] = \sqrt{K_b C} \qquad .....(8.18)$$

Example 8.4

A solution of 0.10M of a weak electrolyte is found to be dissociated to the extent of 1.20% at 25°C . Find the dissociation constant of the acid.

Given that $\alpha = 1.20\% = \frac{1.20}{100} = 1.2 \times 10^{-2}$ $K_a = \alpha^2 c$

$= (1.2 \times 10^{-2})^2 \ (0.1) = 1.44 \times 10^{-4} \times 10^{-1}$

$= 1.44 \times 10^{-5}$

Example 8.5

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

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

For weak acids,

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

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

$=1.34\times10^{-3}M$ $\quad pH=-\log\left(1.34\times10^{-3}\right)$

$=3-\log1.34$

$=3-0.1271$

$=2.8729\simeq2.87$

Evaluate yourself - 7

K_b for NH_4OH is 1.8×10^{-5}. Calculate the percentage of ionisation of 0.06M ammonium hydroxide solution.

8.6 Common Ion Effect

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further. For example, the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the common ion, CH_3COO^-

Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

$$CH_3COOH(aq)\rightleftharpoons H^+(aq)+CH_3COO^-(aq)$$

However, the added salt, sodium acetate, completely dissociates to produce Na^+ and CH_3COO^- ion.

$$CH_3COONa(aq)\rightarrow Na^+(aq)+CH_3COO^-(aq)$$

Hence, the overall concentration of CH_3COO^- is increased, and the acid dissociation equilibrium is disturbed. We know from Le chatelier's principle that when a stress is applied to a system at equilibrium, the system adjusts itself to nullify the effect produced by that stress. So, inorder to maintain the equilibrium, the excess CH_3COO^- ions combines with H^+ ions to produce much more unionized CH_3COOH i.e, the equilibrium will shift towards the left. In other words, the dissociation of CH_3COOH is suppressed. Thus, the dissociation of a weak acid (CH_3COOH) is suppressed in the presence of a salt (CH_3COONa) containing an ion common to the weak electrolyte. It is called the common ion effect.

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8.7 Buffer Solution

Do you know that our blood maintains a constant pH, irrespective of a number of cellular acid – base reactions. Is it possible to maintain a constant hydronium ion concentration in such reactions? Yes, it is possible due to buffer action.

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action. The buffer containing carbonic acid (H_2CO_3) and its conjugate base HCO_3^- is present in our blood. There are two types of buffer solutions.

1. Acidic buffer solution : a solution containing a weak acid and its salt.

Example : solution containing acetic acid and sodium acetate

2. Basic buffer solution : a solution containing a weak base and its salt.

Example : Solution containing NH_4OH and NH_4Cl

8.7.1 Buffer action

To resist changes in its pH on the addition of an acid (or) a base, the buffer solution should contain both acidic as well as basic components so as to neutralize the effect of added acid (or) base and at the same time, these components should not consume each other.

Let us explain the buffer action in a solution containing CH_3COOH and CH_3COONa. The dissociation of the buffer components occurs as below.

$$CH_3COOH\ (aq) \rightleftharpoons CH_3 - COO^-_{(aq)} + H_3O^+(aq)$$

$$CH_3\ COONa\ (s) \xrightarrow{H_2O_{(l)}} CH_3 - COO^-_{(aq)} + Na^+(aq)$$

If an acid is added to this mixture, it will be consumed by the conjugate base CH_3COO^- to form the undissociated weak acid i.e, the increase in the concentration of H^+ does not reduce the pH significantly.

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH\ (aq)$$

If a base is added, it will be neutralized by H_3O^+, and the acetic acid is dissociated to maintain the equlibrium. Hence the pH is not significantly altered.

$$OH^-(aq) + H_3O^+(aq) \longrightarrow H_2O\ (l)$$

$$CH_3COOH\ (aq) \overset{H_2O\ (l)}{\rightleftharpoons} CH_3COO^-(aq) + H_3O^+(aq)$$

$$OH^-(aq) + CH_3COOH\ (aq) \longrightarrow CH_3COO^-(aq) + H_2O\ (l)$$

These neutralization reactions are identical to those reactions that we have already discussed in common ion effect.

Let us analyse the effect of the addition of 0.01 mol of solid sodium hydroxide to one litre of a buffer solution containing 0.8 M CH_3COOH and 0.8 M CH_3COONa. Assume that the volume change due to the addition of NaOH is negligible. (Given: K_a for CH_3COOH is 1.8×10^{-5})

$$\underset{0.8-\alpha}{CH_3\text{-}COOH(aq)} \overset{H_2O}{\rightleftharpoons} \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.8}{CH_3COONa(aq)} \xrightarrow{H_2O} \underset{0.8}{CH_3COO^-(aq)} + \underset{0.8}{Na^+(aq)}$$

The dissociation constant for CH_3COOH is given by

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

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

The above expression shows that the concentration of H^+ is directly proportional to $\frac{[CH_3COOH]}{[CH_3COO^-]}$.

Let the degree of dissociation of CH_3COOH be α then,

$[CH_3COOH]=0.8-\alpha$ and $[CH_3COO^-]=\alpha+0.8$

$$\therefore [H^+] = K_a \frac{(0.8-\alpha)}{(0.8+\alpha)}$$

$\alpha << 0.8$, $\quad \therefore 0.8-\alpha \simeq 0.8$ and $0.8+\alpha \simeq 0.8$

$$[H^+] = \frac{K_a(0.8)}{(0.8)} \Rightarrow [H^+] = K_a$$

Given that

K_a for CH_3COOH is 1.8×10^{-5}

$\therefore [H^+] = 1.8\times10^{-5}$; pH = $-\log(1.8\times10^{-5})$

$= 5 - \log 1.8$

$= 5 - 0.26$

pH $= 4.74$

Calculation of pH after adding 0.01 mol NaOH to 1 litre of buffer.

Given that the volume change due to the addition of NaOH is negligible $\therefore [OH^-] = 0.01M$. The consumption of OH^- are expressed by the following equations.

$$\underset{0.8-\alpha}{CH_3COOH\,(aq)} \rightleftharpoons \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.8}{CH_3COONa(aq)} \rightarrow \underset{0.8}{CH_3COO^-(aq)} + \underset{0.8}{Na^+(aq)}$$

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$$CH_3COOH + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O\ (l)$$

$$\therefore [CH_3COOH] = 0.8 - \alpha - 0.01 = 0.79 - \alpha$$

$$[CH_3COO^-] = \alpha + 0.8 + 0.01 = 0.81 + \alpha \qquad \alpha << 0.8;$$

$$0.79 - \alpha \simeq 0.79 \text{ and } 0.81 + \alpha \simeq 0.81$$

$$\therefore [H^+] = (1.8 \times 10^{-5}) \times \frac{0.79}{0.81}$$

$$[H^+] = 1.76 \times 10^{-5}$$

$$\therefore pH = -\log (1.76 \times 10^{-5})$$

$$= 5 - \log 1.76$$

$$= 5 - 0.25$$

$$pH = 4.75$$

The addition of a strong base (0.01 M NaOH) increased the pH only slightly ie., from 4.74 to 4.75 . So, the buffer action is verified.

Evaluate yourself - 8

a) Explain the buffer action in a basic buffer containing equimolar ammonium hydroxide and ammonium chloride.

b) Calculate the pH of a buffer solution consisting of 0.4M CH_3COOH and 0.4M CH_3COONa . What is the change in the pH after adding 0.01 mol of HCl to 500ml of the above buffer solution. Assume that the addition of HCl causes negligible change in the volume. Given: ($K_a = 1.8 \times 10^{-5}$.)

8.7.2 Buffer capacity and buffer index

The buffering ability of a solution can be measured in terms of buffer capacity. Vanslyke introduced a quantity called buffer index, β, as a quantitative measure of the buffer capacity. It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)} \qquad \text{....(8.19)}$$

Here,

dB = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

8.7.3 Henderson – Hasselbalch equation

We have already learnt that the concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$[H_3O^+] = K_a \frac{[acid]_{eq}}{[base]_{eq}} \qquad \text{....(8.20)}$$

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The weak acid is dissociated only to a small extent. Moreover, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]} \quad \text{....(8.21)}$$

Here [acid] and [salt] represent the initial concentration of the acid and salt, respectively used to prepare the buffer solution

Taking logarithm on both sides of the equation

$$\log [H_3O^+] = \log K_a + \log \frac{[acid]}{[salt]} \quad \text{....(8.22)}$$

reverse the sign on both sides

$$-\log [H_3O^+] = -\log K_a - \log \frac{[acid]}{[salt]} \quad \text{....(8.23)}$$

We know that

$pH = -\log [H_3O^+]$ and $pK_a = -\log K_a$

$$\Rightarrow pH = pK_a - \log \frac{[acid]}{[salt]} \quad \text{....(8.24)}$$

$$\Rightarrow pH = pK_a + \log \frac{[salt]}{[acid]} \quad \text{....(8.25)}$$

Similarly for a basic buffer, $pOH = pK_b + \log \frac{[salt]}{[base]}$ ....(8.26)

Example 8.6

1. Find the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. K_a for acetic acid is 1.8×10^{-5} .

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

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

$$\therefore pK_a = -\log(1.8 \times 10^{-5}) = 5 - \log 1.8$$
$$= 5 - 0.26$$
$$= 4.74$$

$$\therefore pH = 4.74 + \log \frac{0.20}{0.18}$$
$$= 4.74 + \log {}^{10}/_{9} = 4.74 + \log 10 - \log 9$$
$$= 4.74 + 1 - 0.95 = 5.74 - 0.95$$
$$= 4.79$$

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Example 8.7

What is the pH of an aqueous solution obtained by mixing 6 gram of acetic acid and 8.2 gram of sodium acetate making the volume equal to 500 ml. (Given: K_a for acetic acid is 1.8×10^{-5})

According to Henderson – Hasselbalch equation,

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

$$P^{K_a} = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74 \quad \text{(Refer previous example)}$$

$$[Salt] = \frac{\text{Number of moles of sodium acetate}}{\text{Volume of the solution (litre)}}$$

$$\text{Number of moles of sodium acetate} = \frac{\text{mass of sodium acetate}}{\text{molar mass of sodium acetate}}$$

$$= \frac{8.2}{82} = 0.1$$

$$\therefore [Salt] = \frac{0.1 \text{ mole}}{1/2 \text{ Litre}} = 0.2M$$

$$[acid] = \frac{\left(\frac{\text{mass of } CH_3COOH}{\text{molar mass of } CH_3COOH}\right)}{\text{Volume of solution in litre}}$$

$$= \frac{\left(\frac{6}{60}\right)}{1/2}$$

$$= 0.2M$$

$$\therefore pH = 4.74 + \log \frac{(0.2)}{(0.2)}$$

$$pH = 4.74 + \log 1$$

$$pH = 4.74 + 0 = 4.74$$

Evaluate yourself - 9

a) How can you prepare a buffer solution of pH 9. You are provided with 0.1M NH_4OH solution and ammonium chloride crystals. (Given: pK_b for NH_4OH is 4.7 at 25°C.

b) What volume of 0.6M sodium formate solution is required to prepare a buffer solution of pH 4.0 by mixing it with 100ml of 0.8M formic acid. (Given: pK_a for formic acid is 3.75.)

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8.8 Salt Hydrolysis

When an acid reacts with a base, a salt and water are formed and the reaction is called neutralization. Salts completely dissociate in aqueous solutions to give their constituent ions. The ions so produced are hydrated in water. In certain cases, the cation, anion or both react with water and the reaction is called salt hydrolysis. Hence, salt hydrolysis is the reverse of neutralization reaction.

8.8.1 Salts of strong acid and a strong base

Let us consider the reaction between NaOH and nitric acid to give sodium nitrate and water.

$$NaOH(aq)+HNO_3(aq) \rightarrow NaNO_3(aq)+H_2O(l)$$

The salt $NaNO_3$ completely dissociates in water to produce Na^+ and NO_3^- ions.

$$NaNO_3(aq) \rightarrow Na^+(aq)+NO_3^-(aq)$$

Water dissociates to a small extent as

$$H_2O(l) \rightleftharpoons H^+(aq)+OH^-(aq)$$

Since $[H^+]=[OH^-]$, water is neutral

NO_3^- ion is the conjugate base of the strong acid HNO_3 and hence it has no tendency to react with H^+.

Similarly, Na^+ is the conjugate acid of the strong base NaOH and it has no tendency to react with OH^-.

It means that there is no hydrolysis. In such cases $[H^+]=[OH^-]$ pH is maintained and, therefore, the solution is neutral.

8.8.2 Hydrolysis of Salt of strong base and weak acid (Anionic Hydrolysis).

Let us consider the reactions between sodium hydroxide and acetic acid to give sodium acetate and water.

$$NaOH\ (aq) + CH_3COOH(aq) \rightleftharpoons CH_3COONa(aq)+H_2O(l)$$

In aqueous solution, CH_3COONa is completely dissociated as below

$$CH_3COONa\ (aq) \longrightarrow CH_3COO^-(aq)+Na^+(aq)$$

CH_3COO^- is a conjugate base of the weak acid CH_3COOH and it has a tendency to react with H^+ from water to produce unionised acid .

There is no such tendency for Na^+ to react with OH^-.

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH\ (aq) + OH^-(aq)$ and therefore $[OH^-]>[H^+]$, in such cases, the solution is basic due to hydrolysis and the pH is greater than 7.

Let us find a relation between the equilibrium constant for the hydrolysis reaction (hydrolysis constant) and the dissociation constant of the acid.

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$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad .....(1)$$

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad .....(2)$$

(1) × (2)

$$\Rightarrow K_h.K_a = [H^+][OH^-]$$

we know that $[H^+][OH^-] = K_w$

$$K_h.K_a = K_w$$

K_h value in terms of degree of hydrolysis (h) and the concentration of salt (C) for the equilibrium can be obtained as in the case of ostwald's dilution law. $K_h = h^2C$. and

i.e $[OH^-] = \sqrt{K_h.C}$

pH of salt solution in terms of K_a and the concentration of the electrolyte.

$$pH + pOH = 14$$

$$pH = 14 - p\,OH = 14 - \{-\log [OH^-]\}$$

$$= 14 + \log [OH^-]$$

$$\therefore pH = 14 + \log (K_hC)^{1/2}$$

$$pH = 14 + \log \left(\frac{K_wC}{K_a}\right)^{1/2}$$

$$pH = 14 + \left(\tfrac{1}{2} \log K_w + \tfrac{1}{2} \log C - \tfrac{1}{2} \log K_a\right) \quad [\because K_w = 10^{-14}.$$

$$pH = 14 - 7 + \tfrac{1}{2} \log C + \tfrac{1}{2} pK_a \qquad \tfrac{1}{2} \log K_w = \tfrac{1}{2} \times \log 10^{-14} = \frac{-14}{2}(1) = -7.$$

$$pH = 7 + \tfrac{1}{2} pK_a + \tfrac{1}{2} \log C. \qquad -\log K_a = pK_a]$$

8.8.3 Hydrolysis of salt of strong acid and weak base (Cationic Hydrolysis)

Let us consider the reactions between a strong acid, HCl, and a weak base, NH_4OH, to produce a salt, NH_4Cl, and water

$$HCl\ (aq) + NH_4OH\ (aq) \rightleftharpoons NH_4Cl(aq) + H_2O(l)$$

$$NH_4Cl(aq) \rightarrow NH_4^+ + Cl^-(aq)$$

NH_4^+ is a strong conjugate acid of the weak base NH_4OH and it has a tendency to react with OH^- from water to produce unionised NH_4OH shown below.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH\ (aq) + H^+(aq)$$

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There is no such tendency shown by Cl^- and therefore $[H^+] > [OH^-]$; the solution is acidic and the pH is less than 7.

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the K_h and K_b as

$$K_h . K_b = K_w$$

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration of salt

$$K_h = h^2 C \qquad \text{and } [H^+] = \sqrt{K_h . C}$$

$$[H^+] = \sqrt{\frac{K_w}{K_b} . C}$$

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

$$= - \log \left(\frac{K_w . C}{K_b} \right)^{1/2}$$

$$= - \frac{1}{2} \log K_w - \frac{1}{2} \log C + \frac{1}{2} \log K_b$$

$$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C.$$

8.8.4 Hydrolysis of Salt of weak acid and weak base (Anionic & Cationic Hydrolysis).

Let us consider the hydrolysis of ammonium acetate.

$$CH_3COONH_4(aq) \rightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

In this case, both the cation (NH_4^+) and anion (CH_3COO^-) have the tendency to react with water

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

The nature of the solution depends on the strength of acid (or) base i.e, if $K_a > K_b$; then the solution is acidic and pH < 7, if $K_a < K_b$; then the solution is basic and pH > 7, if $K_a = K_b$; then the solution is neutral.

The relation between the dissociation constant (K_a, K_b) and the hydrolysis constant is given by the following expression.

$$K_a . K_b . K_h = K_w$$

pH of the solution

pH of the solution can be calculated using the following expression,

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b .$$

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Example 8.8

Calculate i) degree of hydrolysis, ii) the hydrolysis constant and iii) pH of 0.1M CH_3COONa solution (pK_a for CH_3COOH is 4.74).

Solution (a) CH_3COONa is a salt of weak acid (CH_3COOH) and a strong base (NaOH). Hence, the solutions is alkaline due to hydrolysis.

$$CH_3COO^-(aq) + H_2O(aq) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

i) $h = \sqrt{\frac{K_w}{K_a \times C}}$

$= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}}$

$h = 7.5 \times 10^{-5}$

Give that $pK_a = 4.74$

$pK_a = -\log K_a$

i.e., K_a = antilog of $(-pK_a)$

= antilog of (-4.74)

= antilog of (-5 + 0.26)

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

[antilog of 0.26 = 1.82 $\simeq$ 1.8]

ii) $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$

$= 5.56 \times 10^{-10}$

iii) $pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$

$= 7 + \frac{4.74}{2} + \frac{\log 0.1}{2} = 7 + 2.37 - 0.5$

$= 8.87$

Evaluate yourself - 10

Calculate the i) hydrolysis constant, ii) degree of hydrolysis and iii) pH of 0.05M sodium carbonate solution (pK_a for HCO_3^- is 10.26).

8.9 Solubility Product

We have come across many precipitation reactions in inorganic qualitative analysis. For example, dil HCl is used to precipitate Pb^{2+} ions as $PbCl_2$ which is sparingly soluble in water. Kidney stones are developed over a period of time due to the precipitation of Ca^{2+} (as calcium oxalate etc…). To understand the precipitation, let us consider the solubility equilibria that exist between the undissociated sparingly soluble salt and its constituent ions in solution.

For a general salt X_mY_n,

$$X_mY_n(s) \overset{H_2O}{\rightleftharpoons} mX^{n+}(aq) + nY^{m-}(aq)$$

The equilibrium constant for the above is

$$K = \frac{[X^{n+}]^m [Y^{m-}]^n}{[X_mY_n]}$$

In solubility equilibria, the equilibrium constant is referred as solubility product constant (or) Solubility product.

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In such heterogeneous equilibria, the concentration of the solid is a constant and is omitted in the above expression

$$K_{sp} = [X^{n+}]^m\ [Y^{m-}]^n$$

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

Solubility product finds useful to decide whether an ionic compound gets precipitated when solution that contains the constituent ions are mixed.

When the product of molar concentration of the constituent ions i.e., ionic product, exceeds the solubility product then the compound gets precipitated.

The expression for the solubility product and the ionic product appears to be the same but in the solubility product expression, the molar concentration represents the equilibrium concentration and in ionic product, the initial concentration (or) concentration at a given time 't' is used.

In general we can summarise as,

Ionic product > K_{sp}, precipitation will occur and the solution is super saturated.

Ionic product < K_{sp}, no precipitation and the solution is unsaturated.

Ionic product = K_{sp}, equilibrium exist and the solution is saturated.

Example 8.9

Indicate find out whether lead chloride gets precipitated or not when 1 mL of 0.1M lead nitrate and 0.5 mL of 0.2 M NaCl solution are mixed? K_{sp} of $PbCl_2$ is 1.2×10^{-5}.

$$PbCl_2^{(s)} \underset{}{\overset{H_2O}{\rightleftharpoons}} Pb^{2+}(aq) + 2Cl^-(aq)$$

Ionic product = $[Pb^{2+}][Cl^-]^2$

Total volume = 1.5 mL

$$\underset{0.1M}{Pb(NO_3)_2} \rightleftharpoons \underset{0.1M}{Pb^{2+}} + 2NO_3^-$$

No of moles of Pb^{2+} = Molarity × volume of the solution in litre

$$= 0.1 \times 1 \times 10^{-3} = 10^{-4}$$

$$[Pb^{2+}] = \frac{\text{number of moles of } Pb^{2+}}{\text{Volume of the solution in L}} = \frac{10^{-4}}{1.5 \times 10^{-3}\ mL} = 6.7 \times 10^{-2} M$$

$$\underset{0.2M}{NaCl} \longrightarrow \underset{0.2M}{Na^+} + \underset{0.2M}{Cl^-}$$

No of moles of Cl^- = $0.2 \times 0.5 \times 10^{-3} = 10^{-4}$

$$[Cl^-] = \frac{10^{-4}\ \text{moles}}{1.5 \times 10^{-3}\ L} = 6.7 \times 10^{-2} M$$

Ionic product = $(6.7 \times 10^{-2})(6.7 \times 10^{-2})^2 = 3.01 \times 10^{-4}$

Since, the ionic product 3.01×10^{-4} is greater than the solubility product (1.2×10^{-5}), $PbCl_2$ will get precipitated.

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8.9.1 Determination of solubility product from molar solubility

Solubility product can be calculated from the molar solubility i.e., the maximum number of moles of solute that can be dissolved in one litre of the solution.

For a solute X_mY_n,

$$X_mY_n(s) \rightleftharpoons mX^{n+}(aq) + nY^{m-}(aq)$$

From the above stoichiometrically balanced equation we have come to know that 1 mole of $X_mY_n(s)$ dissociated to furnish 'm' moles of X^{n+} and 'n' moles of Y^{m-} if 's' is molar solubility of X_mY_n, then

$[X^{n+}]=ms$ and $[Y^{m-}]=ns$

$\therefore K_{sp} = [X^{n+}]^m [Y^{m-}]^n$

$K_{sp}=(ms)^m(ns)^n$

$K_{sp}=(m)^m(n)^n(s)^{m+n}$

Example 8.10

- Establish a relationship between the solubility product and molar solubility for the following

a) $BaSO_4$ b) $Ag_2(CrO_4)$

$BaSO_4(s) \overset{H_2O}{\rightleftharpoons} Ba^{2+}(aq)+SO_4^{2-}(aq)$

$K_{sp}=[Ba^{2+}][SO_4^{2-}]$

$= (s)\ (s)$

$K_{sp} = S^2$

$Ag_2CrO_4(s) \overset{H_2O}{\rightleftharpoons} 2Ag^+(aq)+CrO_4^{2-}(aq)$

$K_{sp}=[Ag^+]^2[CrO_4^{2-}]$

$= (2s)^2(s)$

$K_{sp}=4s^3$

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Summary

- According to Arrhenius, an acid is a substance that dissociates to give hydrogen ions in water.
- According to Lowry and Bronsted concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance.
- According to Gilbert . N. Lewis , an acid is a species that accepts an electron pair while base is a species that donates an electron pair.
- ionic product (ionic product constant) of water (K_w)=$[H_3O^+][OH^-]$
- pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = -\log_{10}[H_3O^+]$$

- when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.
- When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further this is known as common ion effect
- Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid.
- Buffer capacity and buffer index is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)}$$

- Henderson – Hasselbalch equation

For Acid buffer

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

For Basic buffer

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

- Hydrolysis of Salt of strong base and weak acid

$$K_h.K_a = K_w$$

$$pH = 7 + \tfrac{1}{2}pK_a + \tfrac{1}{2}\log C.$$

- Hydrolysis of salt of strong acid and weak base

$$K_h.K_b = K_w$$

$$pH = 7 - \tfrac{1}{2}pK_b - \tfrac{1}{2}\log C.$$

- Hydrolysis of Salt of weak acid and weak base

$$K_a.K_b.K_h = K_w$$

$$pH = 7 + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b.$$

- The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

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EVALUATION

ZFOD8

Choose the correct answer:

1. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.24×10^{-4} mol L^{-1} solubility product of $Ag_2C_2O_4$ is (NEET – 2017)

   a) $2.42\times10^{-8}\ mol^3L^{-3}$ b) $2.66\times10^{-12}\ mol^3L^{-3}$

   c) $4.5\times10^{-11}\ mol^3L^{-3}$ d) $5.619\times10^{-12}\ mol^3L^{-3}$

2. Following solutions were prepared by mixing different volumes of NaOH of HCl different concentrations. (NEET – 2018)

   i. 60 mL $\frac{M}{10}$ HCl + 40mL $\frac{M}{10}$ NaOH ii. 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

   iii. 75 mL $\frac{M}{5}$ HCl + 25mL $\frac{M}{5}$ NaOH iv. 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH

   pH of which one of them will be equal to 1?

   a) iv b) i c) ii d) iii

3. The solubility of $BaSO_4$ in water is $2.42\times10^{-3}gL^{-1}$ at 298K. The value of its solubility product (K_{sp}) will be (NEET -2018). (Given molar mass of $BaSO_4$=233g mol^{-1})

   a) $1.08\times10^{-14}mol^2L^{-2}$ b) $1.08\times10^{-12}mol^2L^{-2}$

   c) $1.08\times10^{-10}mol^2L^{-2}$ d) $1.08\times10^{-8}mol^2L^{-2}$

4. pH of a saturated solution of $Ca(OH)_2$ is 9. The Solubility product (K_{sp}) of $Ca(OH)_2$

   a) 0.5×10^{-15} b) 0.25×10^{-10}

   c) 0.125×10^{-15} d) 0.5×10^{-10}

5. Conjugate base for Bronsted acids H_2O and HF are

   a) OH^- and H_2FH^+, respectively b) H_3O^+ and F^-, respectively

   c) OH^- and F^-, respectively d) H_3O^+ and H_2F^+, respectively

6. Which will make basic buffer?

   a) 50 mL of 0.1M NaOH+25mL of 0.1M CH_3COOH

   b) 100 mL of 0.1M CH_3COOH+100 mL of 0.1M NH_4OH

   c) 100 mL of 0.1M HCl+200 mL of 0.1M NH_4OH

   d) 100 mL of 0.1M HCl+100 mL of 0.1M NaOH

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7. Which of the following fluro compounds is most likely to behave as a Lewis base?

(NEET – 2016)

a) BF_3 b) PF_3 c) CF_4 d) SiF_4

8. Which of these is not likely to act as Lewis base?

a) BF_3 b) PF_3 c) CO d) F^-

9. The aqueous solutions of sodium formate, anilinium chloride and potassium cyanide are respectively

a) acidic, acidic, basic b) basic, acidic, basic

c) basic, neutral, basic d) none of these

10. The percentage of pyridine (C_5H_5N) that forms pyridinium ion (C_5H_5NH) in a 0.10M aqueous pyridine solution (K_b for $C_5H_5N = 1.7\times10^{-9}$) is

a) 0.006% b) 0.013% c) 0.77% d) 1.6%

11. Equal volumes of three acid solutions of pH 1,2 and 3 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

a) 3.7×10^{-2} b) 10^{-6} c) 0.111 d) none of these

12. The solubility of AgCl (s) with solubility product 1.6×10^{-10} in 0.1M NaCl solution would be

a) 1.26×10^{-5}M b) 1.6×10^{-9}M c) 1.6×10^{-11}M d) Zero

13. If the solubility product of lead iodide is 3.2×10^{-8}, its solubility will be

a) 2×10^{-3}M b) 4×10^{-4}M c) 1.6×10^{-5}M d) 1.8×10^{-5}M

14. MY and NY_3, are insoluble salts and have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true with regard to MY and NY_3?

a) The salts MY and NY_3 are more soluble in 0.5M KY than in pure water

b) The addition of the salt of KY to the suspension of MY and NY_3 will have no effect on their solubility's

c) The molar solubilities of MY and NY_3 in water are identical

d) The molar solubility of MY in water is less than that of NY_3

15. What is the pH of the resulting solution when equal volumes of 0.1M NaOH and 0.01M HCl are mixed?

a) 2.0 b) 3 c) 7.0 d) 12.65

16. The dissociation constant of a weak acid is 1×10^{-3}. In order to prepare a buffer solution with a pH = 4, the $\frac{[Acid]}{[Salt]}$ ratio should be

a) 4:3 b) 3:4 c) 10:1 d) 1:10

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17. The pH of 10^{-5}M KOH solution will be

a) 9 b) 5 c) 19 d) none of these

18. $H_2PO_4^-$ the conjugate base of

a) PO_4^{3-} b) P_2O_5 c) H_3PO_4 d) HPO_4^{2-}

19. Which of the following can act as Lowry – Bronsted acid as well as base?

a) HCl b) SO_4^{2-} c) HPO_4^{2-} d) Br^-

20. The pH of an aqueous solution is Zero. The solution is

a) slightly acidic b) strongly acidic c) neutral d) basic

21. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its salts is given by

a) $[H^+]=\frac{K_a[acid]}{[salt]}$ b) $[H^+]= K_a[salt]$ c) $[H^+]=K_a[acid]$ d) $[H^+]=\frac{K_a[salt]}{[acid]}$

22. Which of the following relation is correct for degree of hydrolysis of ammonium acetate?

a) $h = \sqrt{\frac{K_h}{C}}$ b) $h = \sqrt{\frac{K_a}{K_b}}$ c) $h = \sqrt{\frac{K_w}{K_a.K_b}}$ d) $h = \sqrt{\frac{K_a.K_b}{K_w}}$

23. Dissociation constant of NH_4OH is 1.8×10^{-5} the hydrolysis constant of NH_4Cl would be

a) 1.8×10^{-19} b) 5.55×10^{-10} c) 5.55×10^{-5} d) 1.80×10^{-5}

Answer the following questions:

1. What are Lewis acids and bases? Give two example for each.
2. Discuss the Lowry – Bronsted concept of acids and bases.
3. Indentify the conjugate acid base pair for the following reaction in aqueous solution

i) $HS^-(aq) + HF \rightleftharpoons F^-(aq) + H_2S(aq)$ ii) $HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-$

iii) $NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$

4. Account for the acidic nature of $HClO_4$ in terms of Bronsted – Lowry theory, identify its conjugate base.
5. When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]^{2+}_{(aq)}+4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$, among H_2O and NH_3 Which is stronger Lewis base.
6. The concentration of hydroxide ion in a water sample is found to be 2.5×10^{-6}M. Identify the nature of the solution.

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7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas at 25°C to get a solution with $[H_3O^+] = 4 \times 10^{-5} M$. Is the solution neutral (or) acidic (or) basic.
8. Calculate the pH of 0.04 M HNO_3 Solution.
9. Define solubility product
10. Define ionic product of water. Give its value at room temperature.
11. Explain common ion effect with an example
12. Derive an expression for Ostwald's dilution law
13. Define pH
14. Calculate the pH of $1.5 \times 10^{-3} M$ solution of $Ba(OH)_2$
15. 50ml of 0.05M HNO_3 is added to 50ml of 0.025M KOH . Calculate the pH of the resultant solution.
16. The K_a value for HCN is 10^{-9} . What is the pH of 0.4M HCN solution?
17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate Given that $K_a = K_b = 1.8 \times 10^{-5}$
18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base
19. Solubility product of Ag_2CrO_4 is 1×10^{-12} . What is the solubility of Ag_2CrO_4 in 0.01M $AgNO_3$ solution?
20. Write the expression for the solubility product of $Ca_3(PO_4)_2$
21. A saturated solution, prepared by dissolving $CaF_2(s)$ in water, has $[Ca^{2+}] = 3.3 \times 10^{-4} M$ What is the K_{sp} of CaF_2 ?
22. K_{sp} of AgCl is 1.8×10^{-10} . Calculate molar solubility in 1 M $AgNO_3$
23. A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+] = 5 \times 10^{-5}$ and $[CrO_4]^{2-} = 4.4 \times 10^{-4} M$. What is the value of K_{sp} for Ag_2CrO_4 ?
24. Write the expression for the solubility product of Hg_2Cl_2.
25. K_{sp} of Ag_2CrO_4 is 1.1×10^{-12}. what is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4 .
26. Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100L of 0.2 M NaCl are mixed? $K_{sp}(PbCl_2) = 1.2 \times 10^{-5}$.
27. K_{sp} of $Al(OH)_3$ is $1 \times 10^{-15} M$. At what pH does $1.0 \times 10^{-3} M$ Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

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ICT Corner

Buffers and pH

By using this tool you can simulate the preparation of a buffer and measure its pH values

Please go to the URL
http://pages.uoregon.edu/tgreenbo/pHbuffer20.html
(or)
Scan the QR code on the right side

G8KRM

Step – 1

Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage as shown in the figure.

Step – 2

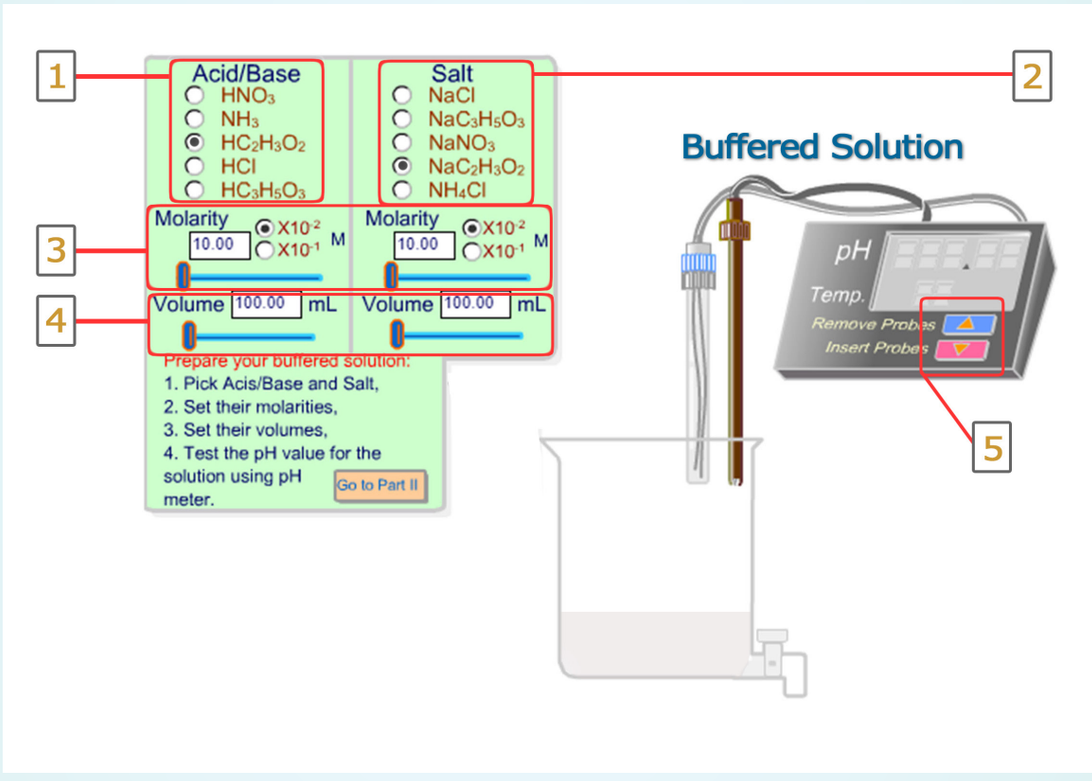
Now you can select a combination of an acid/base (Box 1) and its corresponding salt (Box 2) from the given choices and also select the desired concentrations (Box 3) and volume (Box 4) of these for the buffer.

Step – 3

In order to measure the pH of the made-up buffer click the 'Insert Probe' (Box 5) on the pH meter. Now the pH meter shows the pH. After measuring you need to remove the probe by clicking 'Remove Probe" (Box 5) to make any changes in the composition.

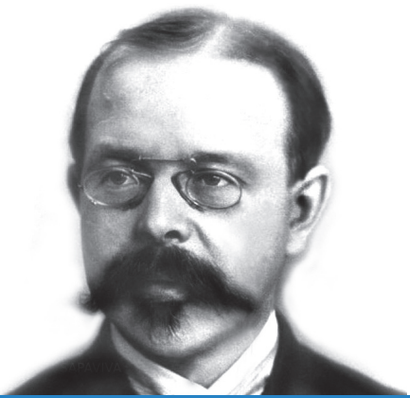
Step – 4

Now you can vary the concentration and volume of the components and see how the pH changes.



UNIT 9

ELECTRO CHEMISTRY



Walther Hermann Nernst

Walther Hermann Nernst, was a German chemist known for his work in thermodynamics, physical chemistry, electrochemistry, and solid state physics. His formulation of the Nernst heat theorem helped to pave the way for the third law of thermodynamics, for which he won the 1920 Nobel Prize in Chemistry. He is also known for developing the Nernst equation in 1887. He also derived the Nernst equation for the electrical potential generated by unequal concentrations of an ion separated by a membrane that is permeable to the ion. His equation is widely used in cell physiology and neurobiology.

WEH6X

Learning Objectives

After learning this unit, the students will be able to

- Recognise the conductivity of electrolylic solution
- Define the terms resistivity, conductivity equivalent and molar conductivity
- Explain the variation of conductivity with concentration
- Apply Kohlrausch law to calculate the conductivity of weak electrolyte at infinite dilution.
- Describe an electrochemical cell
- Differentiate between an electrochemical and electolylic cell
- Represent a galvanic cell using IUPAC cell notation
- Derive Nernst equation and apply it to calculate E_{cell}.
- Define Faraday's Law of electrolysis
- Describe the construction of batteries
- Explain corrosion as an electrochemical process.

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INTRODUCTION

We have come across many materials in our life, and they can be broadly classified into conductors, semiconductors and insulators based on their electrical conductivity. You might have noticed that conducting materials such as copper, aluminium etc., are used to transport electrical energy from one place to another place, and the insulating materials such as PVC, Bakelite etc., in switches, circuit boards etc., Do you know how the electrical energy is generated? We know from first Law of thermodynamics that energy can neither be created nor be destroyed, but one form of energy can be converted into another form. It is not possible to create electrical energy but we can generate electrical energy in many ways i.e., by converting solar energy, wind energy, tidal energy etc.... one such a way is converting chemical energy into electrical energy as in the case of batteries. We cannot imagine a modern technological world without batteries. Hence it is important to know the principles behind this type of energy conversion. The branch of chemistry that deals with the study of electrical energy transport and the inter conversion of electrical and chemical energy is called electrochemistry. Electrochemical reactions are redox reactions and they involve the transfer of electron from one substance to another.

In this unit, we will learn about the electrical conduction, construction of batteries and the thermodynamic principles involved in electro chemical reactions.

9.1 Conductivity of electrolytic solution

We have already learnt that when an electrolyte such as sodium chloride, potassium chloride etc... is dissolved in a solvent like water, the electrolyte is completely dissociated to give its constituent ions (namely cations and anions). When an electric field is applied to such an electrolytic solution, the ions present in the solution carry charge from one electrode to another electrode and thereby they conduct electricity. The conductivity of the electrolytic solution is measured using a conductivity cell. (Fig 9.1)

A conductivity cell consists of two electrodes immersed in an electrolytic solution. It obeys Ohm's law like metallic conductor. i.e., at a constant temperature, the current flowing through the cell (I) is directly proportional to the voltage across the cell (V).

$$\text{i.e., } I \propto V \text{ (or) } I = \frac{V}{R} \Rightarrow V = IR \qquad \text{.....(9.1)}$$

Where 'R' is the resistance of the solution in ohm (Ω)

Here the resistance is the opposition that a cell offers to the flow of electric current through it.

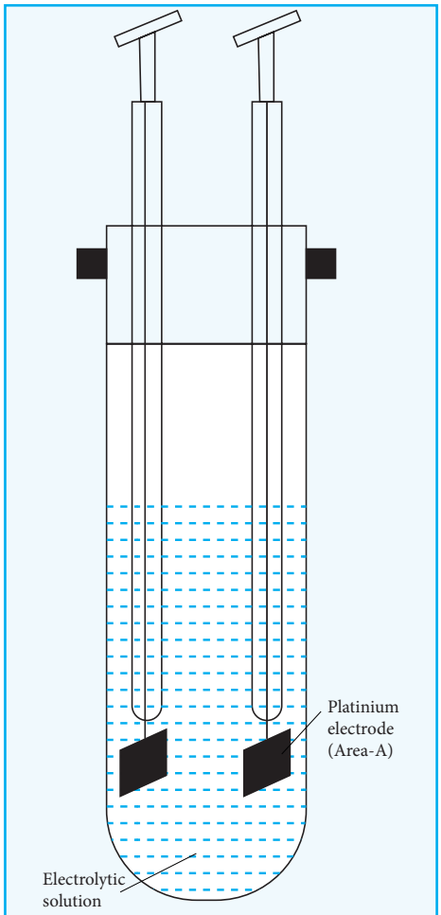


Figure 9.1 conductivity cell

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Resistivity (ρ)

Let us consider a conductivity cell in which the electrolytic solution is confined between the two electrodes having cross sectional area (A) and are separated by a distance 'l' . Like the metallic conductor, the resistance of such an electrolytic solution is also directly proportional to the length (l) and inversely proportional to the cross sectional area (A).

$$R \alpha \frac{l}{A}$$

$$R = \rho \frac{l}{A} \qquad (9.2)$$

Where ρ (rho) is called the specific resistance or resistivity, which depends on the nature of the electrolyte.

If $\frac{l}{A} = 1\ m^{-1}$, then, $\rho = R$. Hence the resistivity is defind as the resistance of an electrolyte confined between two electrodes having unit cross sectional area and are separated by a unit distance. The ratio $\left(\frac{l}{A}\right)$ is called the cell constant, Unit of resistivity is ohm metre (Ωm).

Conductivity

It is more convenient to use conductance rather than resistance. The reciprocal of the resistance $\left(1/R\right)$ gives the conductance of an electrolytic solution. The SI unit of conductance is Siemen (S) .

$$C = \frac{1}{R} \qquad \text{..... (9.3)}$$

Substitude (R) from (9.2) in (9.3)

$$\Rightarrow \text{ i.e., } C = \frac{1}{\rho}.\frac{A}{l} \qquad \text{.....(9.4)}$$

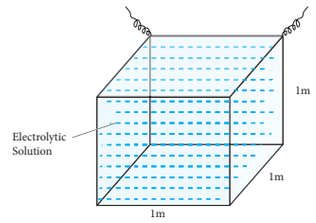


Fig 9.2 conductivity of a cube of an electrolytic solution

The reciprocal of the specific resistance $\left(1/\rho\right)$ is called the specific conductance (or) conductivity. It is represented by the symbol κappa (κ).

Substitute $\frac{1}{\rho} = \kappa$ in equation (9.4) and rearranging

$$\Rightarrow \kappa = C.\left(\frac{l}{A}\right) \qquad \text{.....(9.5)}$$

Unit of κ

$$\kappa = \frac{1}{R} \cdot \frac{l}{A} \left(\frac{1}{\text{ohm}} \cdot \frac{m}{m^2}\right)$$

$$= \text{ohm}^{-1}\ m^{-1} = \text{mho}\ m^{-1} \text{ (or) } Sm^{-1}$$

If $A = 1m^2$ and $l = 1m$; then $\kappa = C$.

The specific conductance is defined as the conductance of a cube of an electrolytic solution of unit dimensions(Fig 9.2). The SI unit of specific conductance is Sm^{-1}.

Example

A conductivity cell has two platinum electrodes separated by a distance 1.5 cm and the cross sectional area of each electrode is 4.5 sq cm. Using this cell, the resistance of 0.5 N

electrolytic solution was measured as 15 Ω . Find the specific conductance of the solution.

Solution

$$\kappa = \frac{1}{R}\left(\frac{l}{A}\right)$$

$$\kappa = \frac{1}{15\Omega} \times \frac{1.5\times10^{-2}\,m}{4.5\times10^{-4}\,m^2}$$

$$= 2.22\ Sm^{-1}$$

$l = 1.5\ cm = 1.5\times10^{-2}m$

$A = 4.5\ cm^2 = 4.5\times(10^{-4})m^2$

$R = 15\Omega$

9.1.1 Molar conductivity (Λ_m)

Solutions of different concentrations have different number of electrolytic ions in a given volume of solution and hence they have different specific conductance. Therefore a new quantity called molar conductance (Λ_m) was introduced.

Let us imagine a conductivity cell in which the electrodes are separated by $1m$ and having $V\ m^3$ of electrolytic solution which contains 1 mole of electrolyte. The conductance of such a system is called the molar conductance (Λ_m)

We have just learnt that the conductance of $1\ m^3$ electrolytic solution is called the specific conductance (κ). Therefore, the conductance of the above mentioned $V\ m^3$ solution (Λ_m) is given by the following expression.

$$(\Lambda_m) = \kappa \times V \qquad .....(9.6)$$

We know that, molarity (M) = $\frac{\text{Number of moles of solute (n)}}{\text{Volume of the solution (V in } dm^3)}$

Therefore, Volume of the solution containing one mole of solute = $\frac{1}{M}\ \left(mol^{-1}\ L\right)$

$$\therefore \text{Volume per } m^3\ (V) = \frac{10^{-3}}{M}\left(mol^{-1}m^3\right)$$

Substitute (9.7) in (9.6)

$$(9.6) \Rightarrow \Lambda_m = \frac{\kappa\ (Sm^{-1}) \times 10^{-3}}{M}\ mol^{-1}m^{-3} \qquad .....(9.8)$$

The above relation defines the molar conductance in terms of the specific conductance and the concentration of the electrolyte.

Example

Calculate the molar conductance of 0.025M aqueous solution of calcium chloride at $25^{\circ}C$. The specific conductance of calcium chloride is $12.04 \times 10^{-2}\ Sm^{-1}$.

$$\text{Molar conductance} = \Lambda_m = \frac{\kappa\ (Sm^{-1}) \times 10^{-3}}{M}\ mol^{-1}m^3$$

$$= \frac{(12.04 \times 10^{-2}\ Sm^{-1}) \times 10^{-3}\left(mol^{-1}m^3\right)}{0.025}$$

$$= 481.6\times10^{-5}\ Sm^2mol^{-1}$$

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Evaluate yourself : 1

Calculate the molar conductance of 0.01M aqueous KCl solution at 25°C . The specific conductance of KC*l* at 25°C is 14.114×10^{-2} Sm^{-1}.

9.1.2 Equivalent conductance (Λ)

Equivalent conductance is defined as the conductance of 'V' m^3 of electrolytic solution containing one gram equivalent of electrolyte in a conductivity cell in which the electrodes are one metre apart.

The relation between the equivalent conductance and the specific conductance is given below.

$$\Lambda = \frac{\kappa\ (Sm^{-1}) \times 10^{-3}\ (\text{gram equivalent})^{-1}\ m^3}{N} \qquad .....(9..9)$$

Where κ the specific conductance and N is the concentration of the electrolytic solution expressed in normality.

Evaluate yourself : 2

The resistance of 0.15N solution of an electrolyte is 50 Ω. The specific conductance of the solution is 2.4 Sm^{-1}. The resistance of 0.5 N solution of the same electrolyte measured using the same conductivity cell is 480 Ω. Find the equivalent conductivity of 0.5 N solution of the electrolyte.

Given that

$R_1 = 50\ \Omega$ $\qquad$ $R_2 = 480\ \Omega$

$\kappa_1 = 2.4\ Sm^{-1}$ $\qquad$ $\kappa_2 = ?$

$N_1 = 0.15\ N$ $\qquad$ $N_2 = 0.5\ N$

$$\Lambda = \frac{\kappa_2\ (Sm^{-1}) \times 10^{-3}\ (\text{gram equivalent})^{-1}\ m^3}{N}$$

$$= \frac{0.25 \times 10^{-3}\ S\ (\text{gram equivalent})^{-1}\ m^2}{0.5}$$

$$\Lambda = 5 \times 10^{-4}\ Sm^2\ \text{gram equivalent}^{-1}$$

we know that

$$\kappa = \frac{\text{Cell constant}}{R}$$

$$\therefore \frac{\kappa_2}{\kappa_1} = \frac{R_1}{R_2}$$

$$\kappa_2 = \kappa_1 \times \frac{R_1}{R_2}$$

$$= 2.4\ Sm^{-1} \times \frac{50\ \Omega}{480\ \Omega}$$

$$= 0.25\ Sm^{-1}$$

9.1.3 Factors affecting electrolytic conductance

If the interionic attraction between the oppositely charged ions of solutes increases, the conductance will decrease.

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- Solvent of higher dielectric constant show high conductance in solution.
- Conductance is inversely proportional to the Viscosity of the medium. i.e., conductivity increases with the decrease in viscosity.
- If the temperature of the electrolytic solution increases, conductance also increases. Increase in temperature increases the kinetic energy of the ions and decreases the attractive force between the oppositely charged ions and hence conductivity increases.
- Molar conductance of a solution increases with increase in dilution. This is because, for a strong electrolyte, interionic forces of attraction decrease with dilution. For a weak electrolyte, degree of dissociation increases with dilution.

9.1.4 Measurement of conductivity of ionic solutions

We have already learnt to measure the specific resistance of a metallic wire using a metre bridge in your physics practical experiment. We know that it works on the principle of wheatstone bridge. Similarly, the conductivity of an electrolytic solution is determined by using a wheatstone bridge arrangement in which one resistance is replaced by a conductivity cell filled with the electrolytic solution of unknown conductivity.

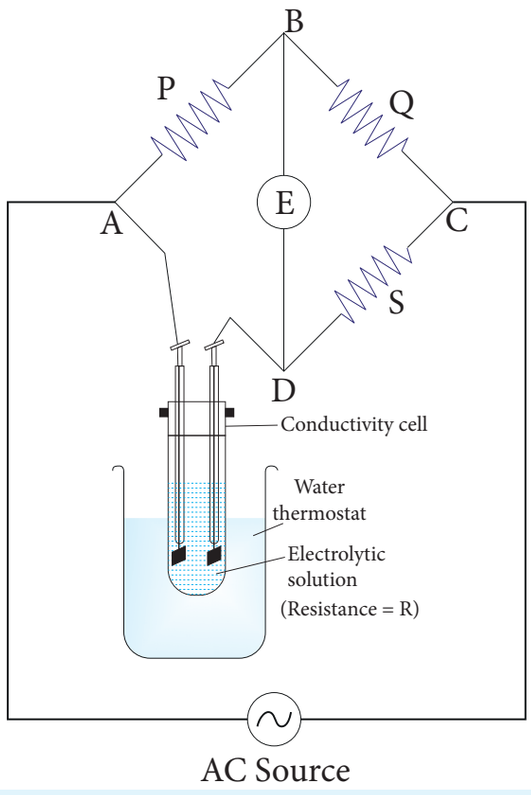


Fig 9.3 Schematic diagram of a conductivity cell in a wheatstone bridge circuit

In the measurement of specific resistance of a metallic wire, a DC power supply is used. Here, if we apply DC current through the conductivity cell, it will lead to the electrolysis of the solution taken in the cell. So, AC current is used for this measurement to prevent electrolysis.

A wheatstone bridge is constituted using known resistances P, Q, a variable resistance S and conductivity cell (Let the resistance of the electrolytic solution taken in it be R) as shown in the figure 9.3. An AC source (550 Hz to 5 KHz) is connected between the junctions A and C. Connect a suitable detector E (Such as the telephone ear piece detector) between the junctions 'B' and 'D'.

The variable resistance 'S' is adjusted until the bridge is balanced and in this conditions there is no current flow through the detector.

Under balanced condition,

$$\frac{P}{Q} = \frac{R}{S}$$

$$\therefore R = \frac{P}{Q} \times S \qquad \text{.....(9.10)}$$

The resistance of the electrolytic solution (R) is calculated from the known resistance values P, Q and the measured 'S' value under balanced condition using the above expression (9.10).

Conductivity calculation

Specific conductance (or) conductivity of an electrolyte can be calculated from the resistance value using the following expression.

$$\kappa = \frac{1}{R}\left(\frac{l}{A}\right) \qquad [\because \text{ equation 9.5}]$$

The value of the cell constant $\frac{l}{A}$ is usually provided by the cell manufacturer. Alternatively the cell constant may be determined using KCl solution whose concentration and specific conductance are known.

Example

The resistance of a conductivity cell is measured as 190 Ω using 0.1M KCl solution (specific conductance of 0.1M KCl is 1.3 Sm^{-1}). When the same cell is filled with 0.003M sodium chloride solution, the measured resistance is 6.3KΩ. Both these measurements are made at a particular temperature. Calculate the specific and molar conductance of NaCl solution.

Given that

$\kappa = 1.3\ Sm^{-1}$ (for 0.1M KCl solution)

$R = 190\ \Omega$

$$\left(\frac{l}{A}\right) = \kappa \,.\, R = (1.3\ Sm^{-1})\ (190\ \Omega)$$

$$= 247\ m^{-1}$$

$$\kappa_{(NaCl)} = \frac{1}{R_{(NaCl)}}\left(\frac{l}{A}\right)$$

$$= \frac{1}{6.3\ K\Omega}\ (247\ m^{-1}) \qquad 6.3K\Omega = 6.3 \times 10^{3}\Omega$$

$$= 39.2 \times 10^{-3}\ Sm^{-1}$$

$$\Lambda_m = \frac{\kappa \times 10^{-3}\ mol^{-1}\ m^3}{M}$$

$$= \frac{39.2 \times 10^{-3}\ (Sm^{-1}) \times 10^{-3}\ (mol^{-1}m^3)}{0.003}$$

$$\Lambda_m = 13.04 \times 10^{-3}\ Sm^2\ mol^{-1}$$

9.2 Variation of molar conductivity with concentration

Friedrich Kohlraush studied the molar conductance of different electrolytes at different concentrations. He observed that, increase of the molar conductance of an electrolytic solution with the increase in the dilution. One such experimental results is given in the following table for better understanding.

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Concentration (M)	Molar conductance ($\times 10^{-3} Sm^2\ mol^{-1}$)		
	NaCl	KCl	HCl
0.1	10.674	12.896	39.132
0.01	11.851	14.127	41.20
0.0001	12.374	14.695	42.136

Based on the above such results, Kohlraush deduced the following empirical relationship between the molar conductance (Λ_m) and the concentration of the electrolyte (C).

$$\Lambda_m = \Lambda_m^\circ - k\sqrt{C} \qquad .....(9.11)$$

The above equation represents a straight line of the form $y = mx + c$. Hence, the plot of Λ_m Vs $\sqrt{C}$ gives a straight line with a negative slope of –k and the y intercept, Λ_m°. Where Λ_m° is called the limiting molar conductivity. i.e., the molar conductance approaches a limiting value in very dilute solutions.

For strong electrolytes such as KCl, NaCl etc., the plot, Λ_m Vs $\sqrt{C}$, gives a straight line as shown in the graph (9.4). It is also observed that the plot is not a linear one for weak electrolytes.

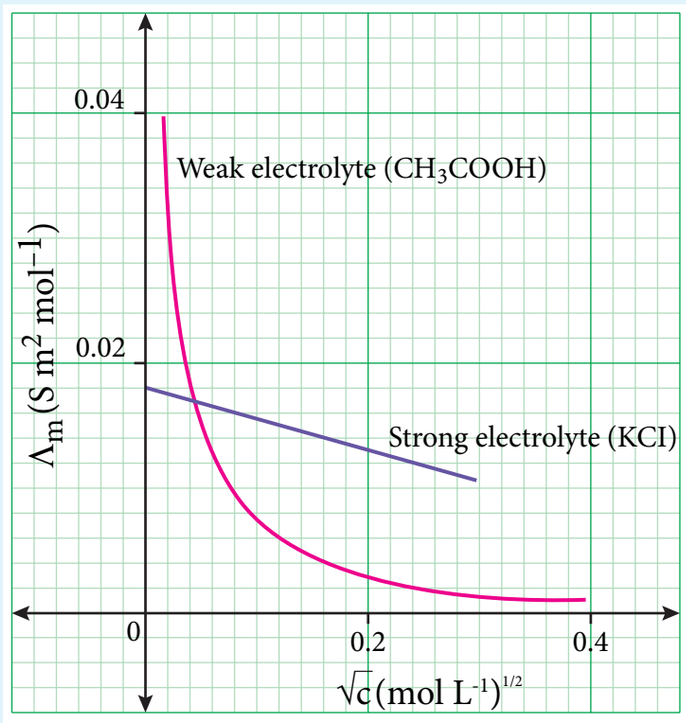


Figure 9.4 Variation of molar conductance with concentration

For a strong electrolyte, at high concentration, the number of constituent ions of the electrolyte in a given volume is high and hence the attractive force between the oppositely charged ions is also high. Moreover the ions also experience a viscous drag due to greater solvation. These factors attribute for the low molar conductivity at high concentration. When the dilution increases, the ions are far apart and the attractive forces decrease. At infinite dilution the ions are so far apart, the interaction between them becomes insignificant and hence, the molar conductivity increases and reaches a maximum value at infinite dilution.

For a weak electrolyte, at high concentration, the plot is almost parallel to concentration axis with slight increase in conductivity as the dilution increases. When the concentration

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approaches zero, there is a sudden increase in the molar conductance and the curve is almost parallel to Λ_m axis. This is due to the fact that the dissociation of the weak electrolyte increases with the increase in dilution (Ostwald dilution law). Λ_m^0 values for strong electrolytes can be obtained by extrapolating the straight line, as shown in figure (9.4). But the same procedure is not applicable for weak electrolytes, as the plot is not a linear one, Λ_m^0 values of the weak electrolytes can be determined using Kohlraush's law.

9.2.1 Debye - Huckel and Onsager equation

We have learnt that at infinite dilution, the interaction between the ions in the electrolyte solution is negligible. Except this condition, electrostatic interaction between the ions alters the properties of the solution from those expected from the free – ions value. The influence of ion-ion interactions on the conductivity of strong electrolytes was studied by Debye and Huckel. They considered that each ion is surrounded by an ionic atmosphere of opposite sign, and derived an expression relating the molar conductance of strong electrolytes with the concentration by assuming complete dissociation. Later, the equation was further developed by Onsager. For a uni – univalent electrolyte the Debye Huckel and Onsager equation is given below.

$$\Lambda_m = \Lambda_m^0 - \left(A + B\,\Lambda_m^0\right)\sqrt{C} \qquad .....(9.12)$$

Where A and B are the constants which depend only on the nature of the solvent and temperature. The expression for A and B are

$$A = \frac{82.4}{\sqrt{DT}\,\eta} \quad ; \quad B = \frac{8.20 \times 10^5}{\sqrt[3]{DT}}$$

Here, D is the dielectric constant of the medium, η the viscosity of the medium and T the temperature in Kelvin.

9.2.2 Kohlraush's law

The limiting molar conductance Λ_m^0 is the basis for kohlraush law. At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the sum of the limiting molar conductivities of its constituent ions. i.e., the molar conductivity is due to the independent migration of cations in one direction and anions in the opposite direction.

For a uni – univalent electrolyte such as NaCl, the Kohlraush's law is expressed as

$$\left(\Lambda_m^0\right)_{NaCl} = \left(\lambda_m^0\right)_{Na^+} + \left(\lambda_m^0\right)_{Cl^-}$$

In general, according to Kohlraush's law, the molar conductivity at infinite dilution for a electrolyte represented by the formula $A_x\ B_y$, is given below.

$$\left(\Lambda_m^0\right)_{A_xB_y} = x\left(\lambda_m^0\right)_{A^{y+}} + y\left(\lambda_m^0\right)_{B^{x-}} \qquad .....(9.13)$$

Kohlraush arrived the above mentioned relationship based on the experimental observations such as the one as shown in the table. These result show that at infinite dilution each constituent ion of the electrolyte makes a definite contribution towards the molar conductance of the electrolyte irrespective of nature of other ion with which it is associated

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i.e.,

$(\Lambda^{\circ}_m)_{KCl} - (\Lambda^{\circ}_m)_{NaCl} = 149.86 - 126.45$

$\{(\lambda^{\circ}_m)_{K^+} + (\lambda^{\circ}_m)_{Cl^-}\} - \{(\lambda^{\circ}_m)_{Na^+} + (\lambda^{\circ}_m)_{Cl^-}\} = 23.41$

$(\lambda^{\circ}_m)_{K^+} - (\lambda^{\circ}_m)_{Na^+} = 23.41$

Similarly, we can conclude that $(\lambda^{\circ}_m)_{Br^-} - (\lambda^{\circ}_m)_{Cl^-} = 2.06$

Electrolyte	Λ^0_m at 298 K	Difference
KCl	149.86	
NaCl	126.45	23.41
KBr	151.92	
NaBr	128.51	23.41
KNO_3	144.96	
$NaNO_3$	121.55	23.41

Electrolyte	Λ^0_m at 298 K	Difference
KBr	151.92	
KCl	149.86	2.06
NaBr	128.51	
NaCl	126.45	2.06
LiBr	117.09	
LiCl	115.03	2.06

Applications of Kohlrausch's Law

1. Calculation of molar conductance at infinite dilution of a weak electrolyte.

It is impossible to determine the molar conductance at infinite dilution for weak electrolytes experimentally. However, the same can be calculated using Kohlraush's Law.

For example, the molar conductance of CH_3COOH, can be calculated using the experimentally determined molar conductivities of strong electrolytes HCl, NaCl and CH_3COONa .

$$\Lambda^{\circ}_{CH_3COONa} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{CH_3COO^-} \quad .....(1)$$

$$\Lambda^{\circ}_{HCl} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} \quad .....(2)$$

$$\Lambda^{\circ}_{NaCl} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} \quad .....(3)$$

Equation (1) + Equation (2) – Equation (3) gives,

$$\left(\Lambda^{\circ}_{CH_3COONa}\right) + \left(\Lambda^{\circ}_{HCl}\right) - \left(\Lambda^{\circ}_{NaCl}\right) = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{CH_3COO^-}$$

$$= \Lambda^{\circ}_{CH_3COOH}$$

2. Calculation of degree of dissociation of weak electrolytes

The degree of dissociation of weak electrolyte can be calculated from the molar conductivity at a given concentration and the molar conductivity at infinite dilution using the following expression

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} \quad .....(9.14)$$

Calculation of dissociation constant using Λ_m values. According to Ostwald dilution Law,

$$K_a = \frac{\alpha^2 C}{(1-\alpha)} \quad .....(9.15)$$

Substitute α value in the above expression (9.15)

$$K_a = \frac{\Lambda^2_m \, C}{\Lambda^{o\,2}_m \left(1 - \frac{\Lambda_m}{\Lambda^{\circ}_m}\right)}$$

$$K_a = \frac{\Lambda_m^2 \, C}{\Lambda_m^{\circ 2} \frac{(\Lambda_m^{\circ} - \Lambda_m)}{\Lambda_m^{\circ}}}$$

$$\Rightarrow K_a = \frac{\Lambda_m^2 C}{\Lambda_m^{\circ} (\Lambda_m^{\circ} - \Lambda_m)} \qquad .....(9.16)$$

3. Calculation of solubility of sparingly soluble salts

Substances like AgCl, $PbSO_4$ etc., are sparingly soluble in water. The solubility product of such substances can be determined using conductivity measurements.

Let us consider AgCl as an example

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-]$$

Let the concentration of $[Ag^+]$ be 'C' $molL^{-1}$.

As per the stoichiometry, if $[Ag^+] = C$, then $[Cl^-]$ also equal to 'C' mol L^{-1}.

$$K_{sp} = C.C$$

$$\Rightarrow K_{sp} = C^2$$

We know that the concentration (in mol dm^{-3}) is related to the molar and specific conductance by the following expressions

$$\Lambda^0 = \frac{\kappa \times 10^{-3}}{C \text{ (in mol } L^{-1})}$$

(or)

$$C = \frac{\kappa \times 10^{-3}}{\Lambda^0}$$

Substitute the concentration value in the relation $K_{sp} = C^2$

$$K_{sp} = \left(\frac{\kappa \times 10^{-3}}{\Lambda^{\circ}} \right)^2 \qquad .....(9.17)$$

9.3 Electrochemical Cell

Electrochemical cell is a device which converts chemical energy into electrical energy and vice versa. It consists of two separate electrodes which are in contact with an electrolyte solution. Electrochemical cells are mainly classified into the following two types.

1. **Galvanic Cell (Voltaic cell)** : It is a device in which a spontaneous chemical reaction generates an electric current i.e., it converts chemical energy into electrical energy. It is commonly known as a battery.
2. **Electrolytic cell** : It is a device in which an electric current from an external source drives a nonspontaneous reaction i.e., it converts electrical energy into chemical energy.

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9.3.1 Galvanic cell

We have already learnt in XI standard that when a zinc metal strip is placed in a copper sulphate solution, the blue colour of the solution fades and the copper is deposited on the zinc strip as red – brown crust due to the following spontaneous chemical reaction.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu\ (s)$$

The energy produced in the above reaction is lost to the surroundings as heat.

In the above redox reaction, Zinc is oxidised to Zn^{2+} ions and the Cu^{2+} ions are reduced to metallic copper. The half reactions are represented as below.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation)}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \quad \text{(reduction)}$$

If we perform the above two half reactions separately in an apparatus as shown in figure 9.5, some of the energy produced in the reaction will be converted into electrical energy. Let us understand the function of a galvanic cell by considering Daniel cell as an example. It uses the above reaction for generation of electrical energy.

The separation of half reaction is the basis for the construction of Daniel cell. It consists of two half cells.

Oxidation half cell

A metallic zinc strip that dips into an aqueous solution of zinc sulphate taken in a beaker, as shown in Figure 9.5.

Reduction half cell

A copper strip that dips into an aqueous solution of copper sulphate taken in a beaker, as shown in Figure 9.5.

Joining the half cells

The zinc and copper strips are externally connected using a wire through a switch (k) and a load (example: volt meter). The electrolytic solution present in the cathodic and anodic compartment are connected using an inverted U tube containing agar-agar gel mixed with an inert electrolytes such as KCl, Na_2SO_4 etc., The ions of inert electrolyte do not react with other ions present in the half cells and they are not either oxidised (or) reduced at the electrodes. The solution in the salt bridge cannot get poured out, but through which the ions can move into (or) out of the half cells.

When the switch (k) closes the circuit, the electrons flows from zinc strip to copper strip. This is due to the following redox reactions which are taking place at the respective electrodes.

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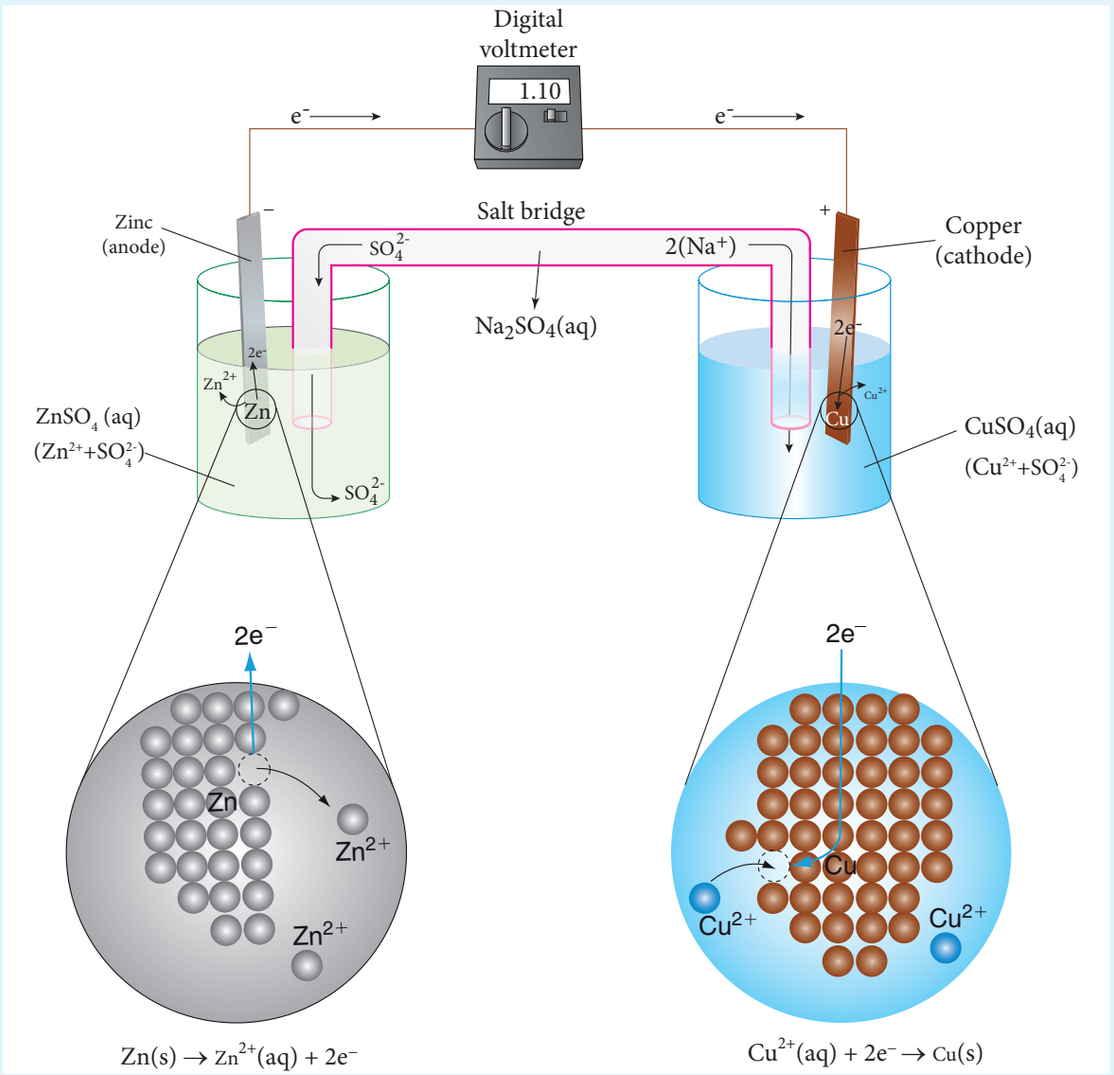


Figure 9.5 : Daniel cell

Anodic oxidation

The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation take place at zinc electrode, i.e., zinc is oxidised to Zn^{2+} ions by loosing its electrons. The Zn^{2+} ions enter the solution and the electrons enter the zinc metal, then flow through the external wire and then enter the copper strip. Electrons are liberated at zinc electrode and hence it is negative (- ve).

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(loss of electron-oxidation)}$$

Cathodic reduction

As discussed earlier, the electrons flow through the circuit from zinc to copper, where the Cu^{2+} ions in the solution accept the electrons, get reduced to copper and the same get deposited on the electrode. Here, the electrons are consumed and hence it is positive (+ve).

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad \text{(gain of electron-reduction)}$$

Salt bridge

The electrolytes present in two half cells are connected using a salt bridge. We have learnt that the anodic oxidation of zinc electrodes results in the increase in concentration of Zn^{2+} in solution. i.e., the solution contains more number of Zn^{2+} ions as compared to SO_4^{2-} and hence the solution in the anodic compartment would become positively charged. Similarly, the solution in the cathodic compartment would become negatively charged as the Cu^{2+} ions are reduced to copper i.e., the cathodic solution contain more number of SO_4^{2-} ions compared to Cu^{2+}.

To maintain the electrical neutrality in both the compartments, the non reactive anions Cl^- (from KCl taken in the salt bridge) move from the salt bridge and enter into the anodic compartment, at the same time some of the K^+ ions move from the salt bridge into the cathodic compartment.

Completion of circuit

Electrons flow from the negatively charged zinc anode into the positively charged copper cathode through the external wire, at the same time, anions move towards anode and cations are move towards the cathode compartment. This completes the circuit.

Consumption of Electrodes

As the Daniel cell operates, the mass of zinc electrode gradually decreases while the mass of the copper electrode increases and hence the cell will function until the entire metallic zinc electrode is converted in to Zn^{2+} or the entire Cu^{2+} ions are converted in to metallic copper.

Unlike Daniel cell, in certain cases, the reactants (or) products cannot serve as electrodes and in such cases inert electrode such as graphite (or) platinum is used which conducts current in the external circuit.

9.3.2 Galvanic cell notation

The galvanic cell is represented by a cell diagram, for example, Daniel cell is represented as

$$Zn\ (s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu\ (s)$$

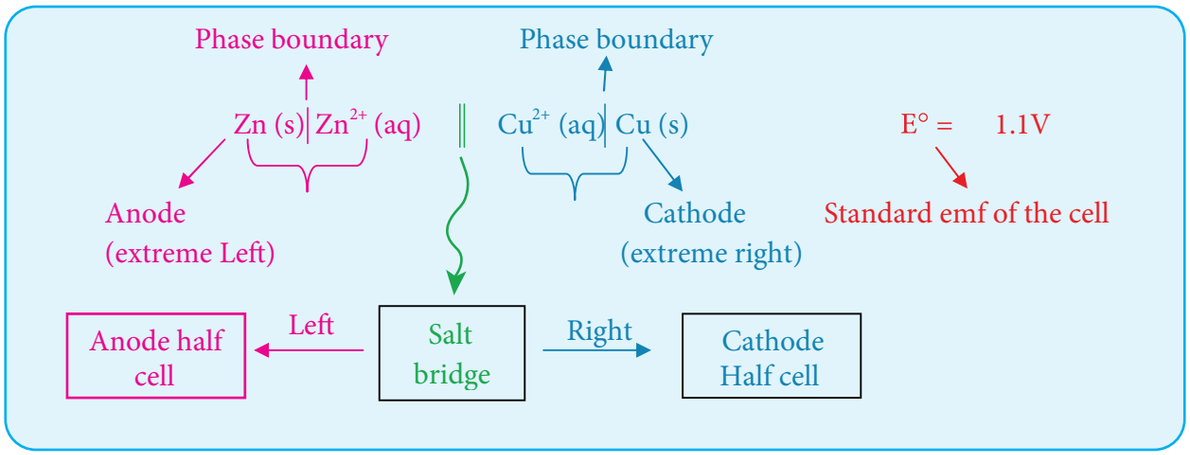
In the above notation, a single vertical bar (|) represents a phase boundary and the double vertical bar (||) represents the salt bridge.

The anode half cell is written on the left side of the salt bridge and the cathode half cell on the right side.

The anode and cathode are written on the extreme left and extreme right, respectively.

The emf of the cell is written on the right side after cell diagram.

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Example

The net redox reaction of a galvanic cell is given below

$2\,Cr\,(s) + 3Cu^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cu\,(s)$

Write the half reactions and describe the cell using cell notation.

Anodic oxidation $2Cr\,(s) \rightarrow 2Cr^{3+}\,(aq) + 6e^{-}$ .....(1)

Cathodic reduction : $3Cu^{2+}\,(aq) + 6e^{-} \rightarrow 3\,Cu\,(s)$ .....(2)

Cell Notation is

$Cr\,(s)\,|\,Cr^{3+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$

9.3.3 *emf* of a Cell

We have learnt that when two half cells of a Daniel cell are connected, a spontaneous redox reaction will take place which results in the flow of electrons from anode to cathode. The force that pushes the electrons away from the anode and pulls them towards cathode is called the electromotive force (emf) (or) the cell potential. The SI unit of cell potential is the volt (v).

When there is one volt difference in electrical potential between the anode and cathode, one joule of energy is released for each columb of charge that moves between them.

i.e., $1J = 1C \times 1V$ .....(9.18)

The cell voltage depends on the nature of the electrodes, the concentration of the electrolytes and the temperature at which the cell is operated. For example

At, $25^{\circ}C$, The emf of the below mentioned Daniel cell is 1.107 Volts

$Zn\,(s)\,|\,Zn^{2+}(aq,1M)\,\|\,Cu^{2+}(aq,1M)\,|\,Cu\,(s)$ $E^{0} = 1.107\ V$

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9.3.4 Measurement of electrode potential

The overall redox reaction can be considered as the sum of two half reactions i.e., oxidation and reduction. Similarly, the emf of a cell can be considered as the sum of the electrode potentials at the cathode and anode,

$$E_{cell} = \left(E_{ox}\right)_{anode} + \left(E_{red}\right)_{cathode} \quad .....(9.19)$$

Here, $\left(E_{ox}\right)_{anode}$ represents the oxidation potential at anode and $\left(E_{red}\right)_{cathode}$ represents the reduction potential at cathode. It is impossible to measure the emf of a single electrode, but we can measure the potential difference between the two electrodes $\left(E_{cell}\right)$ using a voltmeter. If we know the emf of any one of the electrodes which constitute the cell, we can calculate the emf of the other electrode from the measured emf of the cell using the expression (9.19). Hence, we need a reference electrode whose emf is known

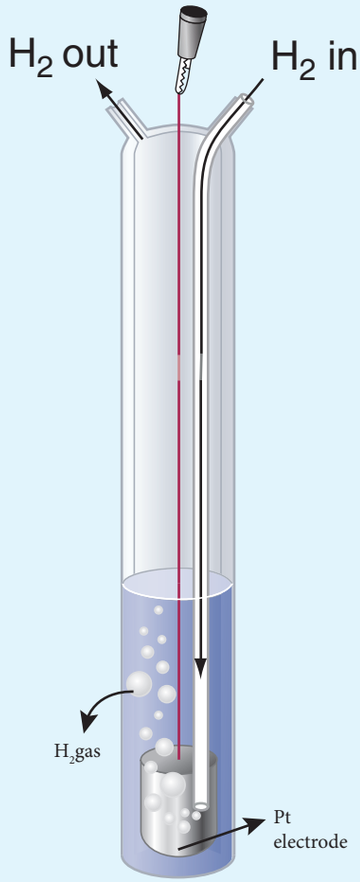
For that purpose, Standard Hydrogen Electrode (**SHE**) is used as the reference electrode. It has been assigned an arbitrary emf of exactly zero volt. It consists of a platinum electrode in contact with 1M HCl solution and 1 atm hydrogen gas. The hydrogen gas is bubbled through the solution at 25°C as shown in the figure 9.6. SHE can act as a cathode as well as an anode. The Half cell reactions are given below.

If SHE is used as a cathode, the reduction reaction is

$$2H^+(aq,1M)+2e^- \rightarrow H_2(g, 1\ atm) \qquad E^o = 0\ volt$$

If SHE is used as an anode, the oxidation reaction is

$$H_2(g,1\ atm) \rightarrow 2H^+(aq, 1M) + 2e^- \qquad E^o = 0\ volt$$



(SHE)

Figure 9.6 Standard Hydrogen electrode

Illustration

Let us calculate the reduction potential of zinc electrode dipped in zinc sulphate solution using SHE.

Step : 1 The following galvanic cell is constructed using SHE

$$Zn\ (s)\ |\ Zn^{2+}\ (aq, 1M)\ ||\ H^+\ (aq, 1M)\ |\ H_2\ (g, 1atm)\ |\ Pt\ (s)$$

Step : 2 The emf of the above galvanic cell is measured using a volt meter. In this case, the measured emf of the above galvanic cell is 0.76V.

Calculation

We know that,

$$E^\circ_{cell} = \left(E^\circ_{ox}\right)_{Zn|\ Zn^{2+}} + \left(E^\circ_{red}\right)_{SHE} \qquad [\text{From equation (9.19)}]$$

$E^\circ_{cell} = 0.76$ and $(E^\circ_{red})_{SHE} = 0V$. Substitute these values in the above equation

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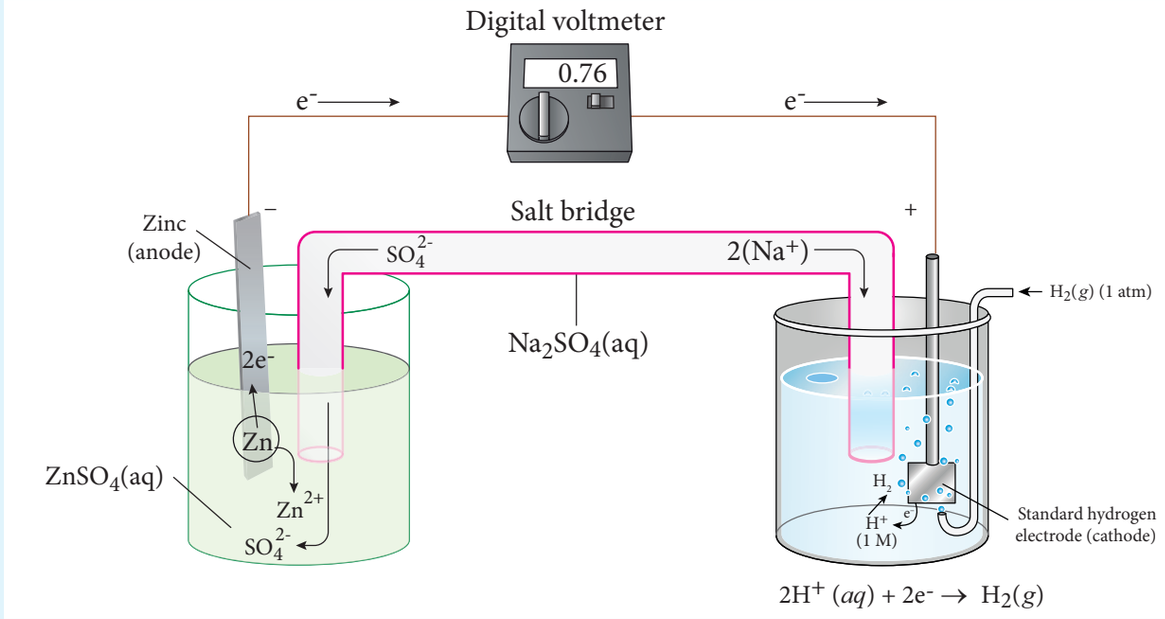


Figure 9.7 *emf* measurement (Zn | Zn^{2+} electrode)

$\Rightarrow$ 0.76V = $(E^{\circ}_{ox})_{Zn|Zn^{2+}}$ + 0V

$\Rightarrow$ $(E^{\circ}_{ox})_{Zn|Zn^{2+}}$ = 0.76V

This oxidation potential corresponds to the below mentioned half cell reaction which takes place at the cathode.

$Zn \rightarrow Zn^{2+} + 2e^{-}$ (Oxidation)

The emf for the reverse reaction will give the reduction potential

$Zn^{2+} + 2e^{-} \rightarrow Zn$; E° = - 0.76V $\quad \therefore (E^{\circ}_{red})_{Zn^{2+}|Zn}$ = -0.76V.

IUPAC definition

Electrode potential (E)

Electromotive force of a cell in which the electrode on the left is a standard hydrogen electrode and the electrode on the right is the electrode in question.

Standard electrode potential, E°

The value of the standard emf of a cell in which molecular hydrogen under standard pressure is oxidised to solvated protons at the left hand electrode.

Evaluate yourself : 3

1. The emf of the following cell at 25°C is equal to 0.34v. Calculate the reduction potential of copper electrode.

   $Pt(s) \mid H_2(g, 1atm) \mid H^{+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$

2. Using the calculated emf value of zinc and copper electrode, calculate the emf of the following cell at 25°C.

   $Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$

Evaluate yourself : 4

Write the overall redox reaction which takes place in the galvanic cell,

$Pt(s)\left|Fe^{2+}(aq),Fe^{3+}(aq)\right\|MnO_4^-(aq),\ H^+(aq),Mn^{2+}(aq)\left|Pt(s)\right.$

9.4 Thermodynamics of cell reactions

We have just learnt that in a galvanic cell, the chemical energy is converted into electrical energy. The electrical energy produced by the cell is equal to the product of the total charge of electrons and the emf of the cell which drives these electrons between the electrodes.

If 'n' is the number of moles of electrons exchanged between the oxidising and reducing agent in the overall cell reaction, then the electrical energy produced by the cell is given as below.

Electrical energy = Charge of 'n' mole of electrons $\times$ E_{cell} .....(9.20)

Charge of 1 mole of electrons = one Faraday (1F)

$\therefore$ Charge of 'n' mole of electrons = nF

Equation (9.20) $\Rightarrow$ Electrical energy = nFE_{cell} .....(9.21)

Charge of one elctron = 1.602×10^{-19} C

$\therefore$ Charge one mole of elctron = $6.023 \times 10^{23} \times 1.602 \times 10^{-19}$ C

= 96488 C

i.e., 1F $\simeq$ 96500 C

This energy is used to do the electric work. Therefore the maximum work that can be obtained from a galvanic cell is

$$(W_{max})_{cell} = - nFE_{cell} \quad .....(9.22)$$

Here the (-) sign is introduced to indicate that the work is done by the system on the surroundings.

We know from the Second Law of thermodynamics that the maximum work done by the system is equal to the change in the Gibbs free energy of the system.

$$\text{i.e.,} \quad W_{max} = \Delta G \quad .....(9.23)$$

From (9.22) and (9.23),

$$\Delta G = - nFE_{cell} \quad .....(9.24)$$

For a spontaneous cell reaction, the ΔG should be negative. The above expression (9.24) indicates that E_{cell} should be positive to get a negative ΔG value.

When all the cell components are in their standard state, the equation (9.24) becomes

$$\Delta G^o = - nFE^o_{cell} \quad .....(9.25)$$

We know that the standard free energy change is related to the equilibrium constant as per the following expression.

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$$\Delta G^{o} = - RT \ln K_{eq} \quad .....(9.26)$$

Comparing (9.25) and (9.26),

$$nFE^{\circ}_{cell} = RT \ln K_{eq}$$

$$\Rightarrow E^{\circ}_{cell} = \frac{2.303\ RT}{nF} \log K_{eq} \quad .....(9.27)$$

9.4.1 Nernst equation

Nernst equation is the one which relates the cell potential and the concentration of the species involved in an electrochemical reaction. Let us consider an electrochemical cell for which the overall redox reaction is,

$xA + yB \rightleftharpoons lC + mD$

The reaction quotient Q for the above reaction is given below

$$Q = \frac{[C]^{l}\ [D]^{m}}{[A]^{x}\ [B]^{y}} \quad .....(9.28)$$

We have already learnt that,

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad .....(9.29)$$

The Gibbs free energy can be related to the cell emf as follows [∴ equation (9.24) and (9.25)]

$$\Delta G = - nFE_{cell} \quad ; \Delta G^{o} = - nFE^{o}_{cell}$$

Substitute these values and Q from (9.28) in the equation (9.29)

$$(9.29) \Rightarrow - nFE_{cell} = - nFE^{o}_{cell} + RT \ln \frac{[C]^{l}[D]^{m}}{[A]^{x}\ [B]^{y}} \quad .....(9.30)$$

Divide the whole equation (9.30) by (-nF)

$$(9.25) \Rightarrow E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[C]^{l}[D]^{m}}{[A]^{x}\ [B]^{y}}$$

$$(or)\ E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^{l}[D]^{m}}{[A]^{x}\ [B]^{y}} \quad .....(9.31)$$

The above equation (9.31) is called the Nernst equation

At 25°C (298K), the above equation (9.31) becomes,

$$E_{cell} = E^{o}_{cell} - \frac{2.303 \times 8.314 \times 298}{n(96500)} \log \frac{[C]^{l}[D]^{m}}{[A]^{x}\ [B]^{y}}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[C]^{l}[D]^{m}}{[A]^{x}\ [B]^{y}} \quad .....(9.32)$$

$$\left[\begin{array}{l} \therefore\ R = 8.314\ JK^{-1}\ mol^{-1} \\ T = 298\ K. \\ 1\ F = 96500\ C\ mol^{-1} \end{array}\right]$$

Let us calculate the emf of the following cell at 25°C using Nernst equation.

$Cu\,(s)\left|Cu^{2+}(0.25\ aq,\ M)\right\|Fe^{3+}(0.005\ aq\ M)\left|Fe^{2+}(0.1\ aq\ M)\right|Pt\,(s)$

Given : $\left(E^{\circ}\right)_{Fe^{3+}|Fe^{2+}} = 0.77V$ and $\left(E^{\circ}\right)_{Cu^{2+}|Cu} = 0.34\ V$

Half reactions are

$Cu\,(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ ..... (1)

$2\,Fe^{3+}(aq) + 2e^{-} \rightarrow 2Fe^{2+}(aq)$ ..... (2)

the overall reaction is

$Cu\,(s) + 2\,Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Fe^{2+}\,(aq)$, and n = 2

Apply Nernst equation at .25°C .

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2} \qquad [\because\ [Cu\,(s)] = 1]$$

$$E^{\circ}_{cell} = \left(E^{\circ}_{ox}\right)_{Cu|Cu^{2+}} + \left(E^{\circ}_{red}\right)_{Fe^{3+}|Fe^{2+}}$$

Given standard reduction potential of $Cu^{2+}|Cu$ is 0.34V

$\therefore\ \left(E^{\circ}_{ox}\right)_{Cu|Cu^{2+}} = -0.34V$

$\left(E^{\circ}_{red}\right)_{Fe^{3+}|Fe^{2+}} = 0.77V$

$\therefore\ E^{\circ}_{cell} = -0.34 + 0.77$

$E^{\circ}_{cell} = 0.43V$

$$\therefore\ E_{cell} = 0.43 - \frac{0.0591}{2}\times\log\frac{(0.25)(0.1)^2}{(0.005)^2}$$

$$= 0.43 - \frac{0.0591}{2}\times 2$$

$$= 0.43 - 0.0591$$

$$= 0.3709V.$$

$$= \log\frac{(0.25)(0.1)^2}{(0.005)^2}$$

$$= \log\frac{25\times10^{-2}\ \times\ 1\times10^{-2}}{25\times10^{-6}}$$

$$= \log 10^2$$

$$= 2\log_{10}10$$

$$= 2.$$

Evaluate yourself : 5

The electrochemical cell reaction of the Daniel cell is

$Zn\,(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu\,(s)$

What is the change in the cell voltage on increasing the ion concentration in the anode compartment by a factor 10?

Electrolytic cell and electrolysis

Electrolysis is a process in which the electrical energy is used to cause a non-spontaneous chemical reaction to occur; the energy is often used to decompose a compound into its elements. The device which is used to carry out the electrolysis is called the electrolytic cell. The electrochemical process occurring in the electrolytic cell and galvanic cell are the reverse of each other. Let us understand the function of a electrolytic cell by considering the electrolysis of molten sodium chloride.

The electrolytic cell consists of two electrodes one is cylindrical steel cathode and another one is graphite anode. They are dipped in molten sodium chloride. They are connected to the external DC power supply via a key as shown in the figure (9.8). The electrode which is attached to the negative end of the power supply is called the cathode, and the one which is attached to the positive end is called the anode. Once the key is closed, the external DC power supply drives the electrons to the cathode and at the same time pull the electrons from the anode.

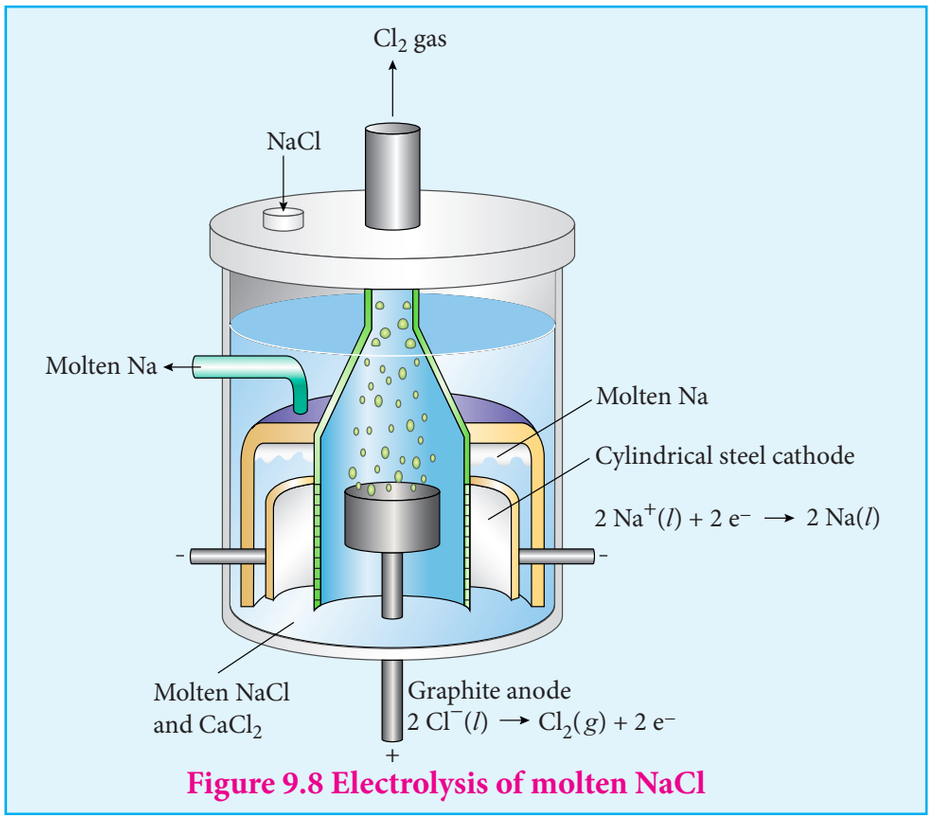


Figure 9.8 Electrolysis of molten NaCl

Cell reactions

Na^+ ions are attracted towards cathode, where they combine with the electrons and reduced to liquid sodium.

Cathode (reduction)

$Na^+(l) + e^- \rightarrow Na(l)$ $\qquad E^\circ = -2.71V$

Similarly, Cl^- ions are attracted towards anode where they lose their electrons and oxidised to chlorine gas.

Anode (oxidation)

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ $\qquad E^\circ = -1.36V$

The overall reaction is,

$$2Na^{+}(l) + 2Cl^{-}(l) \rightarrow 2Na(l) + Cl_2(g) \qquad E^{\circ} = -4.07V$$

The negative E° value shows that the above reaction is a non spontaneous one. Hence, we have to supply a voltage greater than 4.07V to cause the electrolysis of molten NaCl.

In electrolytic cell, oxidation occurs at the anode and reduction occur at the cathode as in a galvanic cell, but the sign of the electrodes is the reverse i.e., in the electrolytic cell cathode is –ve and anode is +ve.

Faraday's Laws of electrolysis

First Law

The mass of the substance (m) liberated at an electrode during electrolysis is directly proportional to the quantity of charge (Q) passed through the cell.

i.e $m \alpha Q$

We know that the charge is related to the current by the equation $I = \frac{Q}{t} \Rightarrow Q = It$

$\therefore \quad m \alpha It$

(or)

$$m = Z\,It \qquad \text{..... (9.33)}$$

Where is Z is known as the electro chemical equivalent of the substance produced of the electrode.

When, I = 1A and t = 1sec, Q = 1C , in such case the equation (9.32) becomes, (9.33)

$$\Rightarrow m = Z \qquad \text{.....(9.34)}$$

Thus, the electrochemical equivalent is defined as the amount of substance deposited or liberated at the electrode by a charge of 1 coulomb.

Electro chemical equivalent and molar mass

Consider the following general electrochemical redox reaction

$M^{n+}(aq) + ne^{-} \rightarrow M(s)$

We can infer from the above equation that 'n' moles of electrons are required to precipitate 1 mole of M^{n+} as M(s).

The quantity of charge required to precipitate one mole of M^{n+} = Charge of 'n' moles of electrons

$$= nF$$

In other words, the mass of substance deposited by one coulomb of charge

$$\text{Electrochemical equivalent of } M^{n+} = \frac{\text{Molarmass of M}}{n\,(96500)}$$

(or)

$$Z = \frac{\text{Equivalent mass}}{96500} \qquad \text{.....(9.35)}$$

Second Law

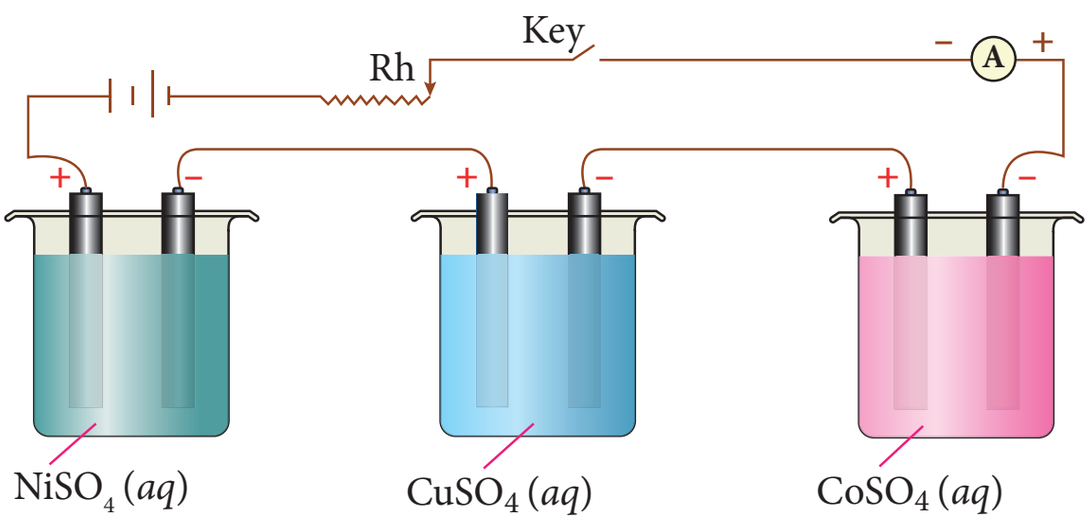


Figure 9.9 Electrolysis of various electrolytes using same quantity of charge

When the same quantity of charge is passed through the solutions of different electrolytes, the amount of substances liberated at the respective electrodes are directly proportional to their electrochemical equivalents.

Let us consider three electrolytic cells connected in series to the same DC electrical source as shown in the figure 9.9. Each cell is filled with a different electrolytes namely $NiSO_4$, $CuSO_4$ and $CoSO_4$, respectively.

When Q coulomb charge is passed through the electrolytic cells the masses of Nickel, copper and cobalt deposited at the respective electrodes be m_{Ni}, m_{Cu} and m_{Co} , respectively.

According to Faraday's second Law,

$$m_{Ni} \propto Z_{Ni},\ m_{Cu} \propto Z_{Cu} \text{ and } m_{Co} \propto Z_{Co}$$

(or)

$$\frac{m_{Ni}}{Z_{Ni}} = \frac{m_{Cu}}{Z_{Cu}} = \frac{m_{Co}}{Z_{Co}} \qquad \text{.....(9.36)}$$

Example

A solution of silver nitrate is electrolysed for 20 minutes with a current of 2 amperes. Calculate the mass of silver deposited at the cathode.

Electrochemical reaction at cathode is $Ag^+ + e^- \rightarrow Ag$ (reduction)

$m = ZIt$

$$m = \frac{108 \text{ gmol}^{-1}}{96500 \text{ C mol}^{-1}} \times 2400\text{C}$$

$m = 2.68$ g.

$$Z = \frac{\text{molarmass of Ag}}{(96500)} = \frac{108}{1 \times 96500}$$

$I = 2\text{A}$

$t = 20 \times 60\text{S} = 1200\text{ S}$

$It = 2\text{A} \times 1200\text{S} = 2400\text{C}$

Evaluate yourself : 6 A solution of a salt of metal was electrolysed for 15 minutes with a current of 0.15 amperes. The mass of the metal deposited at the cathode is 0.783g. calculate the equivalent mass of the metal.

Batteries

Batteries are indispensable in the modern electronic world. For example, Li – ion batteries are used in cell phones, dry cell in flashlight etc…. These batteries are used as a source of direct current at a constant voltage. We can classify them into primary batteries (non – rechargeable) and secondary batteries (rechargeable). In this section, we will briefly discuss the electrochemistry of some batteries.

Leclanche cell

Anode : Zinc container

Cathode : Graphite rod in contact with MnO_2

Electrolyte : ammonium chloride and zinc chloride in water

Emf of the cell is about 1.5V

Cell reaction

Oxidation at anode

$$Zn\,(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad .....(1)$$

Reduction at cathode

$$2\,NH_4^+(aq) + 2e^- \rightarrow 2NH_3\,(aq) + H_2(g) \qquad .....(2)$$

The hydrogen gas is oxidised to water by MnO_2

$$H_2\,(g) + 2\,MnO_2\,(s) \rightarrow Mn_2O_3\,(s) + H_2O\,(l) \qquad .....(3)$$

Equation (1) + (2)+(3) gives the overall redox reaction

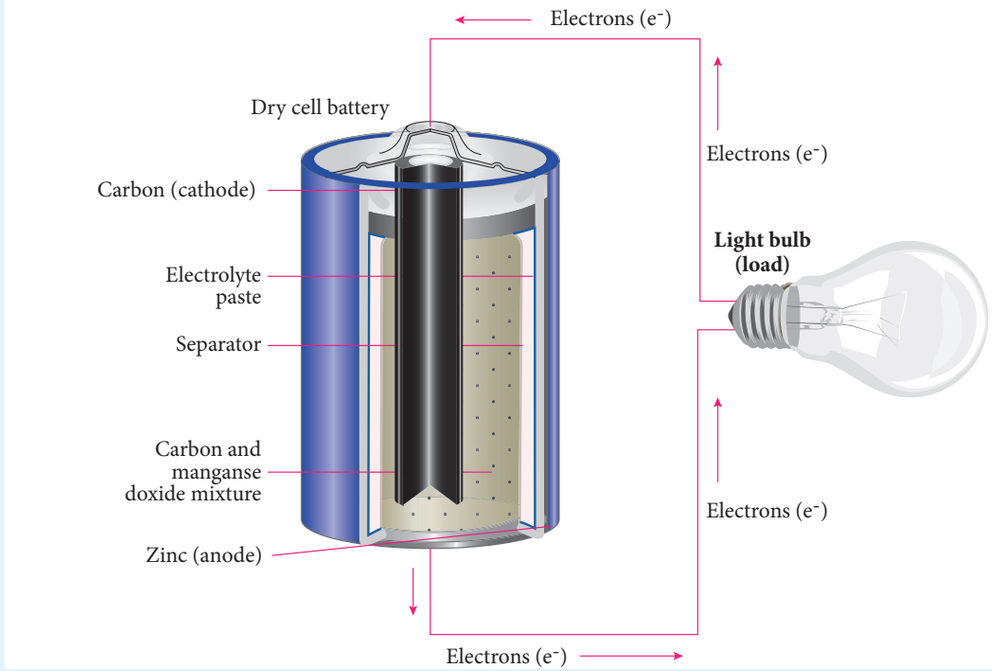


Figure 9.10 Leclanche cell

$$Zn\,(s) + 2NH_4^+\,(aq) + 2\,MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3\,(s) + H_2O\,(l) + 2NH_3 \quad \ldots\ldots (4)$$

Ammonia produced at the cathode combines with Zn^{2+} to form a complex ion $\left[Zn\,(NH_3)_4\right]^{2+}(aq)$. As the reaction proceeds, the concentration of NH_4^+ will decrease and the aqueous NH_3 will increase which lead to the decrease in the emf of cell.

Mercury button cell

Anode	:	zinc amalgamated with mercury
Cathode	:	HgO mixed with graphite
Electrolyte	:	Paste of KOH and ZnO
Oxidation occurs at anode	:	$\overset{0}{Zn}(s) + 2OH^-_{\text{from KOH}}(aq) \rightarrow \overset{+2}{ZnO}(s) + H_2O\,(l) + 2e^-$
Reduction occurs at cathode	:	$\overset{+2}{HgO}(s) + H_2O\,(l) + 2e^- \rightarrow \overset{0}{Hg}(l) + 2OH^-\,(aq)$
Overall reaction	:	$Zn\,(s) + HgO\,(s) \rightarrow ZnO\,(s) + Hg\,(l)$
Cell emf	:	about 1.35V.
Uses	:	It has higher capacity and longer life. Used in pacemakers, electronic watches, cameras etc…

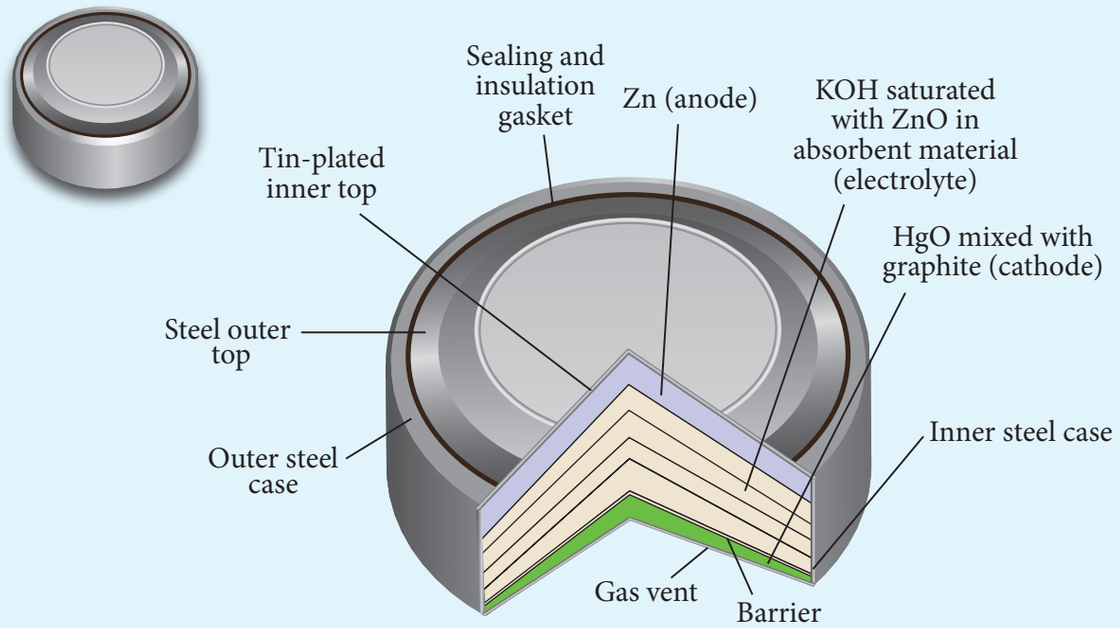


Figure 9.11 Mercury button cell

Secondary batteries

We have already learnt that the electrochemical reactions which take place in a galvanic cell may be reversed by applying a potential slightly greater than the emf generated by the cell. This principle is used in secondary batteries to regenerate the original reactants. Let us understand the function of secondary cell by considering the lead storage battery as an example

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Lead storage battery

Anode : spongy lead

Cathode : lead plate bearing PbO_2

Electrolyte : 38% by mass of H_2SO_4 with density 1.2g / mL.

Oxidation occurs at the anode

$$Pb(s) \rightarrow Pb^{2+}(aq)+2e^- \quad .....(1)$$

The Pb^{2+} ions combine with SO_4^{-2} to form $PbSO_4$ precipitate.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4\ (s) \quad .....(2)$$

Reduction occurs at the cathode

$$PbO_2\ (s) + 4\ H^+(aq) + 2e^- \rightarrow Pb^{2+}\ (aq) + 2H_2O\ (l) \quad .....(3)$$

The Pb^{2+} ions also combine with SO_4^{2-} ions from sulphuric acid to form $PbSO_4$ precipitate.

$$Pb^{2+}\ (aq) + SO_4^{2-}(aq) \rightarrow PbSO_4\,(s) \quad .....(4)$$

The Overall reactions is

Equation (1) + (2) + (3) + (4)

$$Pb\ (s) + PbO_2\ (s) + 4H^+(aq) + 2SO_4^{2-}\ (aq) \rightarrow 2\ PbSO_4\ (s) + 2H_2O\ (l)$$

The emf of a single cell is about 2V . Usually six such cells are combined in series to produce 12volt

The emf of the cell depends on the concentration of H_2SO_4. As the cell reaction uses SO_4^{2-} ions, the concentration H_2SO_4 decreases. When the cell potential falls to about 1.8V, the cell has to be recharged.

Recharge of the cell

As said earlier, a potential greater than 2V is applied across the electrodes, the cell reactions that take place during the discharge process are reversed. During recharge process, the role of anode and cathode is reversed and H_2SO_4 is regenerated.

Oxidation occurs at the cathode (now act as anode)

$$\overset{+2}{Pb}SO_4\ (s) + 2H_2O\ (l) \rightarrow \overset{+4}{Pb}O_2\ (s) + 4\ H^+(aq) + SO_4^{2-}\ (aq) + 2e^-$$

Reduction occurs at the anode (now act as cathode) $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

Overall reaction

$$2PbSO_4\ (s) + 2H_2O\ (l) \rightarrow Pb\ (s) + PbO_2\ (s) + 4H^+(aq) + 2SO_4^{2-}\ (aq).$$

Thus, the overall cell reaction is exactly the reverse of the redox reaction which takes place while discharging .

Uses:

Used in automobiles, trains, inverters etc…

The lithium – ion Battery

Anode : Porus graphite

Cathode : transition metal oxide such as CoO_2.

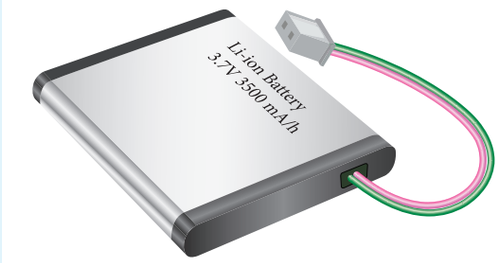


Figure 9.12 lithium – ion Battery

Electrolyte : Lithium salt in an organic solvent

At the anode oxidation occurs

$Li\ (s) \rightarrow Li^+\ (aq) + e^-$

At the cathode reduction occurs

$Li^+ + CoO_2\ (s) + e^- \rightarrow Li\ CoO_2\ (s)$

Overall reactions

$Li\ (s) + CoO_2 \rightarrow LiCoO_2\ (s)$

Both electrodes allow Li^+ ions to move in and out of their structures.

During discharge, the Li^+ ions produced at the anode move towards cathode through the non – aqueous electrolyte. When a potential greater than the emf produced by the cell is applied across the electrode, the cell reaction is reversed and now the Li^+ ions move from cathode to anode where they become embedded on the porous graphite electrode. This is known as intercalation.

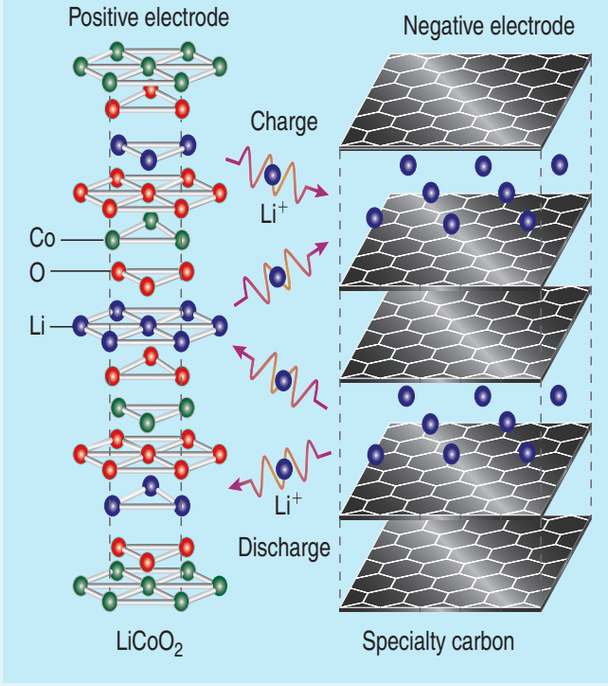


Figure 9.13 Li-ion battery

Uses :

Used in cellular phones, laptops, computers, digital cameras, etc…

Fuel cell

The galvanic cell in which the energy of combustion of fuels is directly converted into electrical energy is called the fuel cell. It requires a continuous supply of reactant to keep functioning. The general representation of a fuel cell is follows

Fuel | Electrode | Electrolyte | Electrode | Oxidant

Let us understand the function of fuel cell by

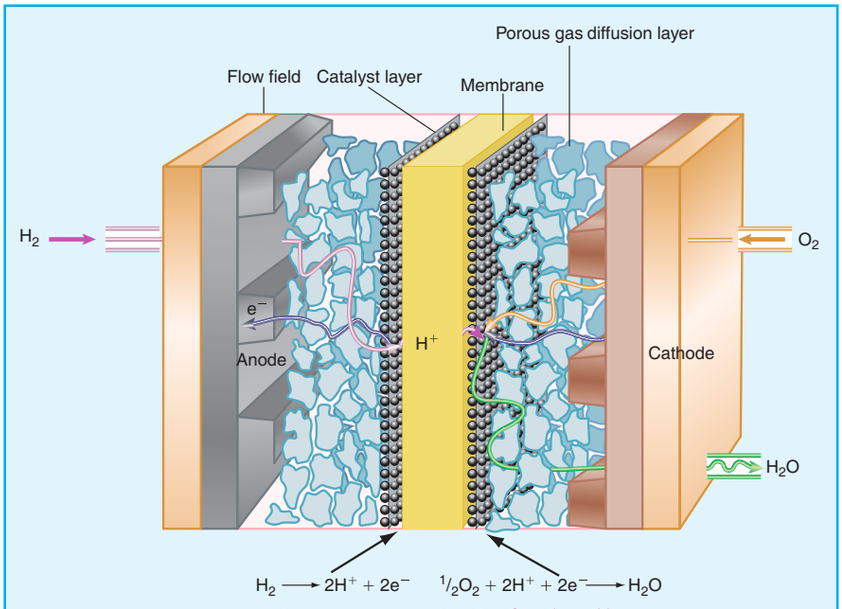


Figure 9.14 H_2O_2 fuel cell

considering hydrogen – oxygen fuel cell. In this case, hydrogen act as a fuel and oxygen as an oxidant and the electrolyte is aqueous KOH maintained at 200°C and 20 – 40 atm. Porous graphite electrode containing Ni and NiO serves as the inert electrodes.

Hydrogen and oxygen gases are bubbled through the anode and cathode, respectively.

Oxidation occurs at the anode:

$2H_2(g) + 4\,OH^-(aq) \rightarrow 4\,H_2O(l) + 4e^-$

Reduction occurs at the cathode $O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$

The overall reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The above reaction is the same as the hydrogen combustion reaction, however, they do not react directly ie., the oxidation and reduction reactions take place separately at the anode and cathode respectively. Like H_2 - O_2 fuel cell other fuel cells like propane –O_2 and methane O_2 have also been developed.

Corrosion

We are familiar with the rusting of iron. Have you ever noticed a green film formed on copper and brass vessels?. In both, the metal is oxidised by oxygen in presence of moisture. This redox process which causes the deterioration of metal is called corrosion. As the corrosion of iron causes damages to our buildings, bridges etc....it is important to know the chemistry of rusting and how to prevent it. Rusting of iron is an electrochemical process.

Electrochemical mechanism of corrosion

The formation of rust requires both oxygen and water. Since it is an electrochemical redox process, it requires an anode and cathode in different places on the surface of iron. The iron surface and a droplet of water on the surface as shown in figure (9.15) form a tiny galvanic cell. The region enclosed by water is exposed to low amount of oxygen and it acts as the anode. The remaining area has high amount of oxygen and it acts as cathode. So based on the oxygen content, an electro chemical cell is formed. corrosion occurs at the anode i,e,. in the region enclosed by the water as discussed below.

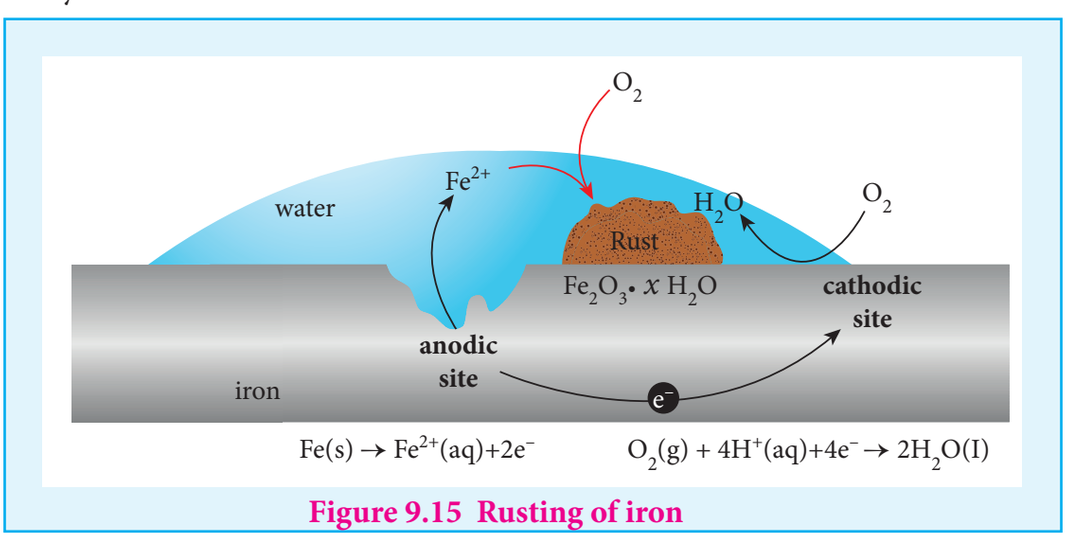


Figure 9.15 Rusting of iron

At anode (oxidation): Iron dissolves in the anode region

$$2Fe(s) \rightarrow 2Fe^{2+}(aq)+4e^{-} \qquad E^{\circ} = 0.44V.$$

The electrons move through the iron metal from the anode to the cathode area where the oxygen dissolved in water, is reduced to water.

At Cathode (reduction)

The reaction of atmospheric carbon dioxide with water gives carbonic acid which furnishes the H^{+} ions for reduction.

$$O_2(g)+4H^{+}(aq)+4e^{-} \rightarrow 2H_2O\,(l) \qquad E^{\circ} = 1.23V$$

The electrical circuit is completed by the migration of ions through water droplet.

The overall redox reactions is,

$$2Fe(s)+O_2(g)+4H^{+}(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) \qquad E^{\circ} = 0.444+1.23 = 1.67V$$

The positive emf value indicates that the reaction is spontaneous.

Fe^{2+} ions are further oxidised to Fe^{3+}, which on further reaction with oxygen form rust.

$$4Fe^{2+}(aq)+O_2(g)+4H^{+}(aq) \rightarrow 4Fe^{3+}(aq)+2H_2O(l)$$

$$2Fe^{3+}(aq)+4H_2O(l) \rightarrow Fe_2O_3.H_2O(s) + 6H^{+}(aq)$$

Other metals such as aluminium, copper and silver also undergo corrosion, but at a slower rate than iron. For example, let us consider the reduction of aluminium,

$$Al(s) \rightarrow Al^{3+}(aq)+3e^{-}$$

Al^{3+}, which reacts with oxygen in air to forms a protective coating of Al_2O_3. This coating act as a protective film for the inner surface. So,further corrosion is prevented.

Protection of metals form corrosion

This can be achieved by the following methods.

i. Coating metal surface by paint.

ii. Galvanizing - by coating with another metal such as zinc. zinc is stronger reducing agent than iron and hence it can be more easily corroded than iron. i.e., instead of iron, the zinc is oxidised.

iii. Cathodic protection - In this technique, unlike galvanising the entire surface of the metal to be protected need not be covered with a protecting metal. Instead, metals such as Mg or zinc which is corroded more easily than iron can be used as a sacrificial anode and the iron material acts as a cathode. So iron is protected, but Mg or Zn is corroded.

Passivation - The metal is treated with strong oxidising agents such as concentrated HNO_3. As a result, a protective oxide layer is formed on the surface of metal.

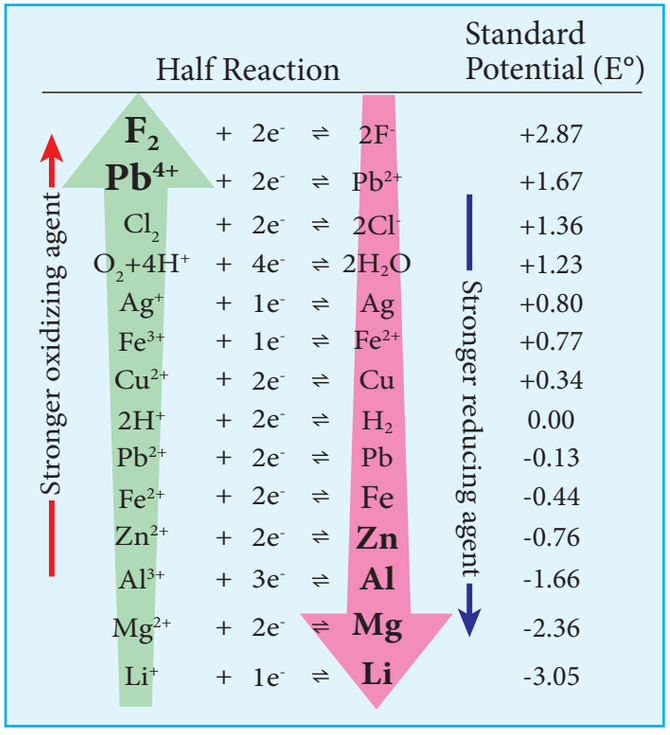
Alloy formation - The oxidising tendency of iron can be reduced by forming its alloy with other more anodic metals.

Example, stainless steel - an alloy of Fe and Cr.

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Electrochemical series

We have already learnt that the standard single electrode potentials are measured using standard hydrogen electrode. The standard electrode potential at 298K for various metal - metal ion electrodes are arranged in the decreasing order of their standard reduction potential values as shown in the figure.



This series is called electrochemical series.

The standard reduction potential (E°) is a measure of the oxidising tendency of the species. The greater the E° value, greater is the tendency shown by the species to accept electrons and undergo reduction. So higher the (E°) Value, lesser is the tendency to undergo corrosion

EVALUATION

Choose the correct answer:

1. The number of electrons that have a total charge of 9650 coulombs is

   a) 6.22×10^{23} b) 6.022×10^{24}

   c) 6.022×10^{22} c) 6.022×10^{-34}

2. Consider the following half cell reactions:

   $Mn^{2+} + 2e^- \rightarrow Mn \quad E^\circ = -1.18V$

   $Mn^{2+} \rightarrow Mn^{3+} + e^- \quad E^\circ = -1.51V$

   The E° for the reaction $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$, and the possibility of the forward reaction are respectively.

   a) 2.69V and spontaneous b) -2.69 and non spontaneous

   c) 0.33V and Spontaneous d) 4.18V and non spontaneous

3. The button cell used in watches function as follows

   $Zn\,(s) + Ag_2O\,(s) + H_2O\,(l) \rightleftharpoons 2\,Ag\,(s) + Zn^{2+}(aq) + 2OH^-\,(aq)$ the half cell potentials are $Ag_2O\,(s) + H_2O\,(l) + 2e^- \rightarrow 2Ag\,(s) + 2\,OH^-\,(aq)$ $E^\circ = 0.34V$ and $Zn\,(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^0 = 0.76\,V$. The cell potential will be

   a) 0.84V b) 1.34V c) 1.10V d) 0.42V

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4. The molar conductivity of a 0.5 mol dm^{-3} solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K is

a) 2.88 S $cm^2 mol^{-1}$ b) 11.52 S $cm^2 mol^{-1}$

c) 0.086 S $cm^2 mol^{-1}$ d) 28.8 S $cm^2 mol^{-1}$

5.

Electrolyte	KCl	KNO_3	HCl	NaOAC	NaCl
Λ_m (S cm^2 mol^{-1})	149.9	145.0	426.2	91.0	126.5

Calculate Λ°_{HOAC} using appropriate molar conductances of the electrolytes listed above at infinite dilution in water at 25°C.

a) 517.2 b) 552.7 c) 390.7 d) 217.5

6. Faraday constant is defined as

a) charge carried by 1 electron

b) charge carried by one mole of electrons

c) charge required to deposit one mole of substance

d) charge carried by 6.22×10^{10} electrons.

7. How many faradays of electricity are required for the following reaction to occur $MnO_4^- \rightarrow Mn^{2+}$

a) 5F b) 3F c) 1F d) 7F

8. A current strength of 3.86 A was passed through molten Calcium oxide for 41minutes and 40 seconds. The mass of Calcium in grams deposited at the cathode is (atomic mass of Ca is 40g / mol and 1F = 96500C).

a) 4 b) 2 c) 8 d) 6

9. During electrolysis of molten sodium chloride, the time required to produce 0.1mole of chlorine gas using a current of 3A is

a) 55 minutes b) 107.2 minutes c) 220 minutes d) 330 minutes

10. The number of electrons delivered at the cathode during electrolysis by a current of 1A in 60 seconds is (charge of electron = 1.6×10^{-19} C)

a) 6.22×10^{23} b) 6.022×10^{20} c) 3.75×10^{20} d) 7.48×10^{23}

11. Which of the following electrolytic solution has the least specific conductance

a) 2N b) 0.002N c) 0.02N d) 0.2N

12. While charging lead storage battery

a) $PbSO_4$ on cathode is reduced to Pb b) $PbSO_4$ on anode is oxidised to PbO_2

c) $PbSO_4$ on anode is reduced to Pb d) $PbSO_4$ on cathode is oxidised to Pb

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13. Among the following cells

I) Leclanche cell
II) Nickel – Cadmium cell
III) Lead storage battery
IV) Mercury cell
Primary cells are

a) I and IV b) I and III c) III and IV d) II and III

14. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because

a) Zinc is lighter than iron

b) Zinc has lower melting point than iron

c) Zinc has lower negative electrode potential than iron

d) Zinc has higher negative electrode potential than iron

15. Assertion : pure iron when heated in dry air is converted with a layer of rust. Reason : Rust has the composition Fe_3O_4

a) if both assertion and reason are true and reason is the correct explanation of assertion.

b) if both assertion and reason are true but reason is not the correct explanation of assertion.

c) assertion is true but reason is false

d) both assertion and reason are false.

16. In H_2-O_2 fuel cell the reaction occurs at cathode is

a) $O_2(g) + 2H_2O\ (l) + 4e^- \rightarrow 4OH^-\ (aq)$

b) $H^+(aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

c) $2H_2(g) + O_2(g) \rightarrow 2H_2O\ (g)$

d) $H^+ + e^- \rightarrow \frac{1}{2} H_2$

17. The equivalent conductance of $\frac{M}{36}$ solution of a weak monobasic acid is 6 mho cm^2 equivalent $^{-1}$ and at infinite dilution is 400 mho cm^2 equivalent $^{-1}$. The dissociation constant of this acid is

a) 1.25×10^{-6} b) 6.25×10^{-6} c) 1.25×10^{-4} d) 6.25×10^{-5}

18. A conductivity cell has been calibrated with a 0.01M, 1:1 electrolytic solution (specific conductance ($\kappa = 1.25\times10^{-3}$ S cm^{-1}) in the cell and the measured resistance was 800 Ω at $25^{\circ}C$. The cell constant is,

a) 10^{-1} c m^{-1} b) 10^{1} c m^{-1} c) 1 c m^{-1} d) 5.7×10^{-12}

19. Conductivity of a saturated solution of a sparingly soluble salt AB (1:1 electrolyte) at 298K is 1.85×10^{-5} S m^{-1}. Solubility product of the salt AB at 298K $\left(\Lambda^{\circ}_{m}\right)_{AB} = 14\times10^{-3}$ S m^{2} mol^{-1}.

a) 5.7×10^{-12} b) 1.32×10^{-12} c) 7.5×10^{-12} d) 1.74×10^{-12}

20. In the electrochemical cell: $Zn|ZnSO_4\ (0.01M)\|CuSO_4(1.0M)|Cu$, the emf of this Daniel cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0M and that $CuSO_4$ changed to 0.01M, the emf changes to E_2. From the above, which one is the relationship between E_1 and E_2?

a) $E_1 < E_2$ b) $E_1 > E_2$ c) $E_2 \geq E_1$ d) $E_1 = E_2$

21. Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram below:

$$BrO_4^- \xrightarrow{1.82V} BrO_3^- \xrightarrow{1.5V} HBrO \xrightarrow{1.595V} Br_2 \xrightarrow{1.0652V} Br^-$$

Then the species undergoing disproportionation is

a) Br_2 b) BrO_4^- c) BrO_3^- d) HBrO

22. For the cell reaction

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

$E^{\circ}_{cell} =$ 0.24V at 298K. The standard Gibbs energy (Δ, G°) of the cell reactions is :

a) -46.32 KJ mol^{-1} b) -23.16 KJ mol^{-1} c) 46.32 KJ mol^{-1} d) 23.16 KJ mol^{-1}

23. A certain current liberated 0.504gm of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time through copper sulphate solution

a) 31.75 b) 15.8 c) 7.5 d) 63.5

24. A gas X at 1 atm is bubbled through a solution containing a mixture of $1MY^-$ and $1MZ^-$ at 25°C. If the reduction potential of Z>Y>X, then

a) Y will oxidize X and not Z b) Y will oxidize Z and not X

d) Y will oxidize both X and Z d) Y will reduce both X and Z

25. Cell equation : $A^{2+} + 2B^- \rightarrow A + 2B$

$A^{2+} + 2e^- \rightarrow A \quad E^{\circ} = +0.34V$ and $\log_{10}K = 15.6$ at 300K for cell reactions find E° for $B^+ + e^- \rightarrow B$ (AIIMS – 2018)

a) 0.80 b) 1.26 c) -0.54 d) -10.94

Short Answer Questions

1. Define anode and cathode
2. Why does conductivity of a solution decrease on dilution of the solution
3. State Kohlrausch Law. How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution.

4. Describe the electrolysis of molten NaCl using inert electrodes
5. State Faraday's Laws of electrolysis
6. Describe the construction of Daniel cell. Write the cell reaction.
7. Why is anode in galvanic cell considered to be negative and cathode positive electrode?
8. The conductivity of a 0.01M solution of a 1 :1 weak electrolyte at 298K is 1.5×10^{-4} S cm^{-1}.

   i) molar conductivity of the solution

   ii) degree of dissociation and the dissociation constant of the weak electrolyte

   Given that

   $\lambda^{\circ}_{cation} = 248.2\ S\ cm^2\ mol^{-1}$

   $\lambda^{\circ}_{anion} = 51.8\ S\ cm^2\ mol^{-1}$
9. Which of 0.1M HCl and 0.1 M KCl do you expect to have greater $\overset{0}{\Lambda}_m$ and why?
10. Arrange the following solutions in the decreasing order of specific conductance.

    i) 0.01M KCl ii) 0.005M KCl iii) 0.1M KCl

    iv) 0.25 M KCl v) 0.5 M KCl
11. Why is AC current used instead of DC in measuring the electrolytic conductance?
12. 0.1M NaCl solution is placed in two different cells having cell constant 0.5 and 0.25cm^{-1} respectively. Which of the two will have greater value of specific conductance.
13. A current of 1.608A is passed through 250 mL of 0.5M solution of copper sulphate for 50 minutes. Calculate the strength of Cu^{2+} after electrolysis assuming volume to be constant and the current efficiency is 100%.
14. Can Fe^{3+} oxidises bromide to bromine under standard conditions?

    Given: $E^{\circ}_{Fe^{3+}|Fe^{2+}} = 0.771$

    $E^{\circ}_{Br_2|Br^-} = 1.09V.$
15. Is it possible to store copper sulphate in an iron vessel for a long time?

    Given : $E^{\circ}_{Cu^{2+}|Cu} = 0.34\,V$ and $E^{\circ}_{Fe^{2+}|Fe} = -0.44V$.
16. Two metals M_1 and M_2 have reduction potential values of $-x$V and +yV respectively. Which will liberate H_2 and H_2SO_4.
17. Reduction potential of two metals M_1 and M_2 are $E^{\circ}_{M_1^{2+}|M_1} = -2.3V$ and $E^{\circ}_{M_2^{2+}|M_2} = 0.2V$ Predict which one is better for coating the surface of iron. Given : $E^{\circ}_{Fe^{2+}|Fe} = -0.44V$
18. Calculate the standard emf 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.

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19. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidised at the anode and O_2 gas is reduced at cathode. If 44.8 litre of H_2 at 25^oC and 1atm pressure reacts in 10 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+}, how many grams of Cu deposited?

20. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 2.935g of Ni was deposited in the first cell. The amount of Cr deposited in the another cell? Give : molar mass of Nickel and chromium are 58.74 and 52 gm^{-1} respectively.

21. A copper electrode is dipped in 0.1M copper sulphate solution at 25^oC. Calculate the electrode potential of copper. [Given: $E^\circ_{Cu^{2+}|Cu} = 0.34\ V$].

22. For the cell $Mg\,(s)|Mg^{2+}(aq)\|Ag^{+}(aq)|Ag\,(s)$, calculate the equilibrium constant at 25^oC and maximum work that can be obtained during operation of cell. Given : $E^\circ_{Mg^{2+}|\,Mg} = -2.37V$ and $E^\circ_{Ag^{+}|Ag} = 0.80V$.

23. 9.2×10^{12} litres of water is available in a lake. A power reactor using the electrolysis of water in the lake, produces electricity at the rate of $2\times10^6\ Cs^{-1}$ at an appropriate voltage. How many years would it take to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.

24. Derive an expression for Nernst equation

25. Write a note on sacrificial protection.

26. Explain the function of H_2 - O_2 fuel cell.

27. Ionic conductance at infinite dilution of Al^{3+} and SO_4^{2-} are 189 and 160 mho cm^2 $equiv^{-1}$. Calculate the equivalent and molar conductance of the electrolyte $Al_2(SO_4)_3$ at infinite dilution.

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ICT Corner

Simulating an Voltaic Cell

By using this tool you can construct an electrochemical cell with using Ag/Cu/Zn electrodes and measure the emf of the cell. You can also learn how the concentration affects the emf value of the cell.

Please go to the URL https://pages.uoregon.edu/tgreenbo/voltaicCellEMF.html
(or)
Scan the QR codeon the right side

Step – 1

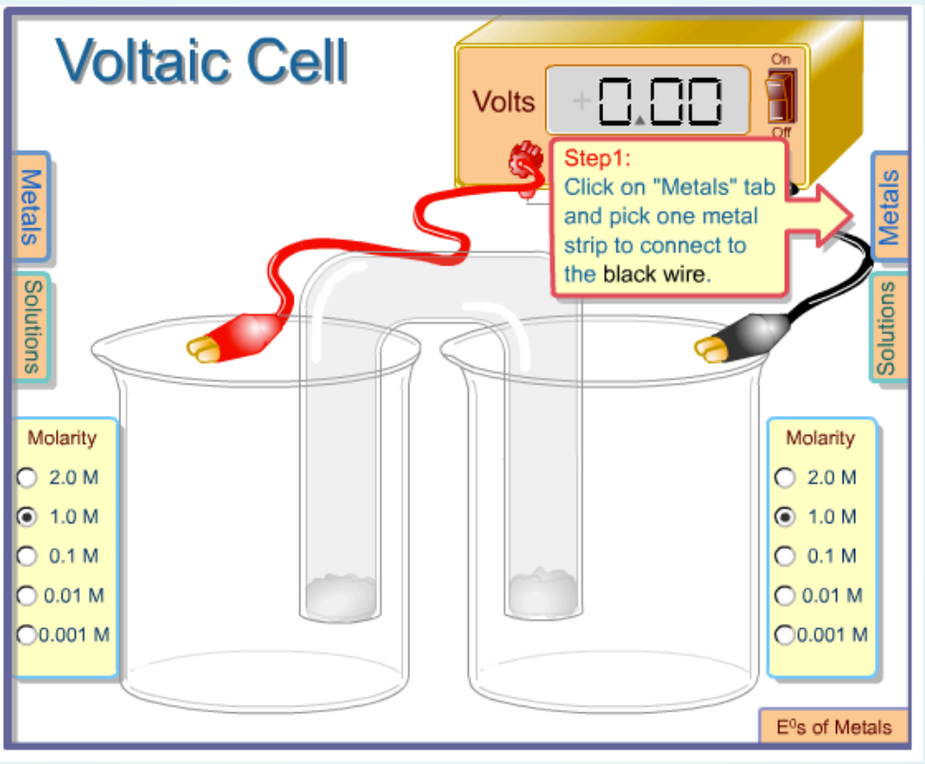
Open the Browser and type the URL given (or) Scan the QR Code. You will see the webpage as shown in the figure.

Step – 2

Choose the metal electrode and appropriate electrolytic solution for both cathode and anode following the on screen instructions. Now switch on the volt meter by clicking the red power switch. Now you can see the flow of electrons and the emf value on the screen.

Step – 3

The above steps can be repeated by varying the concentrations of electrolytic solutions of cathode and anode by selecting appropriate concentration from the list.



UNIT 10

SURFACE CHEMISTRY



Irving Langmuir

Irving Langmuir was an American Chemist and Physicist. He was awarded Nobel Prize in the year 1932 in Chemistry for his works in Surface Chemistry. He outlined the concentric theory of atomic structure. He invented the gas filled incandescent lamp and hydrogen welding technique. The Langmuir Laboratory for Atmospheric Research near Socorro, New Mexico was named in his honor. Langmuir and Tonks discovered electron density waves in plasmas that are now known as Langmuir waves.

3OLDC

Learning Objectives

After studying this unit the student will be able to

- classify adsorption.
- distinguish between absorption and adsorption
- explain Freundlich adsorption isotherm
- understand catalysis and the characteristics of catalysts.
- explain the theories of catalysis and enzyme catalysis.
- classify colloids.
- explain the methods of preparation and purification of colloids.
- discuss the properties of colloidal solution.
- explain the role of colloids and emulsions in daily life.

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INTRODUCTION

Surface chemistry is the branch of chemistry that deals with the processes occurring at interfaces between phases for example, solid and liquid, solid and gas and liquid and liquid. This topic is of immense importance to our everyday life and to numerous industries, from materials and paints to medicine and biotechnology. Surfaces play a key role in heterogeneous catalysis, formation and stability of colloids and electrode reactions. Surfaces of solids are inherently different from their bulk portion. The bonding between the atoms at the mere surface is different from that in the bulk. Hydrogen that exists in the interstellar space are formed on the surfaces of grains and dust particles. Mosquitoes and other small insects can walk on the surface of water but they will drown into the water when soaps are added in the neighbourhood. We are fascinated by the spherical shape of water droplets and mercury droplets. We are also impressed by the non-sticky wings of butterfly and leaves of plants. Blue colour of the sky and red colour of the sunset strongly attract us. In all the above only the surface of matter is important. Many of creams, lotions and other personal care products are complex emulsions. Food companies are interested in developing healthy, tasty and longlasting food products. All these are based on the principles of colloids and surface chemistry. So, surface Chemistry is an exciting topic to learn.

10.1 Adsorption and Absorption

Solid surfaces have the ability to attract the contacting species due to free valency or residual force on them.

For example: charcoal adsorbs ammonia, silica gel adsorbs water., charcoal adsorbs colorants from sugar.

These examples prove that adsorption is a surface phenomenon. In contrast to adsorption, absorption is a bulk phenomenon i.e. the adsorbate molecules are distributed throughout the adsorbent.

- Adsorbent is the material on which adsorption takes place.
- Adsorbed substance is called an adsorbate.
- The surface of separation of the two phases where the concentration of adsorbed molecule is high is known as interface.
- In adsorption, if the concentration of a substance in the interface is high, then it is called positive adsorption. If it is less, then it is called negative adsorption.
- The process of removing an adsorbed substance from the surface is called desorption.
- The gaseous molecules like He, Ne,O_2,N_2,SO_2 and NH_3 and solutions of NaCl or KCl can be adsorbed by suitable adsorbents. These are referred as adsorbates.
- Silica gel and metals like Ni,Cu, Pt, Ag and Pd and certain colloids can act as adsorbents.

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Characteristics of adsorption

1. Adsorption can occur in all interfacial surfaces i.e. the adsorption can occur in between gas-solid, liquid-solid, liquid-liquid, solid- solid and gas-liquid.
2. Adsorption is a spontaneous process and it is always accompanied by decrease in free energy. When ΔG reaches zero, the equilibrium is attained.

   We know, $\Delta G = \Delta H - T\,\Delta S$ where ΔG is Change in Free energy.

   ΔH is Change in enthalpy and ΔS = Change in entropy.
3. When molecules are adsorbed, there is always a decrease in randomness of the molecules.

   ie., $\Delta S<0$, and $T\Delta S$ is negative. Hence, adsorption is exothermic.

   Adsorption is a quick process whereas absorption is a slow process.

M.C. Bain introduced a term 'sorption' to represent the simultaneous adsorption and absorption. T. Graham used a term occlusion for sorption of gases on metal surfaces.

10.1.1 Types of adsorption

Adsorption is classified as physical adsorption and chemical adsorption, depending on the nature of forces acting between adsorbent and adsorbate. In chemical adsorption, gas molecules are held to the surface by formation of chemical bonds. Since strong bond is formed, nearly 400 KJ / mole is given out as heat of adsorption.

Examples

- Adsorption of O_2 on tungsten, Adsorption of H_2 on nickel, Adsorption of ethyl alcohol vapours on nickel.

In physical adsorption, physical forces such as van der waals force of attraction, dipole - dipole interaction, dispersion forces etc., exist between adsorbent and adsorbate. As these forces are weak, heat of adsorption is low, hence physical adsorption occurs at low temperatures.

Examples

(a) Adsorption of N_2 on mica.

(b) Adsorption of gases on charcoal.

The following table 10.1 illustrates the distinction between chemical and physical adsorption.

Table 10.1 Distinction between chemical and physical adsorption

Chemical adsorption or Chemisorption or Activated adsorption	Physical adsorption or van der waals adsorption or Physisorption
1. It is very slow	1. It is instantaneous
2. It is very specific depends on nature of adsorbent and adsorbate.	2. It is non-specific

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3. Chemical adsorption is fast with increase pressure, it can not alter the amount.	3. In Physisorption, when pressure increases the extent of adsorption increases.
4. When temperature is raised chemisorption first increases and then decreases.	4. Physisorption decreases with increase in temperature.
5. Chemisorption involves transfer of electrons between the adsorbent and adsorbate.	5. No transfer of electrons
6. Heat of adsorption is high i.e., from 40-400kJ/mole.	6. Heat of adsorption is low in the order of 40kJ/mole.
7. Monolayer of the adsorbate is formed.	7. Multilayer of the adsorbate is formed on the adsorbent.
8. Adsorption occurs at fixed sites called active centres. It depends on surface area	8. It occurs on all sides.
9. Chemisorption involves the formation of activated complex with appreciable activation energy.	9. Activation energy is insignificant.

10.1.2 Factors affecting adsorption

The adsorption is well understood by considering the various factors affecting it.

Qualitatively, the extent of surface adsorption depends on the following factors

(i) Nature of adsorbent

(ii) Nature of adsorbate

(iii) Pressure

(iv) Concentration at a given temperature.

1. Surface area of adsorbent:

As the adsorption is a surface phenomenon it depends on the surface area of adsorbent. i.e., higher the surface area, higher is the amount adsorbed.

2. Nature of adsorbate

The nature of adsorbate can influence the adsorption. Gases like SO_2,NH_3,HCl and CO_2 are easily liquefiable as they have greater van der waal's force of attraction. On the other hand, permanent gases like H_2,N_2 and O_2 can not be liquefied easily. These permanent gases are having low critical temperature and adsorbed slowly, while gases with high critical temperature are adsorbed readily.

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3. Effect of temperature

When temperature is raised chemisorption first increases and then decreases. whereas physisorption decreases with increase in temperature.

4. Effect of pressure:

chemical adsorption is fast with increase in pressure, it can not alter the amount of adsorption. In Physisorption the extent of adsorption increases with increase in pressure.

10.1.3 Adsorption isotherms and isobars.

Adsorption isotherms represents the variation of adsorption at constant temperature.

When amount of adsorption is plotted versus temperature at constant pressure it is called adsorption isobar.

Adsorption isobars of physisorption and chemisorption are different as represented in the graphs.

Figure 10.1 (a) Physical Adsorption

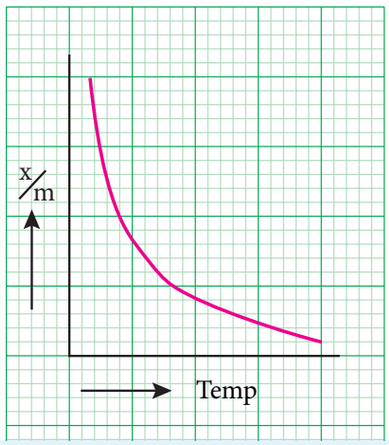
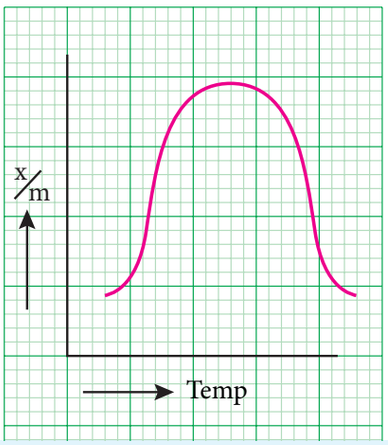


Figure 10.1 (b) Chemical Adsorption



x is the amount of adsorbate adsorbed on 'm' g of adsorbent.

In physical adsorption, $\frac{x}{m}$ decreases with increase in Temprature, But in chemical adsorption, $\frac{x}{m}$ increases with rise in temperature and then decreases. The increase illustrates the requirement of activation of the surface for adsorption is due to fact that formation of activated complex requires certain energy.

The decrease at high temperature is due to desorption, as the kinetic energy of the adsorbate increases.

10.1.3.1 Adsorption isotherms

Adsorption isotherm can be studied quantitatively. A plot between the amount of adsorbate adsorbed and pressure (or concentration of adsorbate) at constant temperature is called adsorption isotherms.

In order to explain these isotherms various equations were suggested as follows:

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(i) Freundlich adsorption isotherm.

According to Freundlich,

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

where x is the amount of adsorbate, adsorbed on 'm' gm of adsorbent at a pressure of p. K and n are constant introduced by freundlich.

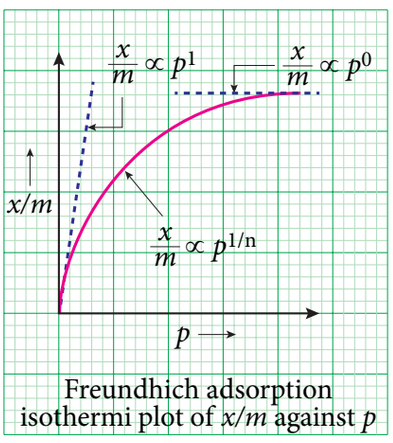
Value n is always less than unity.

This equation is applicable for adsorption of gases on solid surfaces. The same equation becomes $\frac{x}{m} = K\, c^{\frac{1}{n}}$, when used for adsorption in solutions with c as concentration.

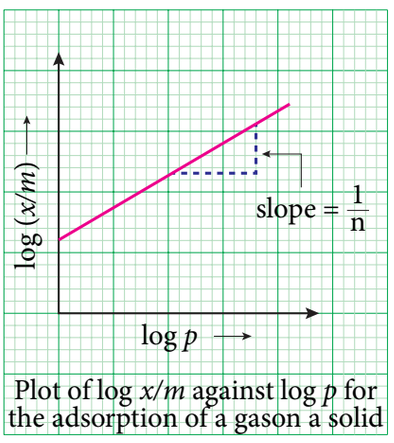
This equation quantitively predicts the effect of pressure(or concentration) on the adsorption of gases(or adsorbates) at constant temperature.

Taking log on both sides of equation $\frac{x}{m} = Kp^{\frac{1}{n}}$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$



Freundhich adsorption isothermi plot of *x/m* against *p*



Plot of log *x/m* against log *p* for the adsorption of a gason a solid

Figure 10.2 $\log \frac{x}{m}$ vs log p **graph**

Hence the intercept represents the value of log k and the slope gives $\frac{1}{n}$.

This equation explains the increase of $\frac{x}{m}$ with increase in pressure. But experimental values show the deviation at low pressure.

Limitations

This equation is purely empirical and valid over a limited pressure range.

The values of constants k and n also found vary with temperature. No theoretical explanations were given.

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10.1.4 Applications of adsorption

Though we have innumerable applications for adsorption, we consider few of them

1. Gas masks: During world war I charcoal gas mask was employed by both the British and American. Activated charcoal was found to be one of the best adsorbents.

2. To create high vacuum in vessels, Tail and Dewar used activated charcoal.For dehydration and also purification of gases like CO_2, N_2, Cl_2, O_2 and He, alumina and silica are employed. In the blast furnace silica gel is also used for drying air.

3. One of the highly important use of adsorption is the softening of hardwater. Permutit is employed for this process which adsorbs Ca^{2+} and Mg^{2+} ions in its surface, there is an ion exchange as shown below it occurs on the surface.

$$Na_2Al_2Si_4O_{12} + CaCl_2 \rightarrow CaAl_2Si_4O_{12} + 2NaCl$$

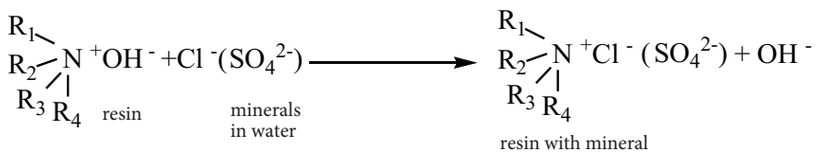
Exhausted permutit is regenerated by adding a solution of common salt.

$$CaAl_2Si_4O_{12} + 2NaCl \rightarrow Na_2Al_2Si_4O_{12} + CaCl_2$$

4. Ion exchange resins

Ion exchange resins are working only based on the process of adsorption. Ion exchange resins are used to demineralise water. This process is carried out by passing water through two columns of cation and anion exchange resins.

$$\underset{\text{resin}}{2\,RSO_3H} + \underset{\text{minerals in water}}{Ca^{2+}(Mg^{2+})} \rightarrow \underset{\text{resin with mineral}}{(RSO_3)_2Ca(Mg)} + 2H^+$$



5. Petroleum refining and refining of vegetable oil

Fuller's earth and silica gel are used for refining process.

6. Decolourisation of Sugar:

Sugar prepared from molasses is decolourised to remove coloured impurities by adding animal charcoal which acts as decolourising material.

7. Chromatography

The chromatographic technique is applied for separation of components in a mixture. It is mainly based on adsorption of components on the surface of adsorbents. This method is very effective and used for identification, detection and estimation of many substances even if they are contained in micro quantities.

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8. Catalysed reaction

Catalysis is an important branch of surface chemistry which is based on the phenomenon of adsorption of materials on the catalyst surface.

Examples:

In the Haber's process, ammonia is manufactured from N_2 and H_2 as shown by the following reactions.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

In this process, Fe is the catalyst and Mo is a promoter. The surface of the Fe catalyses the reaction.

In the hydrogenation of oils to obtain vanaspathi, Nickel is used as a catalyst. Nickel surface catalyses the reaction.

$$\text{vegetable oil} + H_2 \xrightarrow[473K]{\text{Ni catalyst}} \text{vanaspathi}$$

9. Qualitative analysis

When blue litmus solution is added to Al^{3+} ion, a red coloration is seen due to the acidic nature of the solution. Addition of ammonium hydroxide to it gives a blue lake. This is due to the adsorption of blue colour litmus compound on the surface of $Al(OH)_3$ Which is formed during the addition of NH_4OH

10. Medicine:

Drugs cure diseases by adsorption on body tissues.

11. Concentration of Ores of metals

Sulphides ores are concentrated by a process called froth flotation in which light ore particles are wetted by pine oil.

12. Mordants and Dyes

Most of the dyes are adsorbed on the surface of the fabrics. Mordants are the substances used for fixing dyes onto the fabric.

13. Adsorption indicators

In the precipitation titrations, the end point is indicated by an external indicator which changes its colour after getting adsorbed on precipitate. It is used to indicate the end point of the titration.

10.2 Catalysis

In 1836 Berzelius identified certain substances loosen the bond in the reacting molecules and increased the rate of the reaction. But he also found these substances didn't undergo any change chemically. In order to indicate the property, he gave them the name catalyst. (In greek, kata-wholly, lein-to loosen).

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Later it was identified that there were many substances which retarded the speed of a reaction.

Hence a catalyst is defined as a substance which alters the rate of chemical reaction without itself undergoing chemical change. The phenomenon which involves the action of a catalyst is called catalysis.

Positive and negative catalysis:

In positive catalysis, the rate of a reaction is increased by the presence of catalyst but in negative catalysis, the rate of reaction is decreased by the presence of a catalyst.

The two main types of catalysis (i) Homogeneous catalysis and (ii) Heterogeneous catalysis

Homogeneous catalysis

In a homogeneous catalysed reaction, the reactants, products and catalyst are present in the same phase.

Illustration (1):

$$2SO_{2(g)} + O_{2(g)} + [NO]_{(g)} \rightarrow 2SO_{3(g)} + [NO]_{(g)}$$

In this reaction the catalyst NO, reactants, SO_2 and O_2, and product, SO_3 are present in the gaseous form.

Illustration (2):

In the decomposition of acetaldehyde by I_2 catalyst, the reactants and products are all present in the vapour phase.

$$CH_3CHO_{(g)} + [I_2]_{(g)} \rightarrow CH_{4(g)} + CO_{(g)} + [I_2]_{(g)}$$

Let us consider some examples in which the reactants, products and catalyst are present in aqueous solution.

(1) Hydrolysis of cane sugar with a mineral acid as catalyst

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11(l)}} + H_2O_{(l)} \xrightarrow{H_2SO_{4(l)}} \underset{\text{Glucose}}{C_6H_{12}O_{6(l)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(l)}}$$

(2) Ester hydrolysis with acid or alkali as catalyst

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_{5(l)}} + H_2O_{(l)} \xrightarrow{H_2SO_{4(l)}} \underset{\text{acetic acid}}{CH_3COOH_{(l)}} + \underset{\text{ethyl alcohol}}{C_2H_5OH_{(l)}}$$

Heterogeneous catalysis

In a reaction, the catalyst is present in a different phase i.e. it is not present in the same phase as that of reactants or products. This is generally referred as contact catalysis and the catalyst present is in the form of finely divided metal or as gauze

Illustration

(i) In the manufacture of sulphuric acid by contact process SO_3 is prepared by the action of SO_2 and O_2 in the presence of Pt or V_2O_5 as a catalyst.

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$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt_{(s)} \text{ or } V_2O_{5(s)}} 2SO_{3(g)}$$

ii) In the Haber's process for the manufacture of ammonia, iron is used as a catalyst for the reaction between Hydrogen and Nitrogen.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$

iii) Oxidation of ammonia is carried out in presence of platinum gauze

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

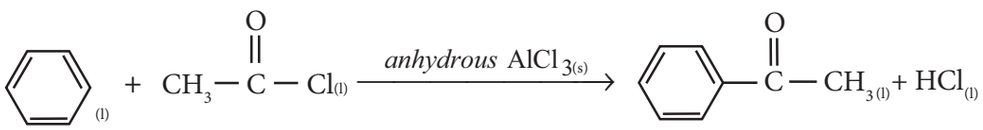
iv) The hydrogenation of unsaturated organic compounds is carried out using finely divided nickel as a catalyst.

$$CH_2{=}CH_{2(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}} CH_3\text{-}CH_{3(g)}$$

v) Decomposition of H_2O_2 occurs in the presence of the Pt catalyst

$$2H_2O_{2(l)} \xrightarrow{Pt_{(s)}} 2H_2O_{(l)} + O_{2(g)}$$

vi) In the presence of anhydrous $AlCl_3$, benzene reacts with ethanoyl chloride to produce acetophenone



acetophenone

10.2.1 Characteristics of catalysts

1. For a chemical reaction, catalyst is needed in very small quantity. Generally, a pinch of catalyst is enough for a reaction in bulk.
2. There may be some physical changes, but the catalyst remains unchanged in mass and chemical composition in a chemical reaction.
3. A catalyst itself cannot initiate a reaction. It means it can not start a reaction which is not taking place. But, if the reaction is taking place in a slow rate it can increase its rate.
4. A solid catalyst will be more effective if it is taken in a finely divided form.
5. A catalyst can catalyse a particular type of reaction, hence they are said to be specific in nature.
6. In an equilibrium reaction, presence of catalyst reduces the time for attainment of equilibrium and hence it does not affect the position of equilibrium and the value of equilibrium constant.
7. A catalyst is highly effective at a particular temperature called as optimum temperature.
8. Presence of a catalyst generally does not change the nature of products

   For example. $2SO_2 + O_2 \rightarrow 2SO_3$

   This reaction is slow in the absence of a catalyst, but fast in the presence of Pt catalyst

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Promoters and catalyst poison

In a catalysed reaction the presence of a certain substance increases the activity of a catalyst. Such a substance is called a promoter.

For example in the Haber's process of manufacture of ammonia, the activity of the iron catalyst is increased by the presence of molybdenum. Hence molybdenum is called a promoter. In the same way Al_2O_3 can also be used as a promoter to increase the activity of the iron catalyst.

On the other hand, certain substances when added to a catalysed reaction decreases or completely destroys the activity of catalyst and they are often known as catalytic poisons.

Few examples,

In the reaction, $2SO_2+O_2 \rightarrow 2SO_3$ with a Pt catalyst, the poison is As_2O_3

i.e., As_2O_3 destroys the activity of Pt. As_2O_3 blocks the activity of the catalyst. So, the activity is lost.

In the Haber's process of the manufacture of ammonia, the Fe catalyst is poisoned by the presence of H_2S.

In the reaction, $2H_2+O_2 \rightarrow 2H_2O$,

CO acts as a catalytic poison for Pt - catalyst

Auto catalysis

In certain reactions one of the products formed acts as a catalyst to the reaction. Initially the rate of reaction will be very slow but with the increase in time the rate of reaction increases.

Auto catalysis is observed in the following reactions.

$$CH_3COOC_2H_5+H_2O \rightarrow CH_3COOH+C_2H_5OH$$

Acetic acid acts as the autocatalyst

$$2AsH_3 \rightarrow 2As+3H_2$$

Arsenic acts as an autocatalyst

Negative Catalysis

In certain reactions, presence of certain substances, decreases the rate of the reaction. Ethanol is a negative catalyst for the following reaction.

(i) $4CHCl_3+3O_2 \rightarrow 4COCl_2+2H_2O+2Cl_2$

Ethanol decreases the rate of the reaction

(ii) $2H_2O_2 \rightarrow 2H_2O+O_2$

In the decomposition of hydrogen peroxide, dilute acid or glycerol acts as a negative catalyst.

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10.2.2 Theories of Catalysis

For a chemical reaction to occur, the reactants are to be activated to form the activated complex. The energy required for the reactants to reach the activated complex is called the activation energy. The activation energy can be decreased by increasing the reaction temperature. In the presence of a catalyst, the reactants are activated at reduced temperatures in otherwords, the activation energy is lowered. The catalyst adsorbs the reactants activates them by weakening the bonds and allows them to react to form the products.

As activation energy is lowered in presence of a catalyst, more molecules take part in the reaction and hence the rate of the reaction increases.

The action of catalysis in chemical reactions is explained mainly by two important theories. They are

(i) the intermediate compound formation theory

(ii) the adsorption theory.

The intermediate compound formation theory

A catalyst acts by providing a new path with low energy of activation. In homogeneous catalysed reactions a catalyst may combine with one or more reactant to form an intermediate which reacts with other reactant or decompose to give products and the catalyst is regenerated.

Consider the reactions:

$A+B \rightarrow AB$ (1)

$A+C \rightarrow AC$ (intermediate) (2)

C is the catalyst

$AC+B \rightarrow AB+C$ (3)

Activation energies for the reactions (2) and (3) are lower compared to that of (1). Hence the formation and decomposition of the intermediate accelerate the rate of the reaction.

Example 1

The mechanism of Fridel crafts reaction is given below

$$C_6H_6+CH_3Cl \xrightarrow[\text{anhydrous}]{AlCl_3} C_6H_5CH_3+HCl$$

The action of catalyst is explained as follows

$$CH_3Cl+AlCl_3 \rightarrow [CH_3]^+[AlCl_4]^-$$

It is an intermediate.

$$C_6H_6+[CH_3^+][AlCl_4]^- \rightarrow C_6H_5CH_3+AlCl_3+HCl$$

Example 2

Thermal decomposition of $KClO_3$ in presence of MnO_2 proceeds as follows.

Steps in the reaction $2KClO_3 \rightarrow 2KCl+3O_2$ can be given as

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$$2KClO_3 + 6MnO_2 \rightarrow 6MnO_3 + 2KCl$$

It is an intermediate.

$$6MnO_3 \rightarrow 6MnO_2 + 3O_2$$

Example 3:

Formation of water due to the reaction of H_2 and O_2 in the presence of Cu proceeds as follows. Steps in the reaction $H_2 + ½O_2 \rightarrow H_2O$ can be given as

$$2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O$$

It is an intermediate.

$$Cu_2O + H_2 \rightarrow H_2O + 2Cu$$

Example 4:

Oxidation of HCl by air in presence of $CuCl_2$ proceeds as follows. Steps in the reaction $4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$ can be given as

$$2CuCl_2 \rightarrow Cl_2 + Cu_2Cl_2$$

$$2Cu_2Cl_2 + O_2 \rightarrow 2Cu_2OCl_2$$

It is an intermediate.

$$2Cu_2OCl_2 + 4HCl \rightarrow 2H_2O + 4CuCl_2$$

This theory describes

(i) the specificity of a catalyst and

(ii) the increase in the rate of the reaction with increase in the concentration of a catalyst.

Limitations

(i) The intermediate compound theory fails to explain the action of catalytic poison and activators (promoters).

(ii) This theory is unable to explain the mechanism of heterogeneous catalysed reactions.

2. Adsorption theory

Langmuir explained the action of catalyst in heterogeneous catalysed reactions based on adsorption. The reactant molecules are adsorbed on the catalyst surfaces, so this can also be called as contact catalysis.

According to this theory, the reactants are adsorbed on the catalyst surface to form an activated complex which subsequently decomposes and gives the product.

The various steps involved in a heterogeneous catalysed reaction are given as follows:

1. Reactant molecules diffuse from bulk to the catalyst surface.
2. The reactant molecules are adsorbed on the surface of the catalyst.
3. The adsorbed reactant molecules are activated and form activated complex which is decomposed to form the products.
4. The product molecules are desorbed.
5. The product diffuse away from the surface of the catalyst.

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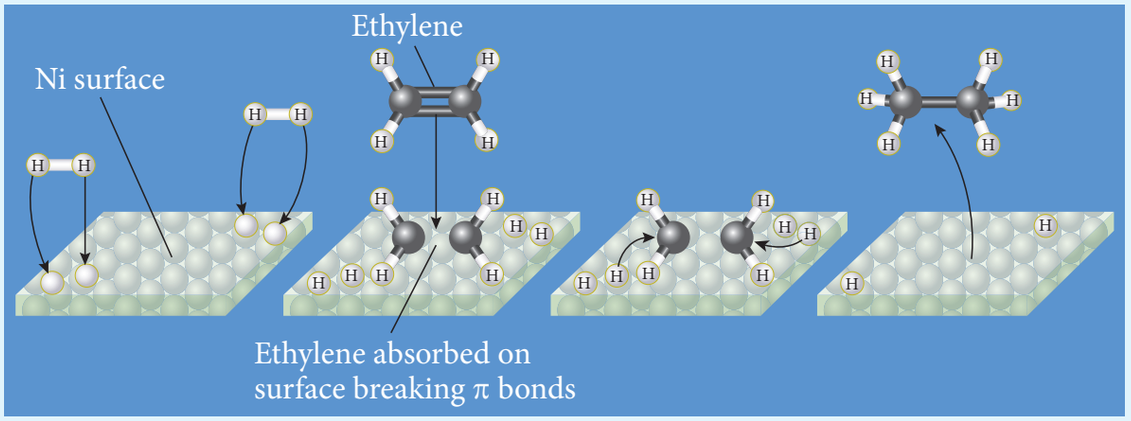


Figure 10.3 Hydrogenation of ethylene in presence of a nickel catalyst.

Active centres

The surface of a catalyst is not smooth. It bears steps, cracks and corners. Hence the atoms on such locations of the surface are co-ordinatively unsaturated. So, they have much residual force of attraction. Such sites are called active centres. So, the surface carries high surface free energy.

The presence of such active centres increases the rate of reaction by adsorbing and activating the reactants.

The adsorption theory explains the following

i. Increase in the surface area of metals and metal oxides by reducing the particle size increases acting of the catalyst and hence the rate of the reaction.

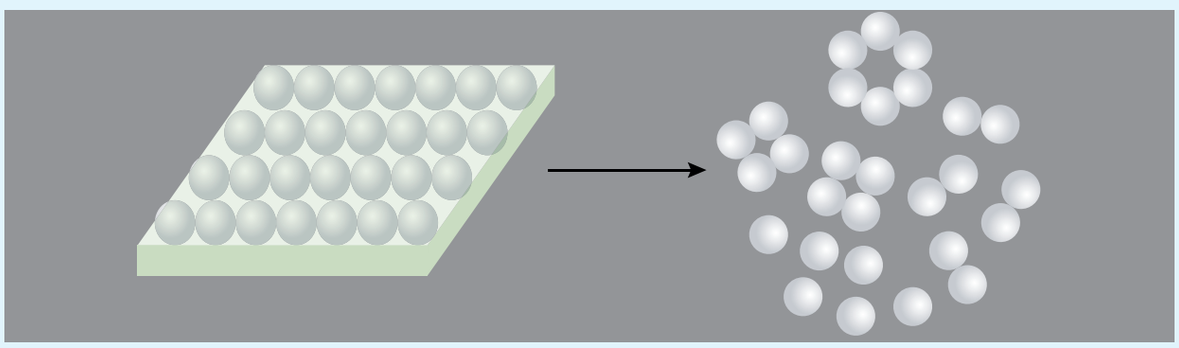


Figure 10.4 Finely divided catalyst is more effective due to increase in the number of active centres.

ii. The action of catalytic poison occurs when the poison blocks the active centres of the catalyst.

iii. A promoter or activator increases the number of active centres on the surfaces.

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10.3 Enzyme Catalysis

Enzymes are complex protein molecules with three dimensional structures. They catalyse the chemical reaction in living organism. They are often present in colloidal state and extremely specific in catalytic action. Each enzyme produced in a particular living cell can catalyse a particular reaction in the cell.

Some common examples for enzyme catalysis

1) The peptide glycyl L-glutamyl L-tyrosin is hydrolysed by an enzyme called pepsin.
2) The enzyme diastase hydrolyses starch into maltose

$$2(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_{12}H_{22}O_{11}$$

3) The yeast contains the enzyme zymase which converts glucose into ethanol.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

4) The enzyme micoderma aceti oxidises alcohol into acetic acid.

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$

5) The enzyme urease present in soya beans hydrolyses the urea.

$$NH_2\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2NH_3 + CO_2$$

10.3.1 Mechanism of enzyme catalysed reaction

The following mechanism is proposed for the enzyme catalysis

$$E + S \rightleftharpoons ES \rightarrow P + E$$

Where E is the enzyme, S the substrate (reactant), ES represents activated complex and P the products.

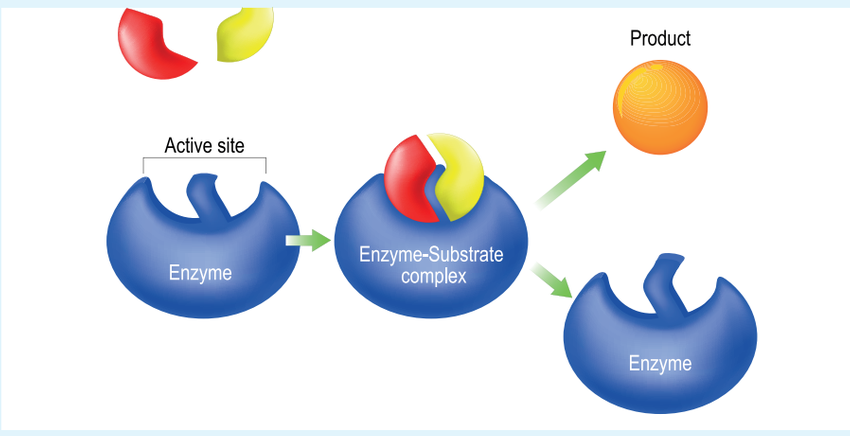


Figure 10.5 Mechanism of Enzyme Catalysis

Enzyme catalysed reaction show certain general special characteristics.

(i) Effective and efficient conversion is the special characteristic of enzyme catalysed reactions. An enzyme may transform a million molecules of reactant into product in a minute.

For eg. $2H_2O_2 \rightarrow 2H_2O + O_2$

For this reaction, the activation energy is 18k cal/mole without a catalyst.

With colloidal platinum as a catalyst the activation energy is 11.7kcal /mole

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But with the enzyme catalyst the activation energy of this reaction is less than 2kcal/mole.

(ii) Enzyme catalysis is highly specific in nature.

$H_2N\text{-}CO\text{-}NH_2 + H_2O \rightarrow 2NH_3 + CO_2$

The enzyme urease which catalyses the reaction of urea does not catalyse the following reaction of methyl urea

$H_2N\text{-}CO\text{-}NH\text{-}CH_3 + H_2O \rightarrow$ No reaction

(3) Enzyme catalysed reaction has maximum rate at optimum temperature. At first rate of reaction increases with the increase of temperature, but above a particular temperature the activity of enzyme is destroyed. The temperature at which enzymic activity is high or maximum is called as optimum temperature.

For example:

- Enzymes involved in human body have an optimum temperature 37°C /98°F
- During high fever, as body temperature rises the enzymatic activity may collapse and lead to danger.

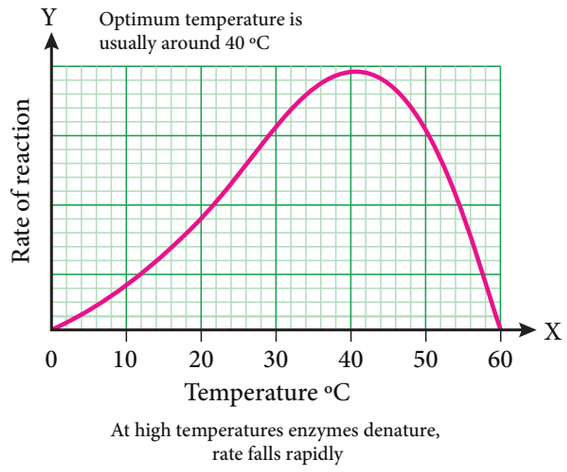


Figure 10.6 Rate vs Temperature

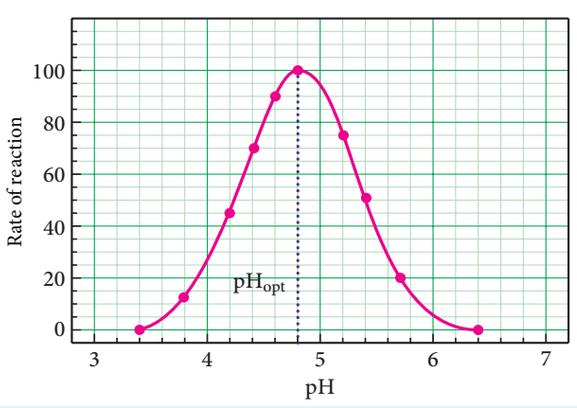


Figure 10.7 Rate vs pH

4. The rate of enzyme catalysed reactions varies with the pH of the system. The rate is maximum at a pH called optimum pH.
5. Enzymes can be inhibited i.e. poisoned.

Activity of an enzyme is decreased and destroyed by a poison.

The physiological action of drugs is related to their inhibiting action.

Example: Sulpha drugs. Penicillin inhibits the action of bacteria and used for curing diseases like pneumonia, dysentery, cholera and other infectious diseases.

6. Catalytic activity of enzymes is increased by coenzymes or activators.

A small non protein (vitamin) called a coenzyme promotes the catalytic activity of enzyme.

10.4 Zeolite Catalysis:

The details of heterogeneous catalysis will be incomplete, if zeolites are not discussed. Zeolites are microporous, crystalline, hydrated, alumino silicates, made of silicon and aluminium tetrahedron. There are about 50 natural zeolites and 150 synthetic zeolites. As

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silicon is tetravalent and aluminium is trivalent, the zeolite matrix carries extra negative charge. To balance the negative charge, there are extra framework cations for example, H^+ or Na^+ ions. Zeolites carrying protons are used as solid acid catalysts and they are extensively used in the petrochemical industry for cracking heavy hydrocarbon fractions into gasoline, diesel,etc., Zeolites carrying Na^+ ions are used as basic catalysts.

One of the most important applications of zeolites is their shape selectivity. In zeolites, the active sites namely protons are lying inside their pores. So, reactions occur only inside the pores of zeolites.

Reactant selectivity:

When bulkier molecules in a reactant mixture are prevented from reaching the active sites within the zeolite crystal, this selectivity is called reactant shape selectivity.

Transition state selectivity:

If the transition state of a reaction is large compared to the pore size of the zeolite, then no product will be formed.

Product selectivity:

It is encountered when certain product molecules are too big to diffuse out of the zeolite pores.

Phase Transfer catalysis:

Suppose the reactant of a reaction is present in one solvent and the other reactant is present in an another solvent. The reaction between them is very slow, if the solvents are immiscible. As the solvents form separate phases, the reactants have to migrate across the boundary to react. But migration of reactants across the boundary is not easy. For such situations a third solvent is added which is miscible with both. So, the phase boundary is eliminated, reactants freely mix and react fast. But for large scale production of any product, use of a third solvent is not convenient as it may be expensive. For such problems phase transfer catalysis provides a simple solution, which avoids the use of solvents. It directs the use a phase transfer catalyst (a phase transfer reagent) to facilitate transport of a reactant in one solvent to the other solvent where the second reactant is present. As the reactants are now brought together, they rapidly react and form the product.

Example:

Substitution of Cl^- and CN^- in the following reaction.

$$\underset{\text{organic phase}}{\text{R-Cl}} + \underset{\text{aqueous phase}}{\text{NaCN}} \rightarrow \underset{\text{organic phase}}{\text{R-CN}} + \underset{\text{aqueous phase}}{\text{NaCl}}$$

R-Cl=1-chlorooctane

R-CN=1-cyanooctane

By direct heating of two phase mixture of organic 1-chlorooctane with aqueous sodium cyanide for several days, 1-cyanooctane is not obtained. However, if a small amount of quaternary ammonium salt like tetraalkylammoniumchloride is added, a rapid transition

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of 1-cyanooctane occurs in about 100% yield after 1 or 2 hours. In this reaction, the tetraalkylammonium cation, which has hydrophobic and hydrophilic ends, transports CN^- from the aqueous phase to the organic phase using its hydrophilic end and facilitates the reaction with 1-chlorooctane as shown below:

$$NaCN + R_4N^+Cl^- \rightarrow R_4N^+CN^- + NaCl$$

aqueous phase — It moves to organic phas e

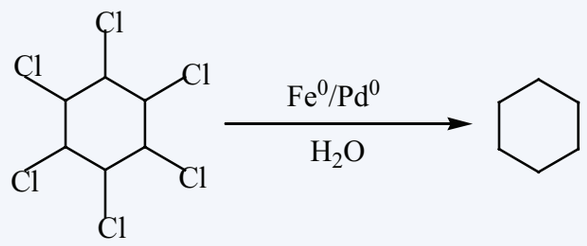
$$R_4N^+CN^- + R\text{-}Cl \rightarrow R\text{-}CN + R_4N^+Cl^-$$

Both in organic phase — organic phase — It moves to aqueous phase, releases Cl^- again pick s up CN^- and transports it.

So phase transfer catalyst, speeds up the reaction by transporting one reactant from one phase to another.

Nano Catalysis:

Nano materials such a metallic nano particles, metal oxides, etc., are used as catalyst in many chemical transformation, Nanocatalysts carry the advantages of both homogeneous and heterogeneous catalyses. Like homogeneous catalysts, the nanocatalysts give 100% selective transformations and excellent yield and show extremely high activity. Like the heterogeneous catalysts, nanocatalysts can be recovered and recycled. Nanocatalysts are actually soluble heterogeneous catalysts. An example for nanoparticles catalysed reaction is given below

(i) 

Lindane — cyclohexane

Fe^0/Pd^0 : Nanobimetallic catalyst (Zerovalent state)

10.5 Colloid, Dispersion phase and dispersion medium

Origin of study of colloid starts with Thomas Graham who observed diffusion of that a solution of sugar, urea or sodium chloride through a membrane but not glue, gelatine or gum. He called the former substances as crystalloids and the latter as colloids (In Greek, kola as gum, eidos-like).

Later it was realised that any substance can be converted into a colloid by reducing its particle size to 1-200nm.

Hence, colloid is a homogeneous mixture of two substances in which one substance (smaller proportion) is dispersed in another substance(large proportion).

In a colloid, the substance present in larger amount is called dispersing medium and the substance present in less amount is called dispersed phase.

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10.5.1 Classifications of Colloidal solution

Probably the most important colloidal systems have dispersed phase as solid and the dispersion medium as liquid.

If the dispersion medium considered is water, then the colloids are referred as hydrosols or aquasols.

If the dispersion medium is an alcohol, the colloid is termed as alcosol, and if benzene is the dispersion medium, it is called as benzosol.

One more type of classification is based on the forces acting between the dispersal phase and dispersion medium.

In lyophillic colloids definite attractive force or affinity exists between dispersion medium and dispersed phase. Examples: sols of protein and starch. They are more stable and will not get precipitated easily. They can be brought back to colloidal solution even after the precipitation by addition of the dispersion medium.

In a lyophobic colloids, no attractive force exists between the dispersed phase and dispersion medium. They are less stable and precipitated readily, but can not be produced again by just adding the dispersion medium. They themselves undergo coagulation after a span of characteristic life time.

They are called irreversible sols

examples: sols of gold, silver, platinum and copper.

The following table lists the types of colloids based on the physical states of dispersed phase and dispersion medium.

Classification of colloids based on the physical state of dispersed phase and dispersion medium.

S.No.	Dispersion medium	Dispersed phase	Name of the colloid	Examples
1.	Gas	Liquid	Liquid Aerosol	Fog Aerosol spray
2.	Gas	Solid	Solid Aerosol	Smoke, Air pollutants like fumes, dust.
3.	Liquid	Gas	Foam	Whipped cream, Shaving cream, Soda water, Froth.
4.	Liquid	Liquid	Emulsion	Milk, Cream, Mayonnaise
5.	Liquid	Solid	Sol	Inks, Paints, colloidal gold.

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6.	Solid	Gas	Solid foam	Pumice stone, Foam rubber bread.
7.	Solid	Liquid	Gel	Butter, cheese
8.	Solid	Solid	Solid sol	Pearls, opals coloured glass alloys colloidal dispersed eutetics.

10.5.2 Preparation of Colloids

Many lyophillic substances are made in their colloidal form by warming with water. Rubber forms colloidal solution with benzene. Soap spontaneously forms a colloidal solution by just mixing with water.

In general, colloidal are prepared by the following methods.

i. Dispersion methods: In this method larger particles are broken to colloidal dimension.

ii. Condensation method: In this method, smaller atom or molecules are converted into larger colloidal sized particles.

1) Dispersion methods

(i) Mechanical Dispersion:

Using a colloid mill, the solid is ground to colloidal dimension. The colloid mill consists of two metal plates rotating in opposite direction at very high speed of nearly 7000 revolution / minute.

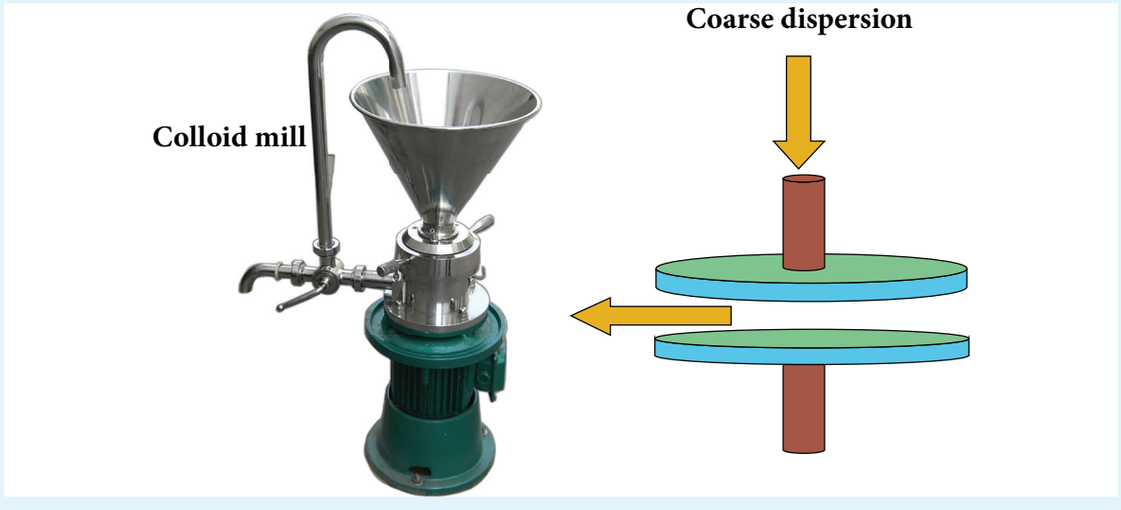


Figure 10.8 Colloid mill

The colloidal particles of required colloidal size is obtained by adjusting the distance between two plates.

By this method, colloidal solutions of ink and graphite are prepared.

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(ii) Electro Dispersion:

A brown colloidal solution of platinum was first prepared by George Bredig in 1898. An electrical arc is struck between electrodes dispersed in water surrounded by ice. When a current of 1 amp /100 V is passed an arc produced forms vapours of metal which immediately condense to form colloidal solution. By this method colloidal solution of many metals like copper, silver, gold, platinum, etc. can be prepared Alkali hydroxide is added as an stabilising agent for the colloidal solution.

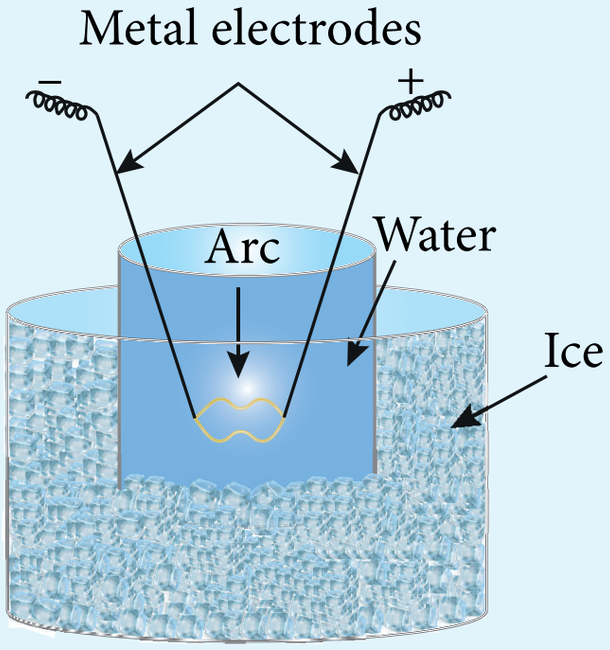


Figure 10.9 Bredig's are method

Svedberg modified this method for the preparation of non aqueous inflammable liquids like pentane, ether and benzene, etc using high frequency alternating current which prevents the decomposition of liquid.

(iii) Ultrasonic dispersion

Sound waves of frequency more than 20kHz (audible limit) could cause transformation of coarse suspension to colloidal dimensions.

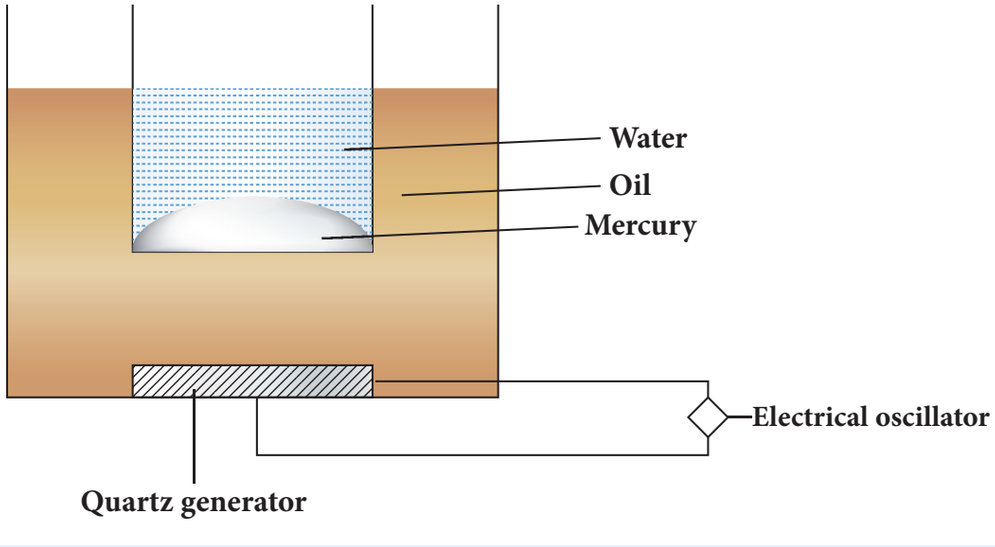


Figure : 10.10 Ultrasonic dispersion

Claus obtained mercury sol by subjecting mercury to sufficiently high frequency ultrasonic vibrations.

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The ultrasonic vibrations produced by generator spread the oil and transfer the vibration to the vessel with mercury in water.

(iv) Peptisation:

By addition of suitable electrolytes, precipitated particles can be brought into colloidal state. The process is termed as peptisation and the electrolyte added is called peptising or dispersing agent.

$$\underset{\text{Precipitate}}{AgCl} \xrightarrow{HCl} \underset{\text{Colloid}}{AgCl}$$

2) Condensation Methods:

When the substance for colloidal particle is present as small sized particle, molecule or ion, they are brought to the colloidal dimension by condensation methods. Here care should be taken to produce the particle with colloidal size otherwise precipitation will occur. Various chemical methods for the formation of colloidal particles.

(i) Oxidation:

Sols of some non metals are prepared by this method.

(a) When hydroiodic acid is treated with iodic acid, I_2 sol is obtained.

$$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2(Sol)$$

(b) When O_2 is passed through H_2Se, a sol of selenium is obtained.

$$2H_2Se + O_2 \rightarrow 2H_2O + 2Se(sol)$$

(ii) Reduction:

Many organic reagents like phenyl hydrazine, formaldehyde, etc are used for the formation of sols. For example: Gold sol is prepared by reduction of auric chloride using formaldehyde.

$$2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au(sol) + 6HCl + 3HCOOH$$

(iii) Hydrolysis

Sols of hydroxides of metals like chromium and aluminium can be produced by this method.

For Example,

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

(iv) Double decomposition

For the preparation of water insoluble sols this method can be used.

When hydrogen sulphide gas is passed through a solution of arsenic oxide, a yellow coloured arsenic sulphide is obtained as a colloidal solution.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

(v) Decomposition

When few drops of an acid is added to a dilute solution of sodium thiosulphate, the insoluble free sulphur produced by decomposition of sodium thiosulphate accumulates into small, clusters which impart various colours blue, yellow and even red to the system depending on their growth within the size of colloidal dimensions.

$$S_2O_3^{2-} + 2H^+ \rightarrow \underset{sol}{S} + H_2O + SO_2$$

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3) By exchange of solvent:

Colloidal solution of few substances like phosphorous or sulphur is obtained by preparing the solutions in alcohol and pouring them into water. As they are insoluble in water, they form colloidal solution.

$$P \text{ in alcohol} + \text{water} \rightarrow P_{sol}.$$

10.5.3 Purification of colloids

The colloidal solutions due to their different methods of preparation may contain impurities. If they are not removed, they may destabilise and precipitate the colloidal solution. This is called coagulation. Hence the impurities mainly electrolytes should be removed to increase the stabilisation of colloid. Purification of colloidal solution can be done by the following methods.

(i) Dialysis (ii) Electrodialysis (iii) Ultrafilteration.

(i) Dialysis

In 1861, T. Graham separated the electrolyte from a colloid using a semipermeable membrane (dialyser). In this method, the colloidal solution is taken in a bag made up of semipermeable membrane. It is suspended in a trough of flowing water, the electrolytes diffuse out of the membrane and they are carried away by water.

Do you Know? Kidney malfunction results in the building up of electrolyte concentration within the blood to toxic levels.

In the Dialysis, recycling of patient's blood is done through considerable length of seimpermeable tube in an isotonic saline solution.

ii) Electrodialysis

The presence of electric field increases the speed of removal of electrolytes from colloidal solution. The colloidal solution containing an electrolyte as impurity is placed between two dialysing membranes enclosed into two compartments filled with water. When current is passed, the impurities pass into water compartment and get removed periodically. This process is faster than dialysis, as the rate of diffusion of electrolytes is increased by the application of electricity.

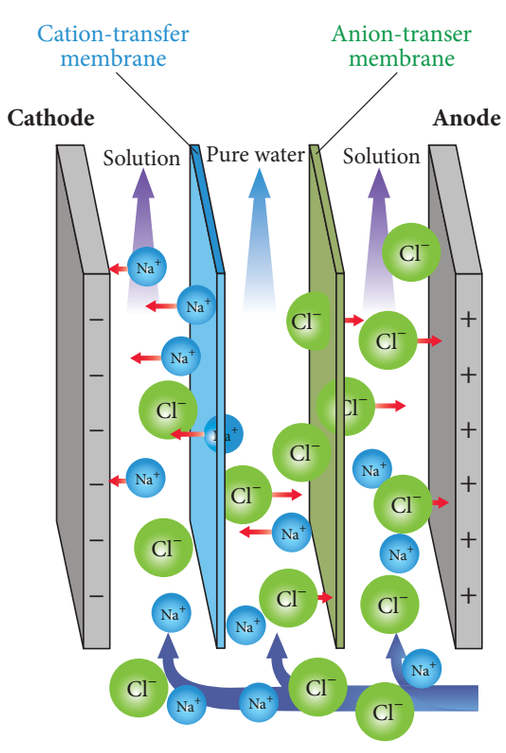


Figure 10.11 Electro Dialysis

iii) Ultrafiltration

The pores of ordinary filter papers permit the passage of colloidal solutions. In ultra filtrations, the membranes are made by using collodion cellophane or visiking. When a colloidal solution is filtered using such a filter,

colloidal particles are separated on the filter and the impurities are removed as washings. This process is quickened by application of pressure. The separation of sol particles from electrolyte by filteration through an ultrafilter is called ultrafiltration. Collodion is 4% solution of nitrocellulose in a mixture of alcohol and water.

10.5.4 Properties of Colloids

1) Colour:

The colour of a sol is not always the same as the colour of the substance in the bulk. For example bluish tinge is given by diluted milk in reflected light and reddish tinge in transmitted light.

Colour of the sol, generally depends on the following factors.

(i) Method of preparation
(ii) Wavelength of source of light.
(iii) Size and shape of colloidal particle
(iv) whether the observer views the reflected light or transmitted light.

2) Size:

The size of colloidal particles ranges from 1nm (10^{-9}m) to 1000 nm (10^{-6}m) diameter.

3) Colloidal solutions are heterogeneous in nature having two distinct phases.

Though experiments like dialysis, ultrafiltration and ultracentrifuging clearly show the heterogeneous nature in the recent times colloidal solution are considered as border line cases.

4) Filtrability:

As the size of pores in ordinary filter paper are large the colloidal particles easily pass through the ordinary filter papers.

5) Non-Setting nature

Colloidal solutions are quite stable i.e. they are not affected by gravity.

6) Concentration and density

When the colloidal solution is dilute, it is stable. When the volume of medium is decreased coagulation occurs. Generally, density of sol decreases with decrease in the concentration.

7) Diffusability

Unlike true solution, colloids diffuse less readily through membranes.

8) Colligative properties

The colloidal solutions show colligative properties i.e. elevation of boiling point, depression in freezing point and osmotic pressure. Measurements of osmotic pressure is used to find molecular weight of colloidal particle.

9) Shape of colloidal particles

It is very interesting to know the various shapes of colloidal particles. Here are some examples

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Colloidal Particles	Shapes
As_2S_3	Spherical
Fe $(OH)_3$sol (blue gold sol)	Disc or plate like
W_3O_5 sol (tungstic acid sol)	Rod like

10) Optical property

Colloids have optical property. When a homogeneous solution is seen in the direction of light, it appears clear but it appears dark, in a perpendicular direction.

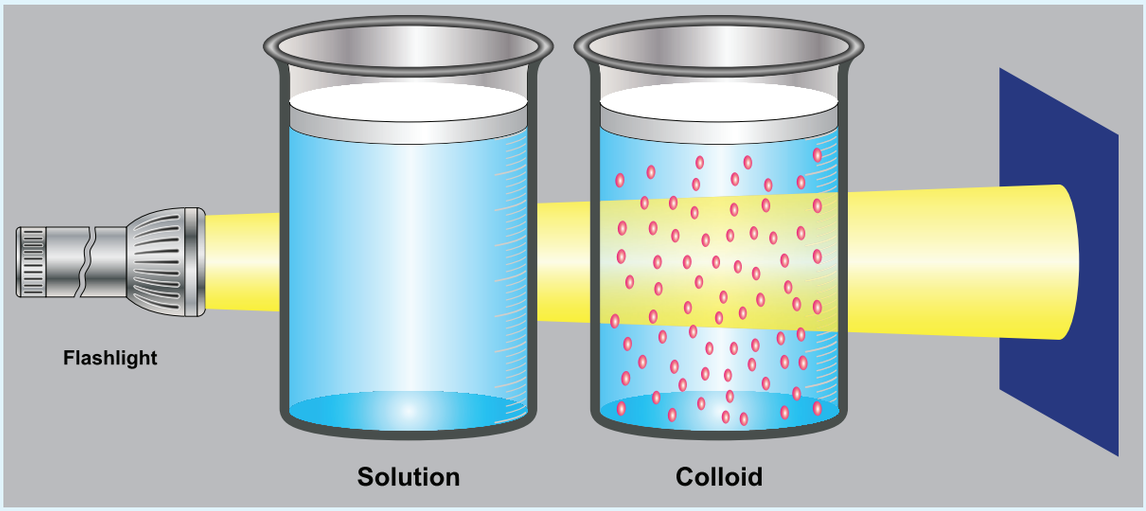


Figure 10.12 Tyndall effect

But when light passes through colloidal solution, it is scattered in all directions. This effect was first observed by Faraday, but investigations are made by Tyndall in detail, hence called as Tyndall effect.

The colloidal particles absorb a portion of light and the remaining portion is scattered from the surface of the colloid. Hence the path of light is made clear.

11) Kinetic property

Robert Brown observed that when the pollen grains suspended in water were viewed through ultra microscope, they showed a random, zigzag ceaseless motion.

This is called Brownian movement of colloidal particles.

This can be explained as follows

The colloidal sol particles are continuously bombarded with the molecules of the dispersion medium and hence they follow a zigzag, random, continuous movement.

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Brownian movement enables us,

I. to calculate Avogadro number.

II. to confirm kinetic theory which considers the ceaseless rapid movement of molecules that increases with increase in temperature.

III. to understand the stability of colloids: As the particles in continuous rapid movement they do not come close and hence not get condensed. That is Brownian movement does not allow the particles to be acted on by force of gravity.

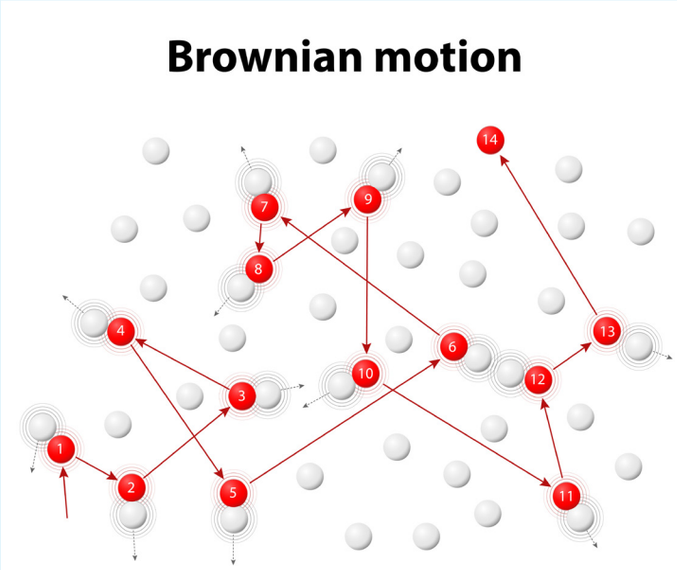


Figure 10. 13 Brownian movement

12) Electrical property

(1) Helmholtz double layer

The surface of colloidal particle adsorbs one type of ion due to preferential adsorption. This layer attracts the oppositely charged ions in the medium and hence at the boundary separating the two electrical double layers are setup. This is called as Helmholtz electrical double layer.

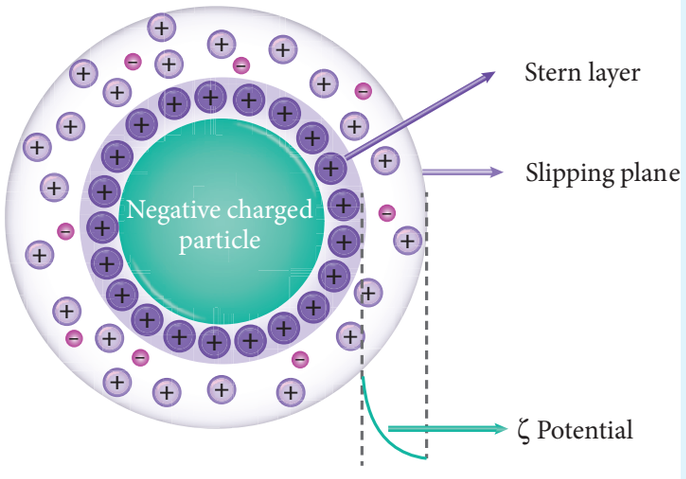


Figure 10.14 Electrical double layer

As the particles nearby are having similar charges, they cannot come close and condense. Hence this helps to explain the stability of a colloid.

(ii) Electrophoresis:

When electric potential is applied across two platinum electrodes dipped in a hydrophilic sol, the dispersed particles move toward one or other electrode.

This migration of sol particles under the influence of electric field is called electrophoresis or cataphoresis. If the sol particles migrate to the cathode, then they posses positive (+) charges,

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and if the sol particles migrate to the anode then they have negative charges(-). Thus from the direction of migration of sol particles we can determine the charge of the sol particles. Hence electrophoresis is used for detection of presence of charges on the sol particles.

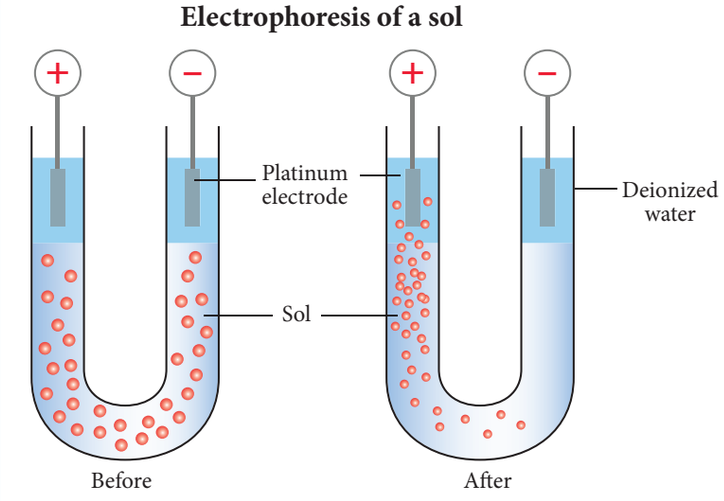


Figure 10.15 Electrophoresis

Few examples of charges of sols detected by electrophoresis are given below:

Positively charged colloids	Negatively charged colloids
Ferric hydroxide	Ag, Au & Pt
Aluminium hydroxide	Arsenic sulphide
Basic dyes	Clay
Haemoglobin	Starch

(iii) Electro osmosis

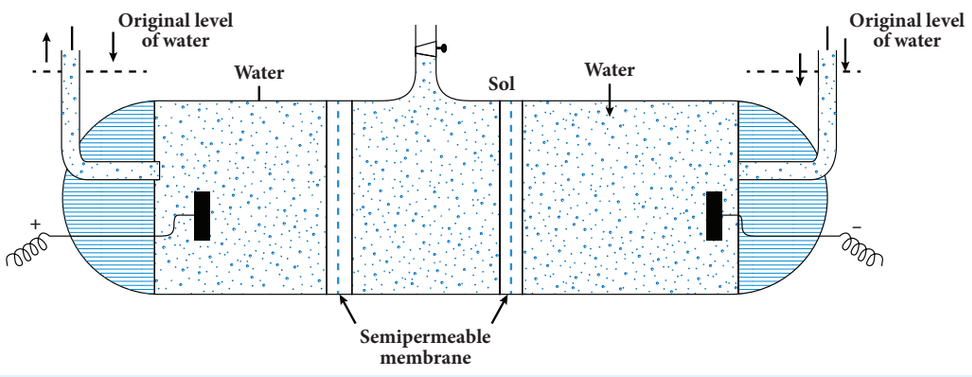


Figure 10.16 Electro osmosis

A sol is electrically neutral. Hence the medium carries an equal but opposite charge to that of dispersed particles. When sol particles are prevented from moving, under the influence of electric field the medium moves in a direction opposite to that of the sol particles. This movement of dispersion medium under the influence of electric potential is called electro osmosis.

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13. Coagulation or precipitation

The flocculation and settling down of the sol particles is called coagulation.

Various method of coagulation are given below:

(i) Addition of electrolytes

(ii) Electrophoresis

(iii) Mixing oppositively charged sols.

(iv) Boiling

(1) Addition of electrolytes

A negative ion causes the precipitation of positively charged sol and vice versa.

When the valency of ion is high, the precipitation power is increased. For example, the precipitation power of some cations and anions varies in the following order

$$Al^{3+} > Ba^{2+} > Na^{+} \text{ , Similarly } [Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^{-}$$

The precipitation power of electrolyte is determined by finding the minimum concentration (millimoles/lit) required to cause precipitation of a sol in 2hours. This value is called flocculation value. The smaller the flocculation value greater will be precipitation.

(ii) Electrophoresis:

In the electrophoresis, charged particles migrate to the electrode of opposite sign. It is due to neutralization of the charge of the colloids. The particles are discharged and so they get precipitated.

(iii) By mixing two oppositively charged sols

When colloidal sols with opposite charges are mixed mutual coagulation takes place. It is due to migration of ions from the surface of the particles.

(iv) By boiling

When boiled due to increased collisions, the sol particles combine and settle down.

14. Protective action

Generally, lyophobic sols are precipitated readily even with small amount of electrolytes. But they are stabilised by addition of a small amount of lyophillic colloid.

A small amount of gelatine sol is added to gold sol to protect the gold sol.

Colloid	Gold number
Gelatin	0.005-0.01
Egg albumin	0.08-0.10
Gum Arabic	0.1-0.15
Potato starch	25

Zsigmondy introduced the term 'gold number' as a measure of protecting power of a colloid. Gold number is defined as the number of milligrams of hydrophilic colloid that will just prevent the precipitation of 10ml of gold sol on the addition of 1ml of 10% NaCl solution. Smaller the gold number greater the protective power.

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10.6 Emulsions

Emulsions are colloidal solution in which a liquid is dispersed in an another liquid.

Generally there are two types of emulsions.

(i) Oil in water (O/W) **(ii) Water in oil (W/O)**

Example:

Milk is example of the oil in water type emulsion.

Stiff greases are emulsion of water in oil i.e. water dispersed in lubricating oil.

The process of preparation of emulsion by the dispersal of one liquid in another liquid is called Emulsification.

A colloid mill can be used as a homogeniser to mix the two liquid. To have a stable emulsion a small amount of emulsifier or emulsification agent is added.

Several types of emulsifiers are known.

i. Most of the lyophillic colloids also act as emulsifiers. Example: glue, gelatine.
ii. Long chain compounds with polar groups like soap and sulphonic acids.
iii. Insoluble powders like clay and lamp black also act as emulsifiers.

Identification of types of emulsion

The two types of emulsions can be identified by the following tests.

(i) Dye test:

A small amount of dye soluble in oil is added to the emulsion. The emulsion is shaken well. The aqueous emulsion will not take the colour whereas oily emulsion will take up the colour of the dye.

(ii)Viscosity test

Viscosity of the emulsion is determined by experiments. Oily emulsions will have higher value than aqueous emulsion.

(iii) Conductivity test

Conductivity of aqueous emulsions are always higher than oily emulsions.

(iv) Spreading test

Oily emulsions spread readily than aqueous emulsion when spread on an oily surface.

10.5.1 Deemulsification:

Emulsion can be separated into two separate layers. The process is called Deemulsification.

Various deemulsification techniques are given below

1. Distilling of one component
2. Adding an electrolyte to destroy the charge.
3. Destroying the emulsifier using chemical methods.

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4. Using solvent extraction to remove one component.
5. By freezing one of the components.
6. By applying centrifugal force.
7. Adding dehydrating agents for water in oil (W/O) type.
8. Using ultrasonic waves.
9. Heating at high pressures.

Inversion of Phase:

The change of W/O emulsion into O/W emulsion is called inversion of phases.

For example:

An oil in water emulsion containing potassium soap as emulsifying agent can be converted into water in oil emulsion by adding $CaCl_2$ or $AlCl_3$. The mechanism of inversion is in the recent developments of research.

10.7 Various application of colloids

In every path of life, colloids play a great role. Human body contains the numerous colloidal solutions. The blood in our body, protoplasma of plant and animal cell, and fats in our intestines are in the form of emulsions. Synthetic polymers like polystyrene silicones and PVC are colloids.

Food

Food stuffs like milk cream, butter, etc are present in colloidal form.

Medicines

Antibodies such as penicillin and streptomycin are produced in colloidal form for suitable injections. Colloidal gold and colloidal calcium are used as tonics. Milk of magnesia is used for stomach troubles. Silver sol protected by gelatine known as Argyrol is used as eye lotion.

In Industry

Colloids find many applications in industries.

(i) Water purification:

Purification of drinking water is activated by coagulation of suspended impurities in water using alums containing Al^{3+}

(ii) In washing:

The cleansing action of soap is due to the formation of emulsion of soap molecules with dirt and grease.

(iii) Tanning of leather

Skin and hides are protein containing positively charged particles which are coagulated by adding tannin to give hardened leather for further application. Chromium salts are used for the purpose. Chrome tanning can produce soft and polishable leather.

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(iv) Rubber industry:

Latex is the emulsion of natural rubber with negative particles. By heating rubber with sulphur, vulcanized rubbers are produced for tyres, tubes, etc.

(v) Sewage disposal

Sewage contains dirt, mud and wastes dispersed in water. The passage of electric current deposits the wastes materials which can be used as a manure.

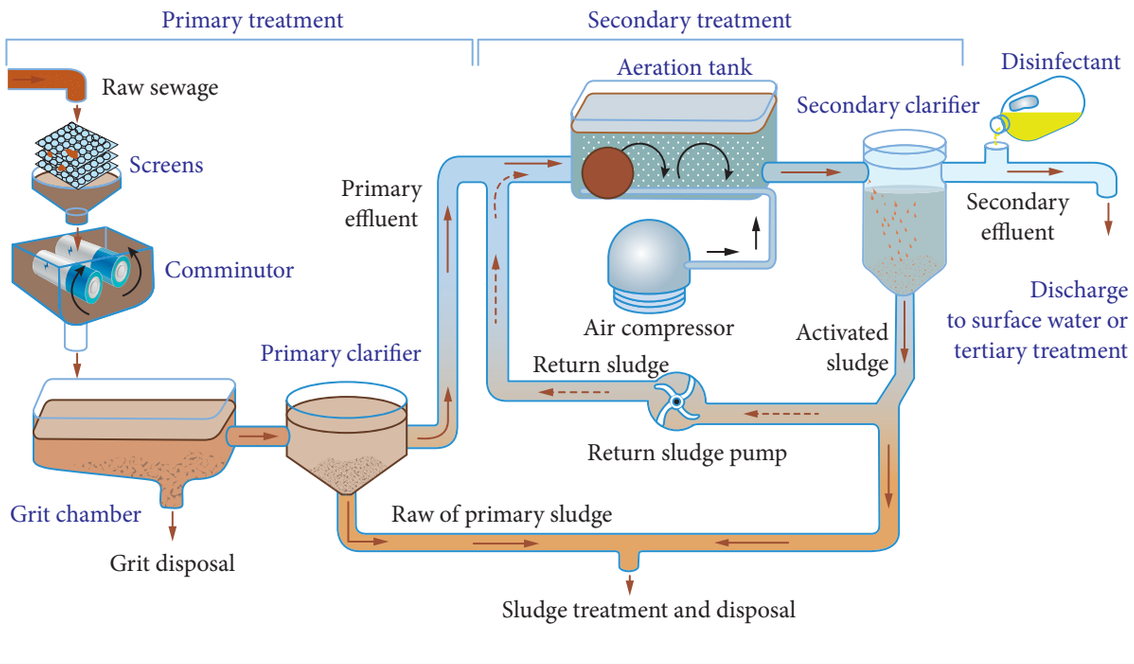


Figure 10.17 Sewage disposal

Vi) Cortrell's precipitator

Carbon dust in air is solidified by cortrell's precipitator. In it, a high potential difference of about 50,000V is used. The charge on carbon is neutralized and solidified. Thus the air is free from carbon particles.

Vii) The blue colour of the sky in nature is due to Tyndall effect of air particles.

Viii) Formation of delta:

The electrolyte in sea and river water coagulates the solid particles in river water at their intersection. So, the earth becomes a fertile land.

Ix) Analytical application

Qualitative and quantitative analysis are based on the various properties of colloids.

Hence we can conclude that in our life, there is hardly any field which is not including the applications of colloids.

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Natural honey is a colloidal sol. It is distinguished from artificial one by adding ammoniacal $AgNO_3$

In case of natural honey a metallic silver is produced, assumes a reddish yellow color due to traces of albumin or ethereal oil which acts as a protective colloid. In case of artificial honey a dark yellow or greenish yellow precipitate is formed.



EVALUATION



Choose the correct answer:

1. For Freundlich isotherm a graph of $\log \frac{x}{m}$ is plotted against log p. The slope of the line and its y – axis intercept respectively corresponds to

   a) $1/n$, k b) $\log 1/n$, k c) $1/n$, log k d) $\log 1/n$, log k

2. Which of the following is incorrect for physisorption?

   a) reversible b) increases with increase in temperature

   c) low heat of adsorption d) increases with increase in surface area

3. Which one of the following characteristics are associated with adsorption? (NEET)

   a) ΔG and ΔH are negative but ΔS is positive

   b) ΔG and ΔS are negative but ΔH is positive

   c) ΔG is negative but ΔH and ΔS are positive d) ΔG, ΔH and ΔS all are negative.

4. Fog is colloidal solution of

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

5. Assertion : Coagulation power of Al^{3+} is more than Na^{+}.

   Reason : greater the valency of the flocculating ion added, greater is its power to cause precipitation

   a) if both assertion and reason are true and reason is the correct explanation of assertion.

   b) if both assertion and reason are true but reason is not the correct explanation of assertion.

   c) assertion is true but reason is false d) both assertion and reason are false.

6. Statement :

   To stop bleeding from an injury, ferric chloride can be applied. Which comment about the statement is justified?

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a) It is not true, ferric chloride is a poison.

b) It is true, Fe^{3+} ions coagulate blood which is a negatively charged sol

c) It is not true; ferric chloride is ionic and gets into the blood stream.

d) It is true, coagulation takes place because of formation of negatively charged sol with Cl^-.

7. Hair cream is

a) gel b) emulsion c) solid sol d) sol.

8. Which one of the following is correctly matched?

a) Emulsion	–	Smoke
b) Gel	–	butter
c) foam	–	Mist
d) whipped cream	–	sol

9. The most effective electrolyte for the coagulation of As_2S_3 Sol is

a) NaCl b) $Ba(NO_3)_2$ c) $K_3[Fe(CN)_6]$ d) $Al_2(SO_4)_3$

10. Which one of the is not a surfactant?

a) $CH_3 — (CH_2)_{15} — \overset{+}{N} — (CH_3)_2\ CH_2Br$

b) $CH_3 — (CH_2)_{15} — NH_2$

c) $CH_3 — (CH_2)_{16} — CH_2\ OSO_2^-\ Na^+$

d) $OHC — (CH_2)_{14} — CH_2 — COO^-\ Na^+$

11. The phenomenon observed when a beam of light is passed through a colloidal solution is

a) Cataphoresis b) Electrophoresis c) Coagulation d) Tyndall effect

12. In an electrical field, the particles of a colloidal system move towards cathode. The coagulation of the same sol is studied using K_2SO_4(i), Na_3PO_4(ii),$K_4[Fe(CN)_6]$ (iii) and NaCl (iv) Their coagulating power should be

a) II > I>IV > III b) III > II > I > IV c) I > II > III > IV d) none of these

13. Collodion is a 4% solution of which one of the following compounds in alcohol – ether mixture?

a) Nitroglycerine b) Cellulose acetate c) Glycoldinitrate d) Nitrocellulose

14. Which one of the following is an example for homogeneous catalysis?

a) manufacture of ammonia by Haber's process

b) manufacture of sulphuric acid by contact process

c) hydrogenation of oil

d) Hydrolysis of sucrose in presence of dil HCl

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15. Match the following

A) V_2O_5	i) High density polyethylene
B) Ziegler – Natta	ii) PAN
C) Peroxide	iii) NH_3
D) Finely divided Fe	iv) H_2SO_4

	A	B	C	D
a)	(iv)	(i)	(ii)	(iii)
b)	(i)	(ii)	(iv)	(iii)
c)	(ii)	(iii)	(iv)	(i)
d)	(iii)	(iv)	(ii)	(i)

16. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below

(I) (NaCl)=52 (II) (($BaCl_2$)=0.69 (III) ($MgSO_4$)=0.22

The correct order of their coagulating power is

a) III > II > I b) I > II > III c) I > III > II d) II > III>I

17. Adsorption of a gas on solid metal surface is spontaneous and exothermic, then

a) ΔH increases b) ΔS increases c) ΔG increases d) ΔS decreases

18. If x is the amount of adsorbate and m is the amount of adsorbent, which of the following relations is not related to adsorption process?

a) x/m =f(P) at constant T b) x/m =f(T) at constant P

c) P = f(T) at constant x/m d) x/m = PT

19. On which of the following properties does the coagulating power of an ion depend ? (NEET – 2018)

a) Both magnitude and sign of the charge on the ion.
b) Size of the ion alone
c) the magnitude of the charge on the ion alone
d) the sign of charge on the ion alone.

20. Match the following

A) Pure nitrogen	i) Chlorine
B) Haber process	ii) Sulphuric acid
C) Contact process	iii) Ammonia
D) Deacons Process	iv) sodium azide (or) Barium azide

Which of the following is the correct option?

	A	B	C	D
a)	(i)	(ii)	(iii)	(iv)
b)	(ii)	(iv)	(i)	(iii)
c)	(iii)	(iv)	(ii)	(i)
d)	(iv)	(iii)	(ii)	(i)

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Short Answer

1. Give two important characteristics of physisorption
2. Differentiate physisorption and chemisorption
3. In case of chemisorption, why adsorption first increases and then decreases with temperature?
4. Which will be adsorbed more readily on the surface of charcoal and why? NH_3 or O_2 ?
5. Heat of adsorption is greater for chemisorptions than physisorption. Why?
6. Peptising agent is added to convert precipitate into colloidal solution. Explain with an example.
7. What happens when a colloidal sol of $Fe(OH)_3$ and As_2S_3 are mixed?
8. What is the difference between a sol and a gel?
9. Why are lyophillic colloidal sols are more stable than lyophobic colloidal sol.
10. Addition of Alum purifies water. Why?
11. What are the factors which influence the adsorption of a gas on a solid?
12. What are enzymes? Write a brief note on the mechanism of enzyme catalysis.
13. What do you mean by activity and selectivity of catalyst?
14. Describe some feature of catalysis by Zeolites.
15. Give three uses of emulsions.
16. Why does bleeding stop by rubbing moist alum
17. Why is desorption important for a substance to act as good catalyst?
18. Comment on the statement: Colloid is not a substance but it is a state of substance.
19. Explain any one method for coagulation
20. Write a note on electro osmosis
21. Write a note on catalytic poison
22. Explain intermediate compound formation theory of catalysis with an example
23. What is the difference between homogenous and hetrogenous catalysis?
24. Describe adsorption theory of catalysis.

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UNIT 11

HYDROXY COMPOUNDS AND ETHERS



Alfred Bernhard Nobel

Alfred Bernhard Nobel was a Swedish chemist, engineer, inventor, and philanthropist. Nobel found that when nitroglycerine was incorporated in an inert absorbent like kieselguhr (diatomaceous earth) it became safer and more convenient to handle. He patented this mixture in 1867 as "dynamite". Nobel prizes were established in accordance with his will. The Nobel prizes is considered as one of the precious awards in the fields of chemistry, literature, peace activism, physics, economics and physiology or medicine.

KOMWX

Learning Objectives

After studying this unit the student will be able to

- describe the important methods of preparation and reactions of alcohols
- explain the mechanism of Nucleophilic substitution reaction of alcohols and ethers.
- explain the elimination reaction of alcohols.
- describe the preparation and properties of phenols
- discuss the preparation of ethers and explain their chemical reactions.
- recognise the uses of alcohols and ethers

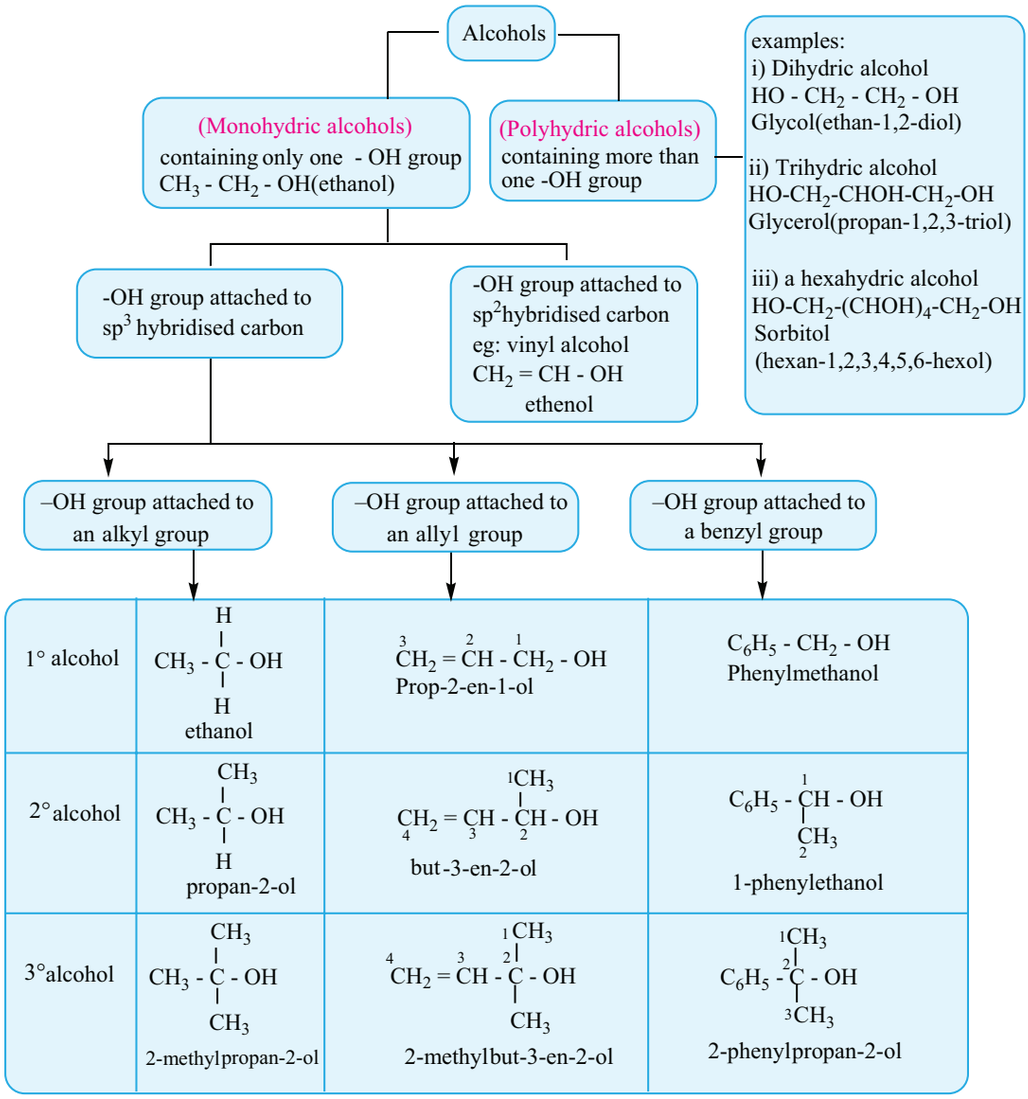
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INTRODUCTION

We have already learnt in eleventh standard that the hydrolysis of an alkyl halide gives an alcohol, an organic compound containing hydroxyl (-OH) functional group. Many organic compounds containing –OH group play an important role in our body. For example, cholesteryl alcohol commonly known as cholesterol is an important component in our cell membrane. Retinol, the storage form of vitamin A, finds application in proper functioning of our eyes. Alcohols also find application in many areas like medicine, industry, etc., For example, methanol is used as an industrial solvent, ethyl alcohol an additive to petrol, isopropyl alcohol as a skin cleanser for injection, etc., The hydroxyl group of alcohol can be converted to many other functional groups. Hence, alcohols are important resource in synthetic organic chemistry. In this unit, we will learn the preparation, properties and uses of alcohols, phenols and ethers.

11.1 Classification of alcohols:

Alcohols can be classified based on the number of hydroxyl groups and the nature of the carbon to which the functional group (–OH) is attached.



1° alcohol	$CH_3 - \underset{H}{\overset{H}{\underset{\vert}{\overset{\vert}{C}}}} - OH$ ethanol	$\overset{3}{C}H_2 = \overset{2}{C}H - \overset{1}{C}H_2 - OH$ Prop-2-en-1-ol	$C_6H_5 - CH_2 - OH$ Phenylmethanol
2°alcohol	$CH_3 - \underset{H}{\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}} - OH$ propan-2-ol	$\overset{4}{C}H_2 = \overset{3}{C}H - \overset{2}{\underset{CH_3}{\overset{^1CH_3}{C}}} - OH$ but-3-en-2-ol	$C_6H_5 - \underset{CH_3}{\overset{1}{CH}} - OH$ 1-phenylethanol
3°alcohol	$CH_3 - \underset{CH_3}{\overset{CH_3}{\underset{\vert}{\overset{\vert}{C}}}} - OH$ 2-methylpropan-2-ol	$\overset{4}{C}H_2 = \overset{3}{C}H - \overset{2}{\underset{CH_3}{\overset{^1CH_3}{C}}} - OH$ 2-methylbut-3-en-2-ol	$C_6H_5 - \underset{^3CH_3}{\overset{^1CH_3}{\overset{2}{C}}} - OH$ 2-phenylpropan-2-ol

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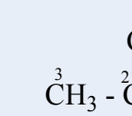
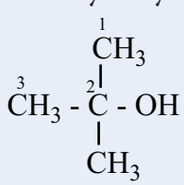
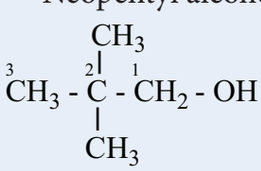
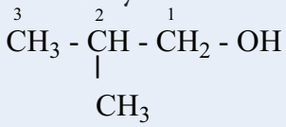
11.2 IUPAC Nomenclature

We have already learnt about naming the organic compounds according to IUPAC guidelines in XI standard. Let us recall the basic rules to name the alcohols.

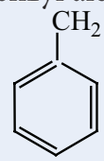
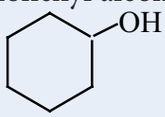
1. Select the longest continuous chain of carbon atoms (root word) containing the functional group (-OH).
2. Number the carbon atoms in the chain so that the carbon bearing the -OH group has the lowest possible number.
3. Name the substituent (if any)
4. Write the name of the alcohol as below.

Prefix + Root word + Primary suffix + Secondary suffix
(substituents) (longest chain) (Saturation /unsaturation) (ol)

The following table illustrates the IUPAC nomenclature of alcohols.

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Isopropyl alcohol  Propan-2-ol	-	Prop	ane	2-ol
Tertiary butyl alcohol  2-methylpropan-2-ol	2-methyl	Prop	ane	2-ol
Neopentyl alcohol  2,2-dimethylpropan-1-ol	2,2-dimethyl	Prop	ane	1-ol
Isobutyl alcohol  2-methylpropan-1-ol	2-methyl	Prop	ane	1-ol

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Benzyl alcohol  Phenylmethanol	Phenyl	Meth	ane	ol
Allyl alcohol $^{3}CH_2=\overset{2}{C}H-\overset{1}{C}H_2-OH$ Prop-2-en-1-ol	-	Prop	2-ene	1-ol
Cyclohexyl alcohol  Cyclohexanol	-	Cyclohex	ane	ol
Glycerol $HO-CH_2-CH(OH)-CH_2-OH$ Propane – 1,2,3 – triol	-	Prop	ane	1,2,3 – triol

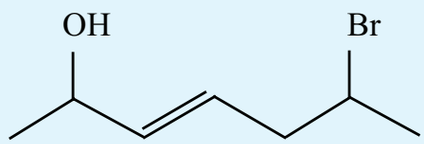
Evaluate Yourself:

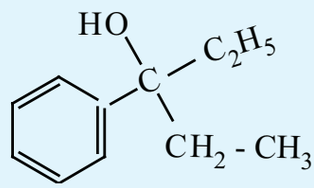
1. Classify the following alcohols as 1°, 2°, and 3° and give their IUPAC Names.

a) $CH_3-CH_2-CH(OH)CH_2-\overset{Br}{\overset{|}{C}}(CH_3)_2$

b) $(C_2H_5)_3COH$

c) $CH_2=C(Cl)-CH(OH)CH_3$

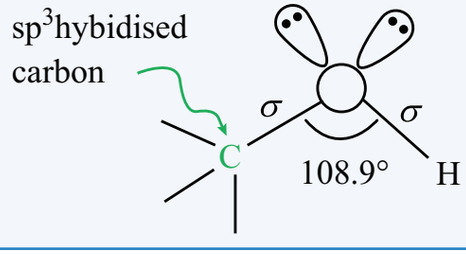
d) 

e) 

2. Write all the possible isomers of an alcohol having the molecular formula $C_5H_{12}O$ and give their IUPAC names.

Structure of the functional group of alcohol.

The structure of -O-H group which is attached to a sp^3 hybridised carbon is similar to the structure of -O-H group attached to a hydrogen in water. i.e., 'V' shaped. In such alcohols, one of the sp^3 hybridised orbital of



oxygen linearly overlap with the sp^3 hybridised orbital of carbon to form a C-O, 'σ' bond and another sp^3 hybridised orbital linearly overlap with 1s orbital of hydrogen to form a O-H 'σ' bond. The remaining two sp^3 hybridised orbitals of oxygen are occupied by two lone pairs of electrons. Due to the lone pair – lone pair repulsion, the C-O-H bond angle in methanol is reduced to $108.9°$ from the regular tetrahedral bond angle of $109.5°$.

Preparation of alcohols:

We have already learnt that the nucleophilic substitution reactions of alkyl halides with dilute alkali, conversion of alkenes to alcohols by hydration and the preparation of alcohols using Grignard reagent in XI standard. These reactions are summarised below.

1. **From Alkyl halides:** Alkyl halides on heating with dilute aqueous NaOH gives alcohols. Primary alkyl halides undergo substitution by SN^2 reaction. Secondary and tertiary alkyl halides usually undergo nucleophilic substitution by SN^1 mechanism.

$$R\text{-}X + NaOH(aq) \xrightarrow{\Delta} R\text{-}OH + NaX$$

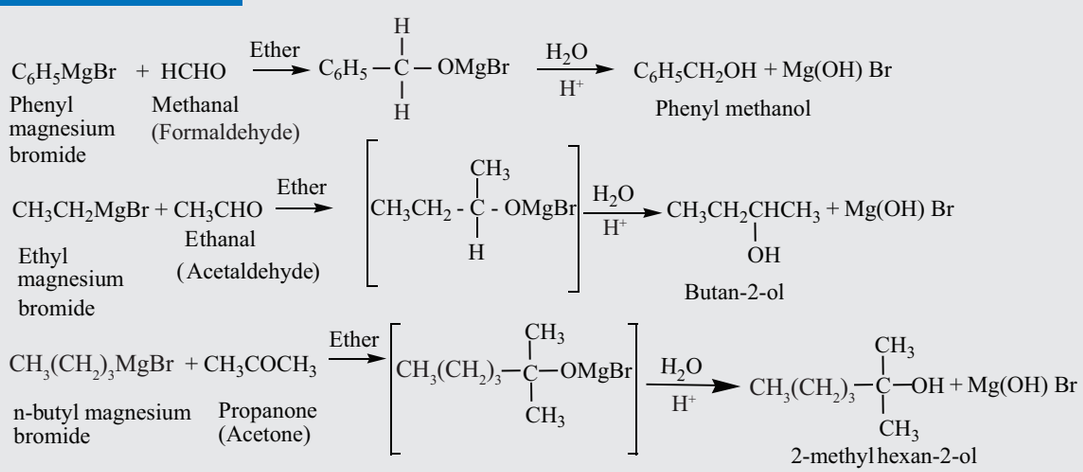
If R =t-butyl, the reaction proceeds through the formation of t-butyl carbocation

2. **From alkenes:** Addition of water across the double bond of an alkene in presence of concentrated sulphuric acid gives alcohols. This addition reaction follows Markownikoff's rule.

Example:
$$\underset{\text{propylene}}{CH_3\text{-}CH=CH_2} + H_2O \xrightarrow{Conc.H_2SO_4} \underset{\text{propan-2-ol}}{CH_3\text{-}CH(OH)\text{-}CH_3}$$

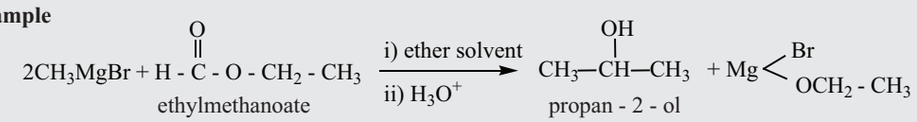
3. **From Grignard reagent:** Nucleophilic addition of Grignard reagent to aldehydes/ketones in presence of dry ether followed by the acid hydrolysis gives alcohols. Formaldehyde gives primary alcohol and other aldehydes give secondary alcohols. Ketones give tertiary alcohols.

Examples



Formate ester is used to prepare a secondary alcohol with identical alkyl groups

Example



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4. Hydroboration:

Diborane reacts with an alkene to form trialkyl borane which on treatment with H_2O_2 in presence of NaOH gives an alcohol. (Refer reactions of diborane) The overall reaction is hydration of an alkene. This reaction yields an anti-Markownikoff's product.

$$6CH_3-CH=CH_2 + B_2H_6 \longrightarrow \underset{\text{Tripropylborane}}{2(CH_3-CH_2-CH_2)_3B}$$

$$(CH_3-CH_2-CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} \underset{\text{propan-1-ol}}{3CH_3-CH_2-CH_2-OH} + B(OH)_3$$

5. Reduction of carbonyl compounds:

Reduction of aldehydes/ketones with $LiAlH_4$ in the presence of solvents like THF (Tetrahydrofuran) followed by hydrolysis gives alcohols. Unlike other reducing agents such as Raney Ni, Na-Hg/H_2O, the lithium aluminium hydride does not reduce the carbon–carbon double bond present in unsaturated carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.

Examples

$$\underset{\text{acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} \xrightarrow[ii)\ H_2O]{i)\ LiAlH_4} \underset{\text{propan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-H}$$

$$C_6H_5-COOH \xrightarrow[(ii)H_2O]{(i)LiAlH_4} C_6H_5CH_2OH$$

Benzoic acid — Phenyl methanol(Benzyl alcohol)

$$CH_3COOCH_2CH_3 \xrightarrow[(ii)H_2O]{(i)LiAlH_4} 2CH_3CH_2OH$$

Ethyl ethanoate (ethyl acetate) — Ethanol

$$CH_3-CH=CH-CHO \xrightarrow[(ii)H_2O]{(i)LiAlH_4} CH_3-CH=CH-CH_2OH$$

crotonaldehyde (but-2-enal) — crotyl alcohol (but-2-en-1-ol)

When two or more functional groups are present in a molecule a less vigorous sodium borohydride is used as a reducing agent to reduce the more reactive group. For example, if a compound contains both carbonyl and carboxyl group, it preferentially reduces the carbonyl group.

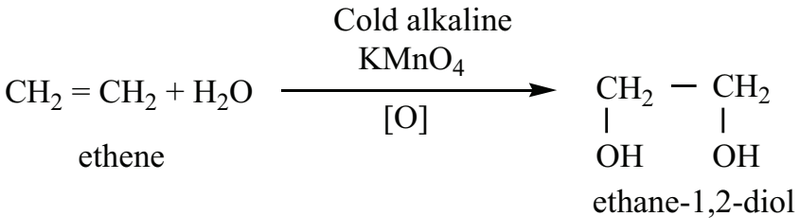
$$RCOCH_2CH_2COOH \xrightarrow[H_3O^+]{NaBH_4} RCHOH-CH_2CH_2COOH$$

4-alkyl- 4- hydroxybutanoic acid

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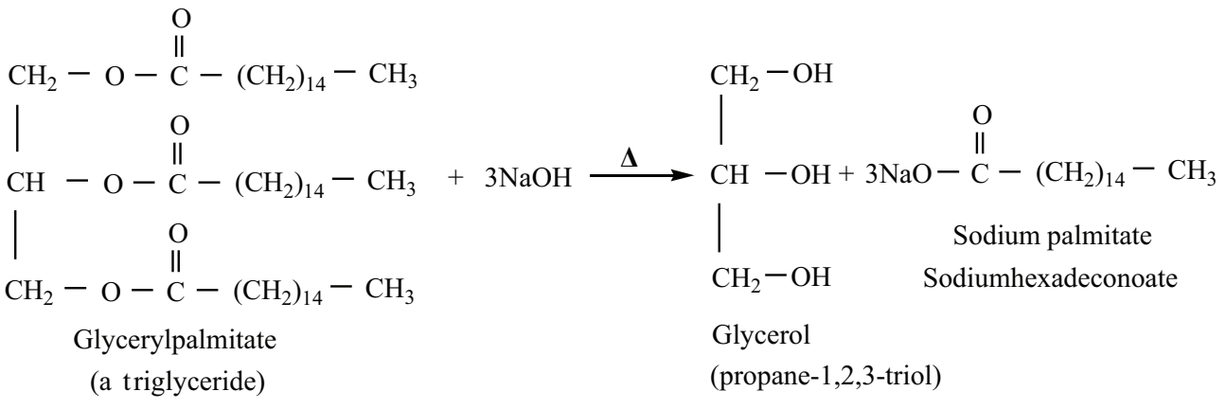
Preparation of glycol

We have already learnt that the hydroxylation of ethylene using cold alkaline solution of potassium permanganate (Baeyer's reagent) gives ethylene glycol.



Preparation of glycerol

Glycerol occurs in many natural fats and it is also found in long chain fatty acids in the form of glyceryl esters (Triglycerides). The alkaline hydrolysis of these fats gives glycerol and the reaction is known as saponification.



Evaluate Yourself?

1. Suggest a suitable carbonyl compound for the preparation of pent-2-en-1-ol using $LiAlH_4$.
2. 2-methylpropene $\xrightarrow{H_2SO_4/H_2O}$?
3. How will you prepare the following using Grignard reagent.
   i) t-butyl alcohol
   ii) allyl alcohol

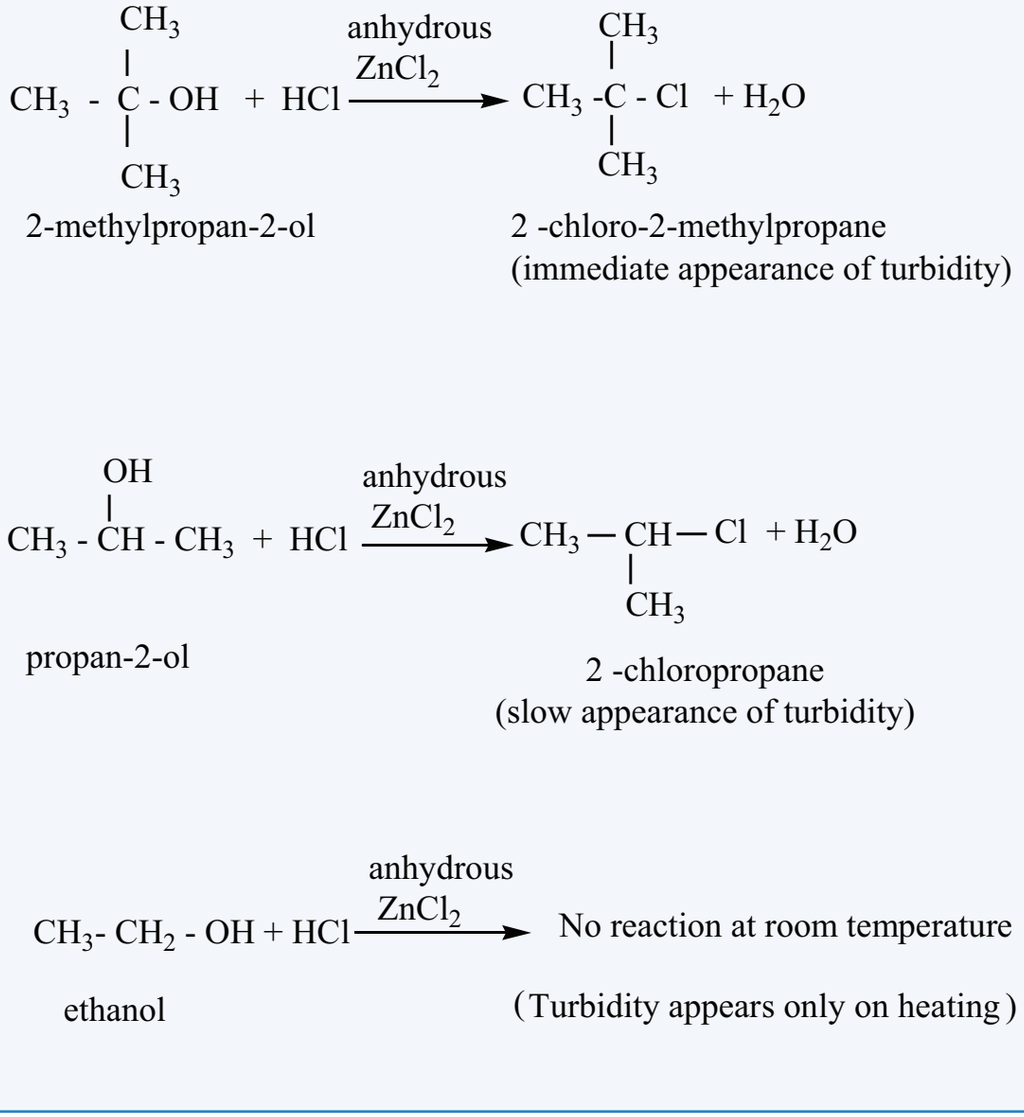
Methods to differentiate primary, secondary and tertiary alcohols.

The following tests are used to distinguish between 1°, 2° and 3° alcohols.

a) Lucas test:

When alcohols are treated with Lucas agent (a mixture of concentrated HCl and anhydrous $ZnCl_2$) at room temperature, tertiary alcohols react immediately to form a turbidity due to the formation of alkyl chloride which is insoluble in the medium. Secondary alcohols react within 10 minutes to form a turbidity of alkyl chloride where primary alcohols do not react at room temperature.

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b) Victor Meyer's test:

This test is based on the behaviour of the different nitro alkanes formed by the three types of alcohols with nitrous acid and it consists of the following steps.

i) Alcohols are converted into alkyl iodide by treating it with I_2/P.

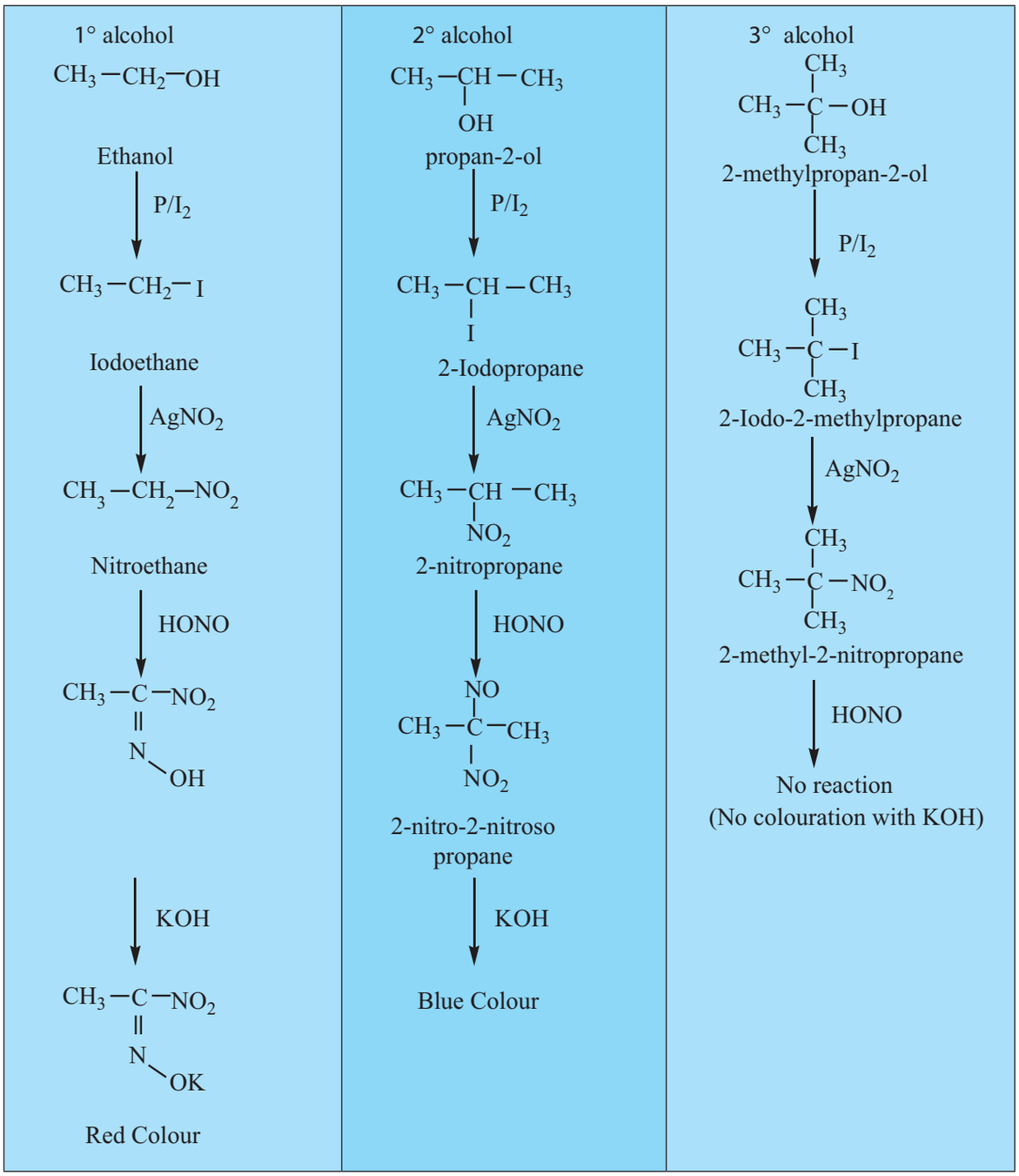
ii) Alkyl iodide so formed is then treated with $AgNO_2$ to form nitro alkanes.

ii) Nitro alkanes are finally treated with HNO_2 (mixture of $NaNO_2$ / HCl) and the resultant solution is made alkaline with KOH.

Result:

- Primary alcohol gives red colour • Secondary alcohol gives blue colour.
- No colouration will be observed in case of tertiary alcohol.

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Properties of alcohols

Physical properties

i. Lower alcohols are colourless liquids and the higher members are waxy solids.

ii. They have higher boiling points than the corresponding other organic compounds such as alkanes, aldehydes, ethers etc., this is due to the presence of intermolecular hydrogen bonding present in alcohols.

iii. Among isomeric alcohols primary alcohols have higher boiling point and the tertiary alcohols have lower boiling points.

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iv. The lower members are highly soluble in water due to the formation of intermolecular hydrogen bonding with water.

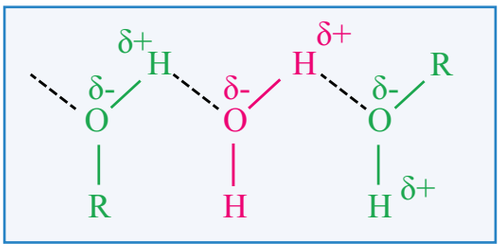


Table : Boiling point of alcohols in comparision with other organic compounds.

S.No.	Compound	Molecule formula	Molar mass	Boiling point (K)
1	Butane	CH_3-CH_2-CH_2-CH_3	58	272.5
2	Propanal	CH_3-CH_2-CHO	58	322
3	Methoxyethane	CH_3-O-CH_2-CH_3	60	283.8
4	Prapan – 1- ol	CH_3-CH_2-CH_2-OH	60	370.4
5	Propan – 2- ol	CH_3-CH(OH)-CH_3	60	355.5

Chemical properties of alcohols

Nucleophilic substitution reactions of alcohols

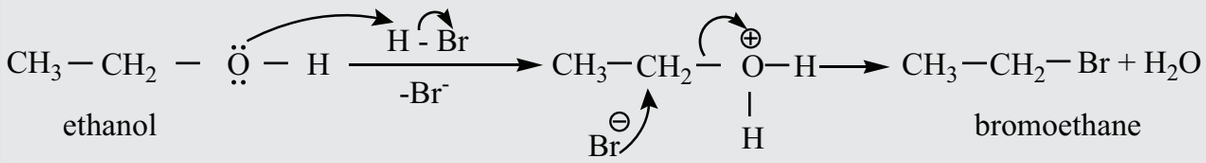
Alcohol has a strong basic leaving group (OH^-). So, –OH group is first converted into $-\overset{+}{O}H_2$ group by adding an acid. The $-\overset{+}{O}H_2$ group in the protonated alcohol can be easily displaced by a nucleophile such as Br^- to give alkyl halides.

Example: Alcohols undergo nucleophilic substitution reaction with hydro halic acids to form alkyl halides. In case of tertiary alcohols heating is required.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[-\,H_2O]{HBr} \underset{\text{Bromoethane}}{CH_3-CH_2-Br}$$

Alkyl halide formation from primary alcohols follow S_N2 mechanism

Example

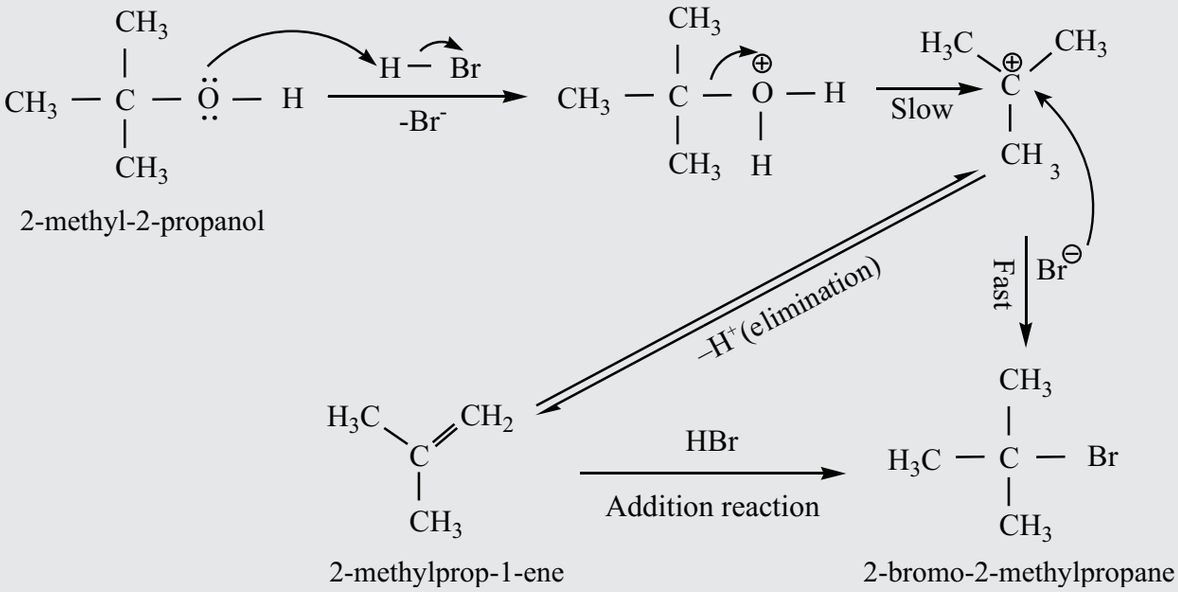


Nucleophilic attack of Br^- and leaving of H_2O takes place simultaneously.

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Alkyl halide formation of tertiary alcohols follow S_N1 mechanism.

Example



Here, the carbocation formed can undergo elimination to give an alkene. However the alkene can again undergo addition reaction with HBr to give the substituted product.

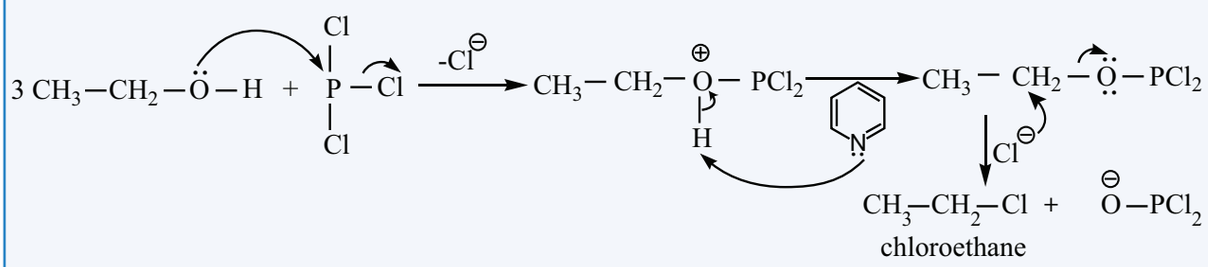
Conversion of alcohol into alkyl halides: Other methods

Alcohols can also be converted into an alkyl halides using PCl_3, PBr_3.

$$CH_3CH_2OH \xrightarrow[\text{pyridine}]{PCl_3} CH_3CH_2Cl$$

ethanol → chloroethane

Mechanism : S_N2 reaction on phosphorous tri chloride



The conversion of an alcohol to alkyl halide can also be effected using thionyl chloride

$$CH_3-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-Cl + HCl + SO_2$$

Methanol + Thionyl chloride → chloromethane

This reaction also follows the S_Ni mechanism in the presence of pyridine.

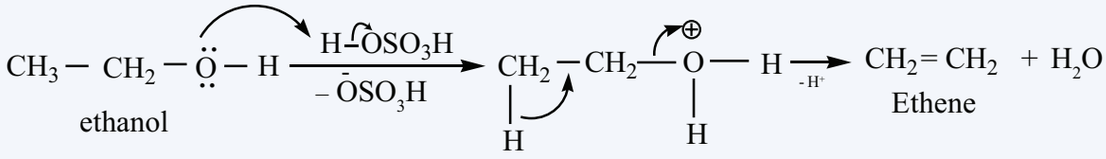
2. Elimination reactions of alcohols

When alcohols are heated with a suitable dehydrating agents like sulphuric acid, the H and OH present in the adjacent carbons of alcohols are lost, and it results in the formation of a carbon – carbon double bond. Phosphoric acid, anhydrous $ZnCl_2$, alumina etc., can also be used as dehydrating agents.

Example $CH_3 - CH_2 - OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$

Mechanism

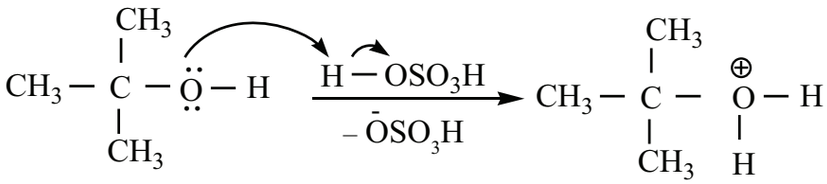
Primary alcohols undergo dehydration by E_2 mechanism



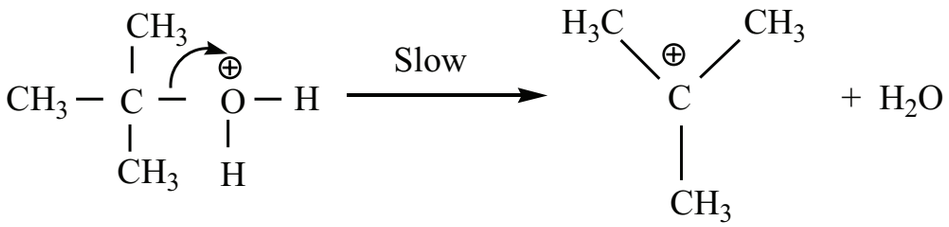
Tertiary alcohols undergo dehydration by E_1 mechanism. It involves the formation of a carbocation.

Protonation of alcohol

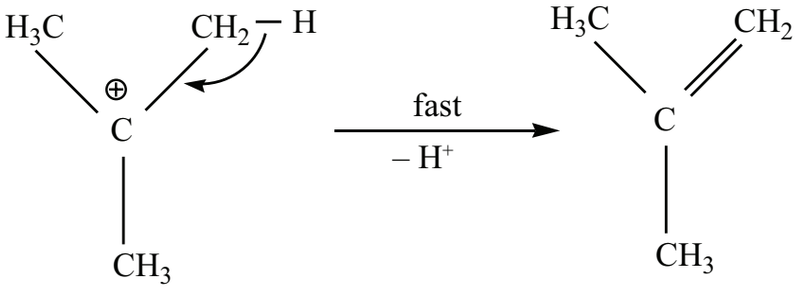
Step 1 :



Step 2 : Dissociation of oxonium ion to form a carbocation.



Step 3 : Deprotonation of carbocation to form an alkene



2 - methylprop - 1- ene

Order of reactivity:

The relative reactivities of alcohols in the dehydration reaction follows the order

primary < secondary < tertiary

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Evaluate yourself

Identify the products in the following reactions. Write their IUPAC names and mention the mechanism involved in the reactions.

i) cyclopentanol $\xrightarrow[\Delta]{H_2SO_4}$?

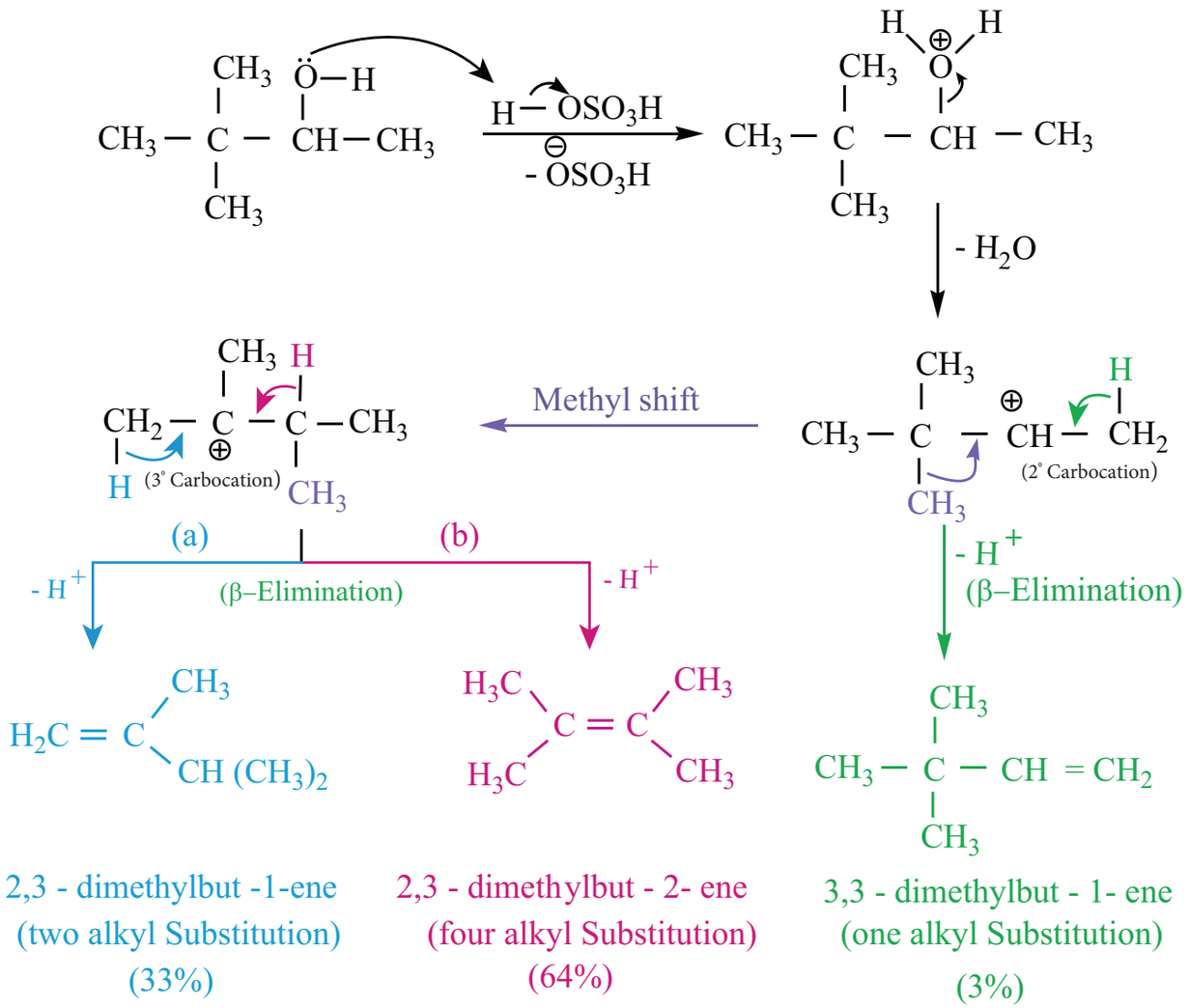
ii) butan–1–ol $\xrightarrow[H_2SO_4]{NaBr}$?

iii) neopentyl alcohol $\xrightarrow{PCl_5}$?

Saytzeff's rule

During intramolecular dehydration, if there is a possibility to form a carbon – carbon double bond at different locations, the preferred location is the one that gives the more (highly) substituted alkene i.e., the stable alkene.

For example, the dehydration of 3,3 – dimethyl – 2- butanol gives a mixture of alkenes. The secondary carbocation formed in this reaction undergoes rearrangement to form a more stable tertiary carbocation.



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Evaluate yourself : What is the major product obtained when 2,3 – dimethyl pentan -3 – ol is heated in the presence of H_2SO_4.

Oxidation of alcohols

The important reactions of alcohols are their oxidation to give carbonyl compounds. The commonly used oxidising agent is acidified sodiumdichromate. Oxidation of primary alcohols give an aldehyde which on further oxidation gives the carboxylic acids. To stop the oxidation reaction at the aldehyde / ketone stage, pyridinium chlorochromate (PCC) is used as an oxidising agent.

Example

$$CH_3 - CH_2 - OH \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3 - CHO \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3 - COOH$$

ethanol — ethanal — ethanoicacid

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Propan - 2- ol — Propanone — ethanoicacid

$$CH_3 - CH_2 - CH_2 - OH \xrightarrow{PCC} CH_3 - CH_2 - CHO$$

Propan - 1- ol — Propanal

Tertiary alcohols do not undergo oxidation reaction under normal conditions, but at elevated temperatures, under strong oxidising agent cleavage of C –C bond takes place to give a mixture of carboxylic acid.

Swern oxidation

In this method, dimethyl sulfoxide (DMSO) is used as the oxidising agent, which converts alcohols to ketones / aldehydes.

In this method an alcohol is treated with DMSO and oxalyl chloride followed by the addition of triethylamine.

$$\underset{\text{Propan - 2- ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + \underset{\text{DMSO}}{H_3C-\overset{\overset{O}{\|}}{S}-CH_3} + \underset{\text{Oxalylchloride}}{Cl-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow{Et_3N} \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + (CH_3)_2S + CO_2 + CO + 2HCl$$

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Biological oxidation

The fermentation of the food consumed by an animal produces alcohol. To detoxify the alcohol, the liver produces an enzyme called alcohol dehydrogenase (ADH). Nicotinamide adenine dinucleotide (NAD) present in the animals act as an oxidising agent and ADH catalyses the oxidation of toxic alcohols into non-toxic aldehyde.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + NAD^+ \xrightarrow{ADH} \underset{\text{ethanal}}{CH_3CHO} + NADH + H^+$$

Catalytic dehydrogenation

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573K, dehydrogenation takes place to form aldehyde or ketone.

$$\underset{\text{ethanol}}{CH_3 - CH_2 - OH} \xrightarrow[573\ K]{Cu} \underset{\text{ethanal}}{CH_3 - CHO} + H_2$$

$$\underset{\text{Propan - 2- ol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3} \xrightarrow[573\ K]{Cu} \underset{\text{propanone}}{CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3} + H_2$$

Tertiary alcohols undergo dehydration reaction to give alkenes.

$$\underset{\text{2 - methylpropan - 2- ol}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH} \xrightarrow[573\ K]{Cu} \underset{\text{2 - methylprop - 1- ene}}{\begin{matrix} H_3C \\ \diagdown \\ \quad C = CH_2 \\ \diagup \\ H_3C \end{matrix}} + H_2O$$

Esterification

Alcohols react with carboxylic acids in the presence of an acid to give esters

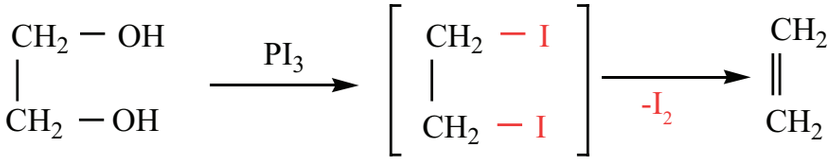
Example

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + HO-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow{H^+} \underset{\text{ethylethanoate}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-CH_3}$$

Reactions of Glycol

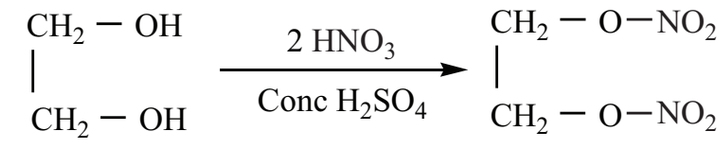
Ethylene glycol contains two primary alcoholic groups and it exhibits the usual reactions of hydroxyl group. Like other primary alcohols, it reacts with metallic sodium to form monosodium glycolate and disodium glycolate. The hydroxyl groups can be converted to the halide groups by treating glycol with halic acid (or with PCl_5 / PCl_3 / $SOCl_2$.)

When ethylene glycol is treated with HI or P/I_2, 1,2 – diiodoethane is first formed which decomposes to give ethene.



ethane - 1,2 - diol 1,2 - diiodoethane ethene

On heating with conc HNO_3 in the presence of Con. H_2SO_4, ethylene glycol forms dinitroglycol.

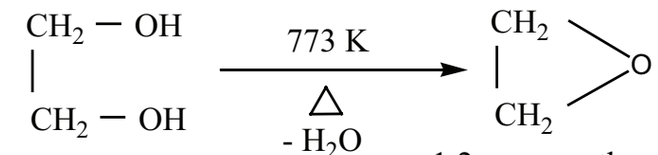


ethane - 1,2 - diol 1,2 - dinitroxyethene (dinitroglycol)

Dehydration reaction

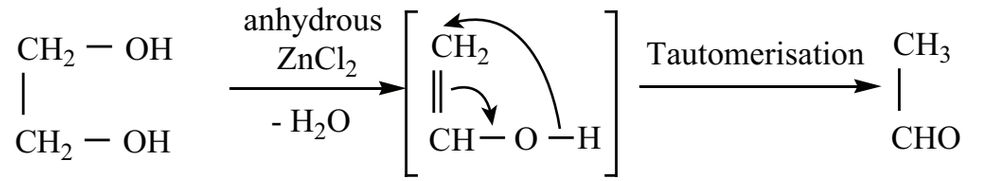
Ethyleneglycol undergoes dehydration reaction under different conditions to form different products.

1. When heated to 773K, it forms epoxides.



ethane - 1,2 - diol 1,2 - epoxyethane (Oxirane)

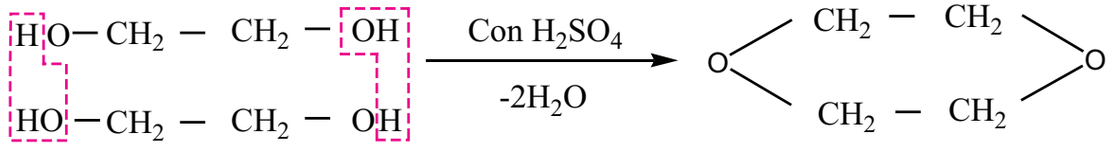
2. When heated with dilute sulphuric acid (or) anhydrous $ZnCl_2$ under pressure in a sealed tube, it gives acetaldehyde.



ethane-1,2 - diol ethenol (Vinylalcohol) Ethanal

XII U11-Hydroxy compounds.indd 119 16-12-2022 19:42:06

3. When distilled with Conc. H_2SO_4, glycol forms dioxane



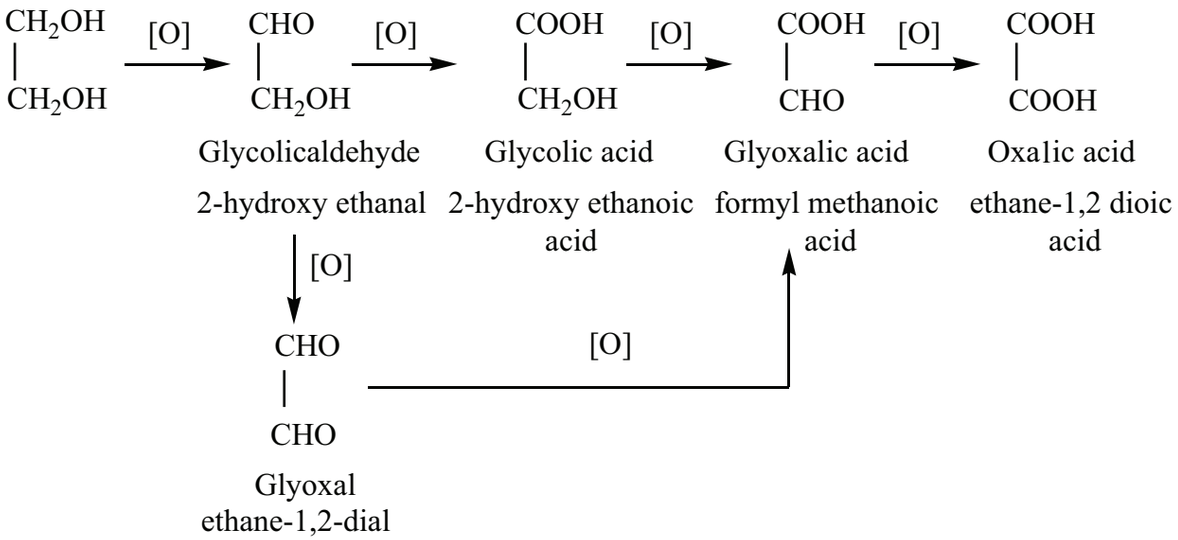
ethane - 1,2 - diol

1,4 - dioxane

Oxidation of glycol

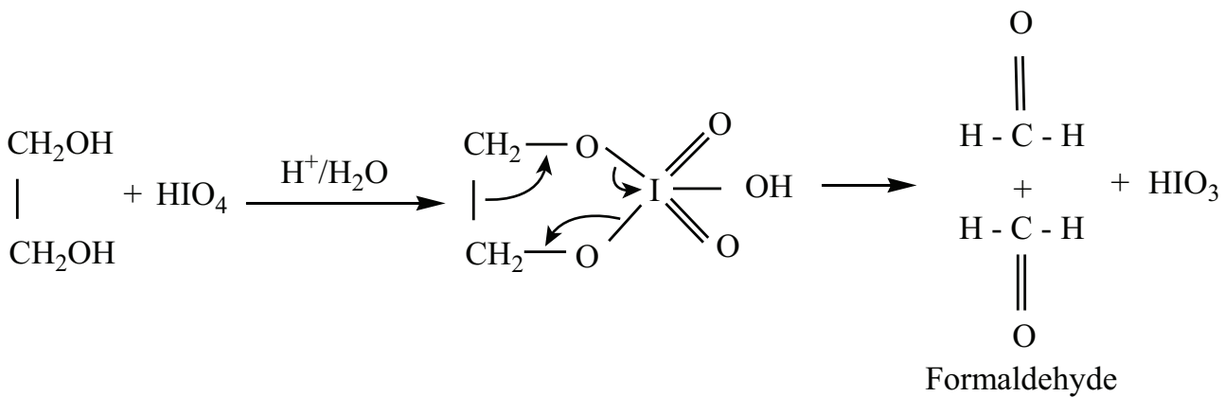
On oxidation, glycol gives a variety of products depending on the nature of oxidizing agent and other reaction conditions.

i) When nitric acid (or) alkaline potassium permanganate is used as the oxidizing agent, the following products are obtained.



ii) **Oxidation of glycol with periodic acid**

Ethylene glycol on treatment with periodic acid gives formaldehyde. This reaction is selective for vicinal 1,2 – diols and it proceeds through a cyclic periodate ester intermediate.

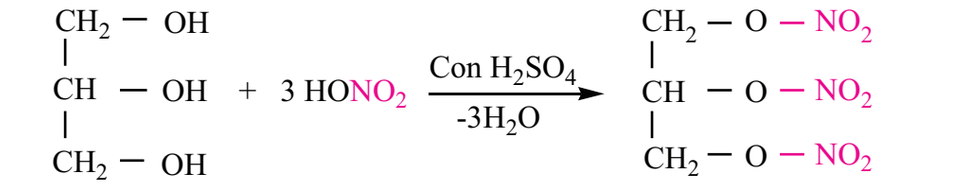


Formaldehyde

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Reaction of Glycerol

Nitration: Glycerol reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form TNG (nitroglycerine).

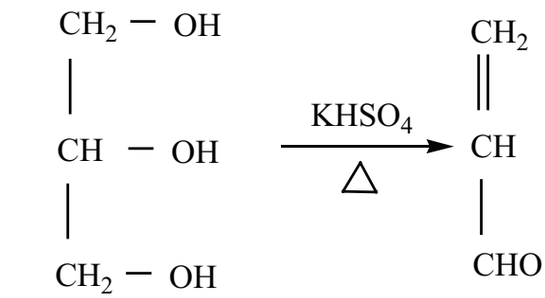


Propan - 1,2,3 - triol
glycerol

1,2,3 - trinitroxy propane

Dehydration

When glycerol is heated with dehydrating agents such as Con H_2SO_4,$KHSO_4$ etc…., it undergoes dehydration to form acrolein.



Propane - 1,2,3 - triol

Prop - 2- enal (acrolein)

Oxidation

Glycerol can give rise to a variety of oxidation products depending on the nature of the oxidising agent used for oxidation.

a) Oxidation of glycerol with dil. HNO_3 gives glyceric acid and tartronic acid.

b) Oxidation of glycerol with Conc. HNO_3 gives mainly glyceric acid.

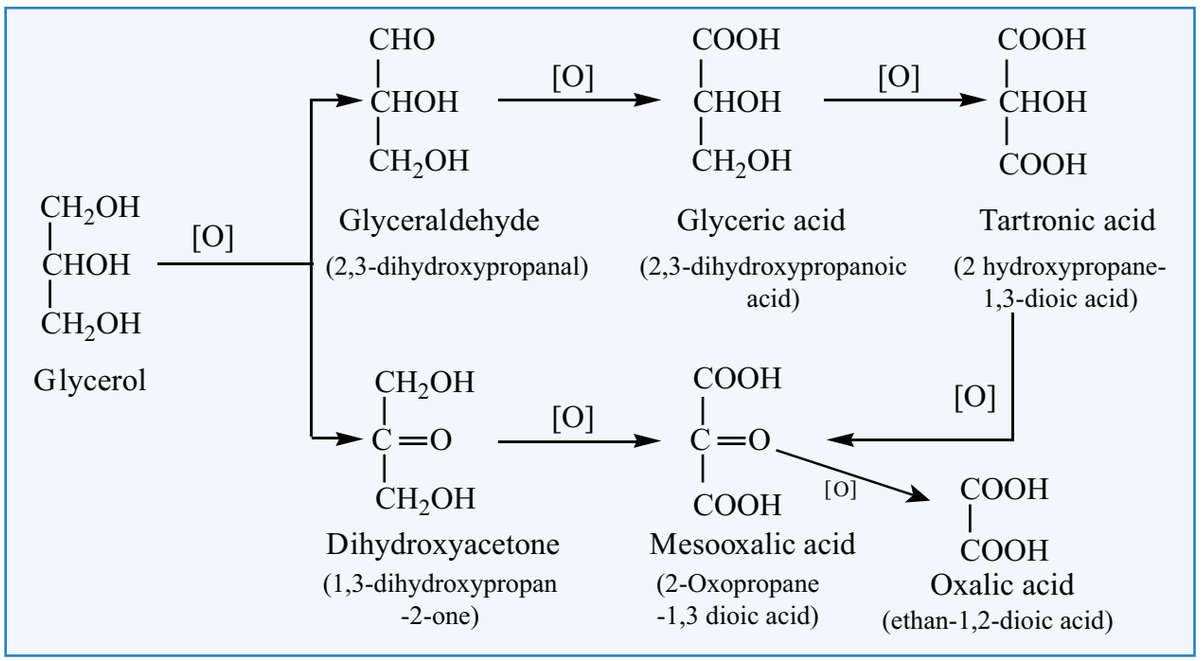
c) Oxidation of glycerol with bismuth nitrate gives as meso oxalic acid.

d) Oxidation of glycerol with Br_2/H_2O (or) NaOBr (or) Fenton's reagent ($FeSO_4 + H_2O_2$) gives a mixture of glyceraldehyde and dihydroxy acetone(This mixture is named as glycerose).

e) On oxidation with HIO_4 or Lead tetra acetate (LTA) it gives formaldehyde and formic acid.

f) Acidified $KMnO_4$ oxidises glycerol into oxalicacid.

XII U11-Hydroxy compounds.indd 121 16-12-2022 19:42:06



Uses of alcohols

Uses of methanol :

1. Methanol is used as a solvent for paints, varnishes, shellac, gums, cement, etc.
2. In the manufacture of dyes, drugs, perfumes and formaldehyde.

Uses of ethanol:

1. It is also used in the preparation of
   a) Paints and varnishes.
   b) Organic compounds like ether, chloroform, iodoform, etc.,
   c) Dyes, transparent soaps.
2. As a substitute for petrol under the name power alcohol used as fuel for aeroplane
3. It is used as a preservative for biological specimens.

Uses of ethylene glycol:

1. Ethylene glycol is used as an antifreeze in automobile radiator
2. Its dinitrate is used as an explosive with TNG.

Uses of glycerol

1. Glycerol is used as a sweetening agent in confectionary and beverages.
2. It is used in the manufacture of cosmetics and transparent soaps.
3. It is used in making printing inks and stamp pad ink and lubricant for watches and clocks.
4. It is used in the manufacture of explosive like dynamite and cordite by mixing it with china clay

XII U11-Hydroxy compounds.indd 122 16-12-2022 19:42:07

Acidity of alcohols

According to Bronsted theory, an acid is defined as a proton donor and the acid strength is the tendency to give up a proton. Alcohols are weakly acidic and their acidity is comparable with water. Except methanol, all other alcohols are weaker acid than water. The K_a value for water is 1.8×10^{-16} where as for alcohols, the K_a value in the order 10^{-18} to 10^{-16}.

Alcohols react with active metals such as sodium, aluminium etc… to form the corresponding alkoxides with the liberation of hydrogen gas and similar reaction to give alkoxide is not observed in the reaction of alcohol with NaOH.

$$2C_2H_5\text{-}OH + 2Na \rightarrow 2C_2H_5ONa + H_2 \uparrow$$

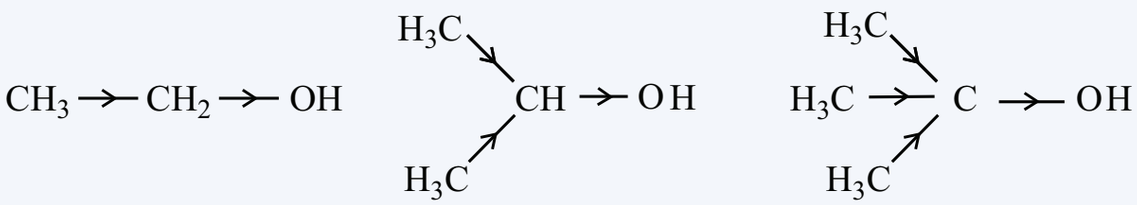
The above reaction explains the acidic nature of alcohols.

Comparison of acidity of 1°, 2°and 3° alcohols

The acidic nature of the alcohol is due to the polar nature of O –H bond. When an electron withdrawing -I groups such as -Cl, - F etc… is attached to the carbon bearing the OH group, it withdraws the electron density towards itself and thereby facilitating the proton donation. In contrast, the electron releasing group such as alkyl group increases the electron density on oxygen and decreases the polar nature of O – H bond, Hence it results in the decrease in acidity. on moving from primary to secondary and tertiary alcohols, the number of alkyl groups which attached to the carbon bearing -OH group increases, which results in the following order of acidity.

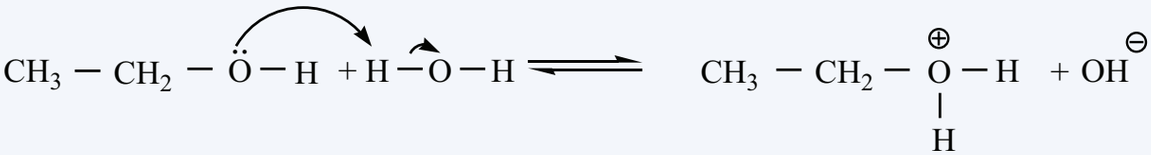
1° alcohol > 2° alcohol > 3° alcohol

For example



$K_a = 1.3\times10^{-16}$ $K_a = 3.2\times10^{-17}$ $K_a = 1\times10^{-18}$

Alcohols can also act as a Bronsted bases. It is due to the presence of unshared electron pairs on oxygen which make them proton acceptors.



XII U11-Hydroxy compounds.indd 123 16-12-2022 19:42:08

Acidity of Phenol

Phenol is more acidic than aliphatic alcohols. Unlike alcohols it reacts with bases like sodium hydroxide to form sodium phenoxide. This explains the acidic behaviour of phenol.let us consider the aqueous solution of phenol in which the following equilibrium exists.

$$C_6H_5 - OH + H.OH \rightleftharpoons C_6H_5 - O^{\ominus} + H_3O^{\oplus}$$

K_a value for the above equilibrium is 1×10^{-10} at $25^{o}C$. This Ka value indicates that it is more acidic than aliphatic alcohols. This increased acidic behaviour can be explained on the basis of the stability of phenoxide ion. We have already learnt in XI standard that the phenoxide is more stabilised by resonance than phenol.

In substituted phenols, the electron withdrawing groups such as $-NO_2$,-Cl enhances the acidic nature of phenol especially when they are present at ortho and para positions. In such cases,there is a possibility for the extended delocalisation of negative charge on the phenoxide ion. On the other hand the alkyl substitued phenols show a decreased acidity due to the electron releasing +I effect of alkyl group.

Table: pK_a Values of some alcohols and phenols

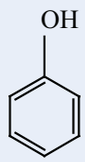
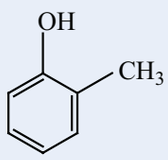
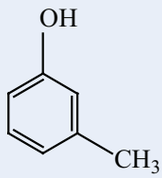
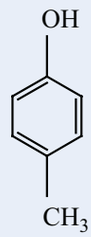
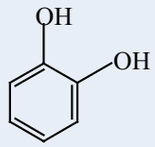
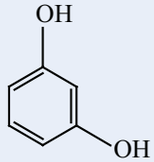
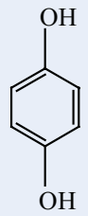
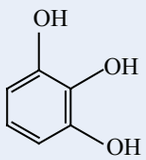
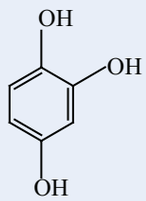
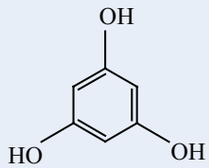
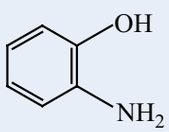
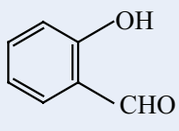
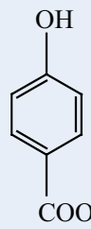
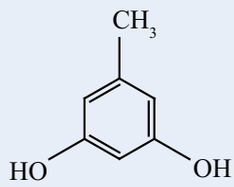
S.No.	Compound	pK_a Value
1	methanol	15.5
2	ethanol	15.9
3	propan – 2- ol	16.5
4	2 – methyl propan 2 - ol	18.0
5	Cyclohexanol	18.0
6	Phenol	10.0
7	o – nitrophenol	7.2
8	p – nitrophenol	7.1
9	m - nitrophenol	8.3
10	o – cresol	10.2
11	m – cresol	10.1
12	p – cresol	10.2

XII U11-Hydroxy compounds.indd 124 16-12-2022 19:42:09

Phenols:

Phenols are organic compounds in which a -OH group is directly attached to a benzene ring. The carbon bearing the -OH group is sp^2 hybridized.

Table: Classification of phenols

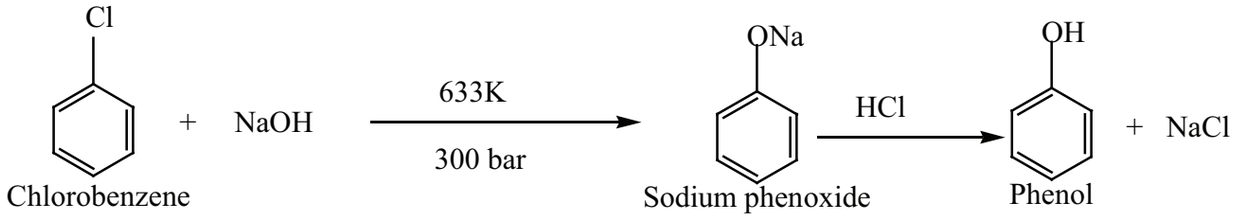
Monohydric Phenol	Monohydric phenols			 
	Common Name:	Phenol	o -cresol	m-cresol	p-cresol
	IUPAC Name :	Phenol	2-methyl phenol	3-methyl phenol	4-methyl phenol
Dihydric Phenol	Dihydric phenols			
	Common Name:	Catechol	Resorcinol	Quinol
	IUPAC Name:	1,2-dihydroxybenzene	1,3-dihydroxybenzene	1,4-dihydroxybenzene
Trihydric Phenol	Trihydric phenols			
	Common Name:	Pyrogallol	Hydroxyquinol	Phloroglucinol
	IUPAC Name:	1,2,3-trihydroxybenzene	1,2,4-trihydroxybenzene	1,3,5-trihydroxybenzene
Substituted phenol	Substituted phenols				
		o-amino phenol	o-hydroxy Benzaldehyde	p-hydroxy benzoic acid	Orcinol(or) 3,5-Dihydroxy toluene

XII U11-Hydroxy compounds.indd 125 16-12-2022 19:42:10

Preparation of Phenols

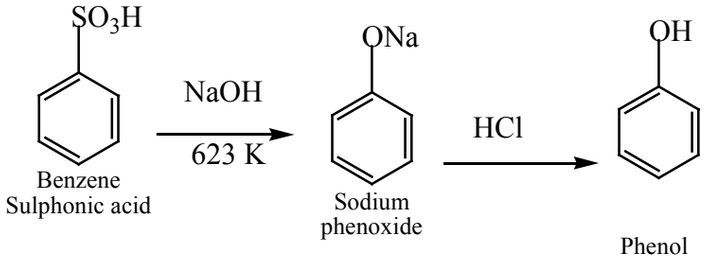
a) From halo arenes(Dows process)

When Chlorobenzene is hydrolysed with 6-8% NaOH at 300 bar and 633K in a closed vessel,sodium phenoxide is formed which on treatment with dilute HCl gives phenol.



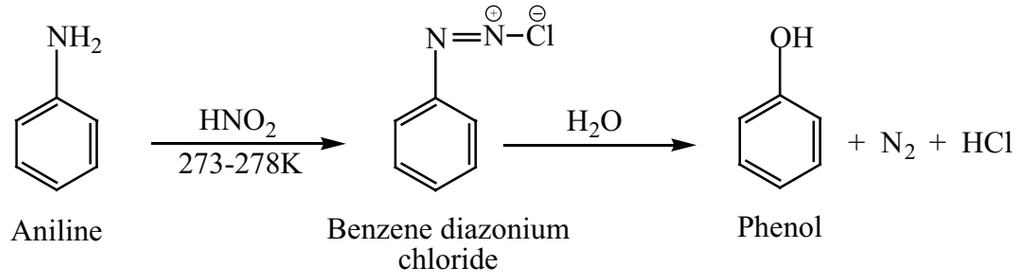
b) From benzene sulphonic acid

Benzene is sulphonated with oleum and the benzene sulphonic acid so formed is heated with molten NaOH at 623K gives sodium phenoxide which on acidification gives phenol.



c) From aniline

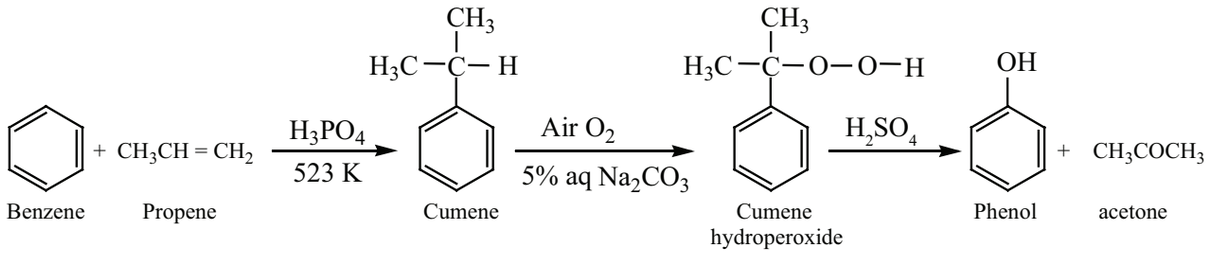
Aniline is diazotized with nitrous acid ($NaNO_2$+HCl) at 273-278K to give benzene diazonium chloride which on further treatment with hot water in the presence of mineral acid gives phenol.



d) From cumene

A mixture of benzene and propene is heated at 523K in a closed vessel in presence of H_3PO_4 catalyst gives cumene (isopropylbenzene). On passing air to a mixture of cumene and 5% aqueous sodium carbonate solution, cumene hydro peroxide is formed by oxidation. It is treated with dilute acid to get phenol and acetone. Acetone is also an important byproduct in this reaction.

XII U11-Hydroxy compounds.indd 126 16-12-2022 19:42:11



Physical Properties

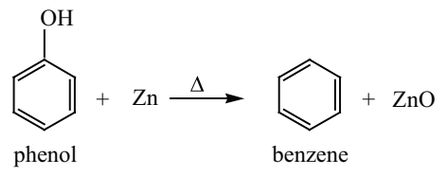
Phenol is colourless, needle shaped crystal, hygroscopic, corrosive and poisonous. It turns pink on exposure to air and light. The simplest phenols are liquids or low melting solids, they have quite high boiling points. Phenol is slightly soluble in water because of hydrogen bonding. However other substituted phenols are essentially insoluble in water.

Chemical Properties:

Reactions involving -OH group.

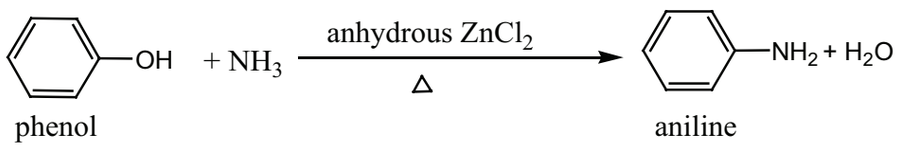
a) Reaction with Zn dust:

Phenol is converted to benzene on heating with zinc dust. In this reaction the hydroxyl group which is attached to the aromatic ring is eliminated.



b) Reaction with ammonia:

Phenol on heating with ammonia in presence of anhydrous $ZnCl_2$ gives aniline.



c) Formation of esters:

Schotten-Baumann reaction :

Phenol on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called Schotten-Baumann reaction.

$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{acetyl chloride}}{CH_3COCl} \xrightarrow[Py]{NaOH} \underset{\text{phenyl ethanoate}}{CH_3\text{-}COOC_6H_5} + HCl$$

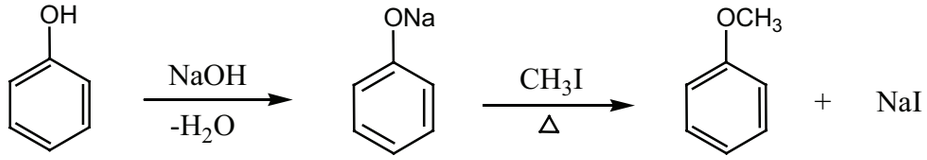
$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{benzoyl chloride}}{C_6H_5COCl} \xrightarrow[Py]{NaOH} \underset{\text{phenyl benzoate}}{C_6H_5\text{-}COOC_6H_5} + HCl$$

d) Formation of ethers:

Williamson ether synthesis:

An alkaline solution of phenol reacts with alkyl halide to form phenyl ethers. The alkyl halide undergoes nucleophilic substitution by the phenoxide ion in the presence of alkali.

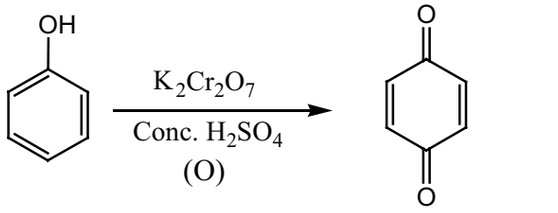
XII U11-Hydroxy compounds.indd 127 16-12-2022 19:42:12



Phenol — Sodium Phenoxide — Anisole (methoxybenzene)

d) Oxidation:

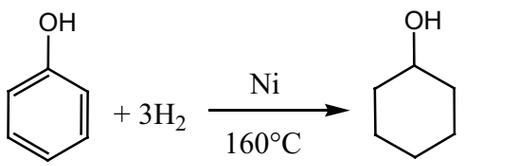
Phenol undergoes oxidation with air or acidified $K_2Cr_2O_7$ with conc. H_2SO_4 to form 1,4-benzoquinone.



Phenol — 1,4-benzoquinone

e) Reduction:

Phenol on catalytic hydrogenation gives cyclohexanol.



Phenol — cyclohexanol

Reactions of benzene ring:

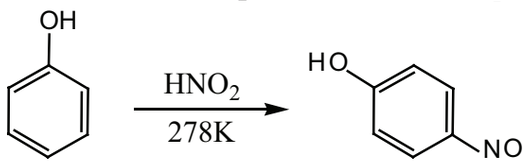
Electrophilic aromatic substitution:

We have already learnt in XI standard that the groups like -$\ddot{O}H$, -$\ddot{N}H_2$, etc., which when directly attached to the benzene ring, activate the ring towards electrophilic substitution reaction and direct the incoming electrophile to occupy either the ortho or para position.

Common electrophilic aromatic substitutions are as follows:

i) Nitrosation:

Phenol can be readily nitrosoated at low temperature with HNO_2.

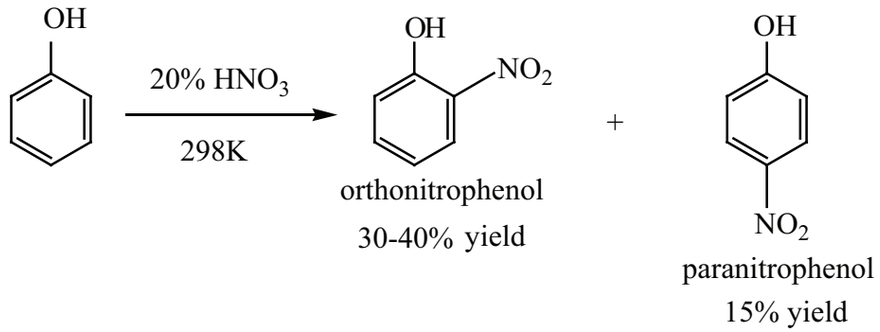


phenol — p-nitroso phenol

XII U11-Hydroxy compounds.indd 128 16-12-2022 19:42:13

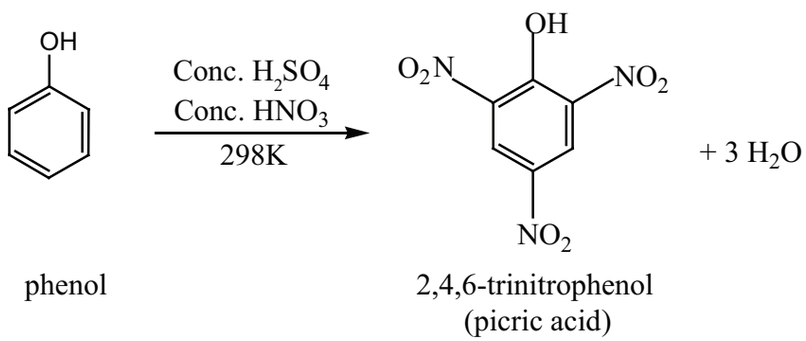
ii) Nitration:

Phenol can be nitrated using 20% nitric acid even at room temperature, a mixture of ortho and para nitro phenols are formed.



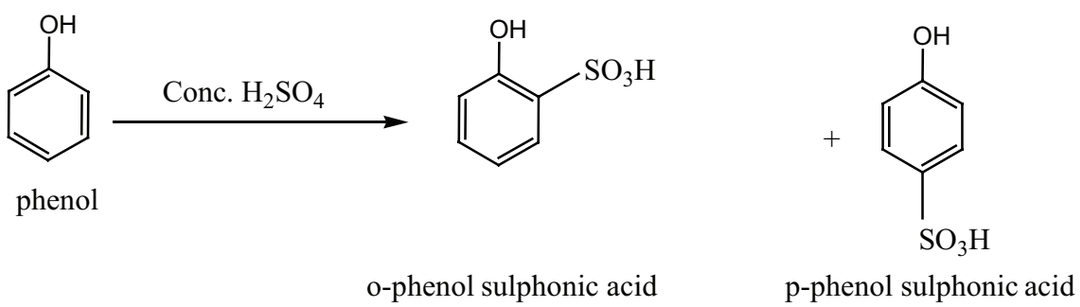
The ortho and para isomers are separated by steam distillation, as o-nitro phenol is slightly soluble in water and more volatile due to intra molecular hydrogen bonding, whereas p-nitro phenol is more soluble in water and less volatile due to intermolecular hydrogen bonding.

Nitration with Conc. HNO_3 + con. H_2SO_4 gives picric acid.



iii) Sulphonation:

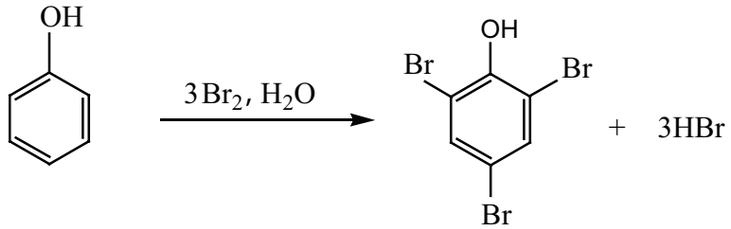
Phenol reacts with con. H_2SO_4 at 280K to form o-phenol sulphonic acid as the major product. When the reaction is carried out at 373K the major product is p-phenol sulphonic acid.



XII U11-Hydroxy compounds.indd 129 16-12-2022 19:42:13

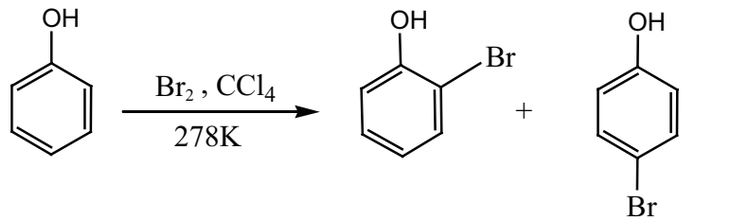
iv) Halogenation:

Phenol reacts with bromine water to give a white precipitate of 2,4,6-tri bromo phenol.



Phenol 2,4,6-tribromophenol

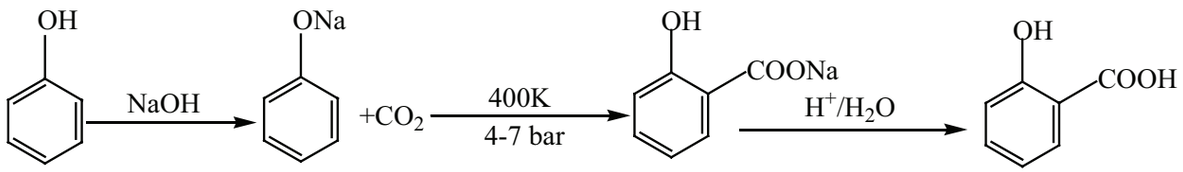
If the reaction is carried out in CS_2 or CCl_4 at 278K, a mixture of ortho and para bromo phenols are formed.



phenol o -bromo phenol p- bromo phenol

v) Kolbe's (or) Kolbe's Schmit reaction:

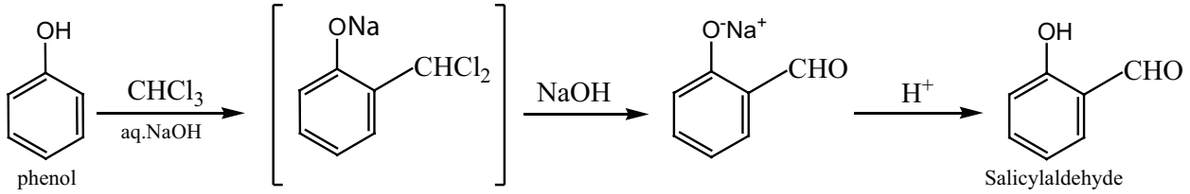
In this reaction, phenol is first converted into sodium phenoxide which is more reactive than phenol towards electrophilic substitution reaction with CO_2. Treatment of sodium phenoxide with CO_2 at 400K, 4-7 bar pressure followed by acid hydrolysis gives salicylic acid.



phenol sodium phenoxide sodium salicylate Salicyclic acid

vi) Riemer – Tiemann Reaction:

On treating phenol with $CHCl_3$/NaOH, a -CHO group is introduced at ortho position. This reaction proceeds through the formation of substituted benzal chloride intermediate.

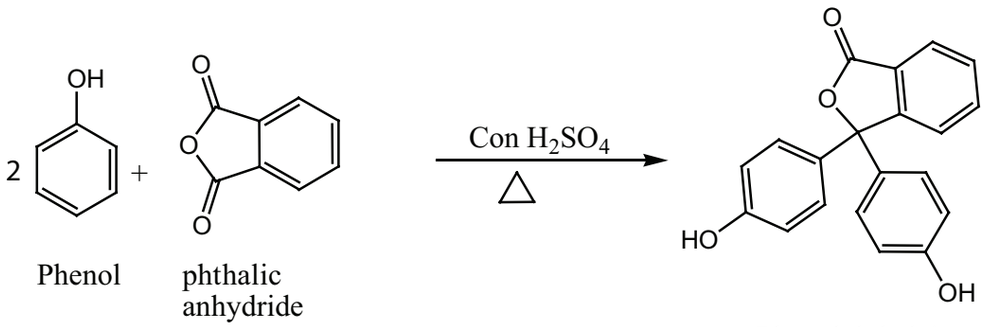


phenol Salicylaldehyde

XII U11-Hydroxy compounds.indd 130 16-12-2022 19:42:14

vii) Phthalein reaction:

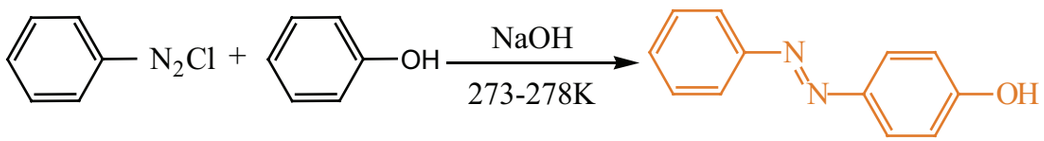
On heating phenol with phthalic anhydride in presence of con.H_2SO_4, phenolphthalein is obtained.



Phenol | phthalic anhydride | Phenolphthalein

viii) Coupling reaction:

Phenol couples with benzene diazonium chloride in an alkaline solution to form p-hydroxy azobenzene(a red orange dye).



Benzene diazonium chloride | Phenol | p-hydroxy azobenzene

Test to differentiate alcohol and phenols

i) Phenol react with benzene diazonium chloride to form a red orange dye, but ethanol has no reaction with it.

ii) Phenol gives purple colouration with neutral ferric chloride solution, alcohols do not give such coloration with $FeCl_3$.

iii) Phenol reacts with NaOH to give sodium phenoxide. Ethyl alcohol does not react with NaOH.

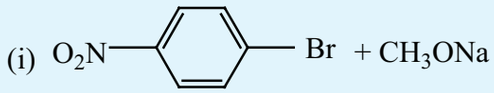
Uses of phenol

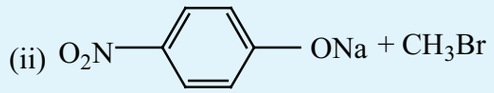
1) About half of world production of phenol is used for making phenol formaldehyde resin. (Bakelite).
2) Phenol is a starting material for the preparation of
   i) drugs such as phenacetin, Salol, aspirin, etc.
   ii) phenolphthalein indicator.
   iii) explosive like picric acid.
3) It is used as an antiseptic-carbolic lotion and carbolic soaps.

XII U11-Hydroxy compounds.indd 131 16-12-2022 19:42:15

Evaluate Yourself

1. Which of the following set of reactants will give 1-methoxy-4-nitrobenzene.

(i) 

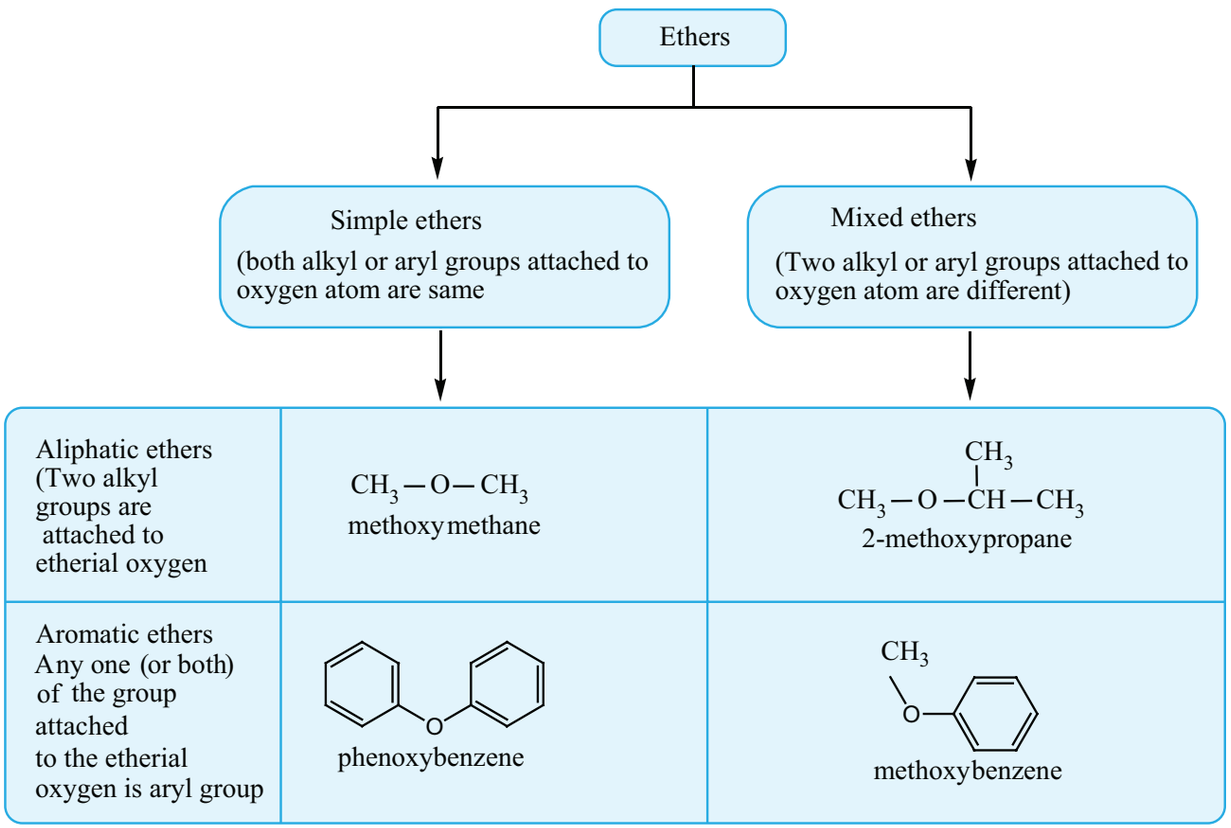
(ii) 

2. what happens when m-cresol is treated with acidic solution of sodium dichromate?
3. when phenol is treated with propan-2-ol in the presence of HF, Friedel-Craft reaction takes place . Identify the products.

Ethers:

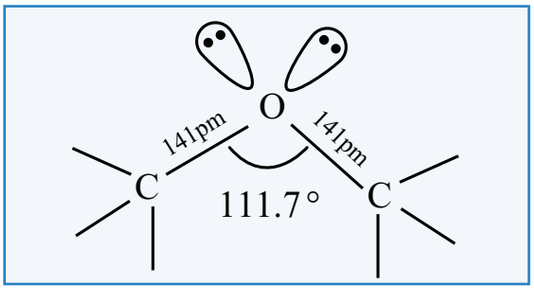
Ethers are a class of organic compound in which an oxygen atom is connected to two alkyl/aryl groups (R - $\ddot{O}$ - R) . Ethers can be considered as the derivatives of hydrocarbon in which one hydrogen atom is replaced by an alkoxy (-OR) or an aryloxy(-OAr) group. The general formula of aliphatic ether is $C_nH_{2n+2}O$.

Classification:



XII U11-Hydroxy compounds.indd 132 16-12-2022 19:42:16

Structure of functional group



The structure of ethereal oxygen which is attached to two alkyl groups is similar to the structure of -O-H group of alcohol. The oxygen atom is sp^3 hybridized. Two sp^3 hybridized orbitals of oxygen linearly overlap with two sp^3 hybrid orbitals of the carbon which are directly attached to the oxygen forming two C-O 'σ ' bonds. The C-O-C bond angle is slightly greater than the tetrahedral bond angle due to the repulsive interaction between the two bulkier alkyl groups.

IUPAC System:

Let us recall the naming of ethers according to IUPAC nomenclature.

Compound (Common Name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Dimethyl ether $CH_3—O—CH_3$ Methoxymethane	Methoxy	Meth	ane	–
Isopropyl methyl ether $CH_3—O—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_3$ 2-methoxypropane	2-methoxy	prop	ane	–
t-butylmethyl ether $CH_3-O-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_3$ 2-methoxy-2-methyl propane	2-methoxy 2-methyl	prop	ane	–
Methylphenylether(Anisole) $C_6H_5—O—CH_3$ Methoxybenzene	Methoxy	benzene	–	–
Ethylphenylether(phenetole) $C_6H_5—O—CH_2CH_3$ Ethoxybenzene	Ethoxy	benzene	–	–
Diphenylether or phenylether $C_6H_5—O—C_6H_5$ Phenoxybenzene	Phenoxy	benzene	–	–

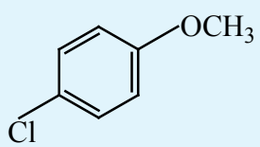
XII U11-Hydroxy compounds.indd 133 16-12-2022 19:42:17

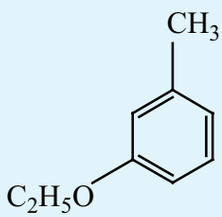
n-heptyl phenyl ether $C_6H_5-O-(CH_2)_6CH_3$ 1-phenoxyheptane	1-phenoxy	hept	ane	–
Isopentylphenylether C_6H_5 - O - CH_2 - CH_2 - CH(-CH_3) - CH_3 1-butoxy-3-methyl benzene	1-butoxy-3-methyl	benzene	–	–
Dimethylglycolate $CH_3-O-CH_2-CH_2-OCH_3$ 1,2-dimethoxyethane.	1,2-dimethoxy	eth	ane	–

Evaluate yourself

Give the IUPAC name for the following ethers and classify them as simple or mixed.

(i) $CH_3-CH_2-O-(CH_2)_3-CH_3$

(ii) 

(iii) 

(iv) $(CH_3)_3C-O-C(CH_3)_3$

(v) $CH_2=CH-CH(Cl)-O-CH_3$

(vi) dibenzyl ether

(vii) vinyl allyl ether

Preparation of ethers:

1. Inter molecular dehydration of alcohol.

We have already learnt that when ethanol is treated with con.H_2SO_4 at 443K, elimination takes place to form ethene. If the same reaction is carried out at 413K, substitution competes over elimination to form ethers.

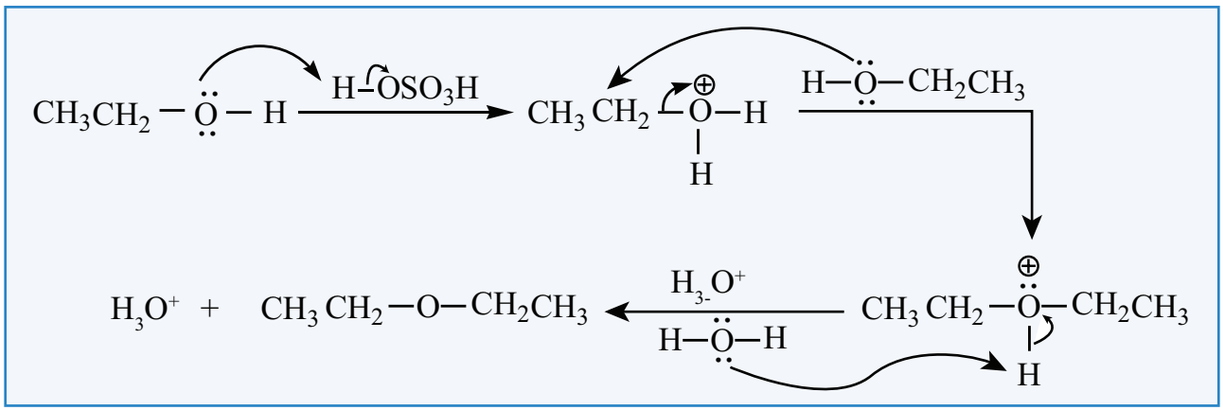
$$2CH_3\text{-}CH_2\text{-}OH \xrightarrow[413K]{H_2SO_4} CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$$

ethanol → diethylether

Mechanism:

This method is useful for the preparation of simple ethers and not suitable for preparing mixed ethers. If a mixture of two different alcohols is used, mixture of different ethers will be formed and they are difficult to separate.

XII U11-Hydroxy compounds.indd 134 16-12-2022 19:42:18



2. Williamsons synthesis:

When an alkyl halide is heated with an alcoholic solution of sodium alkoxide, the corresponding ethers are obtained. The reaction involves SN^2 mechanism.

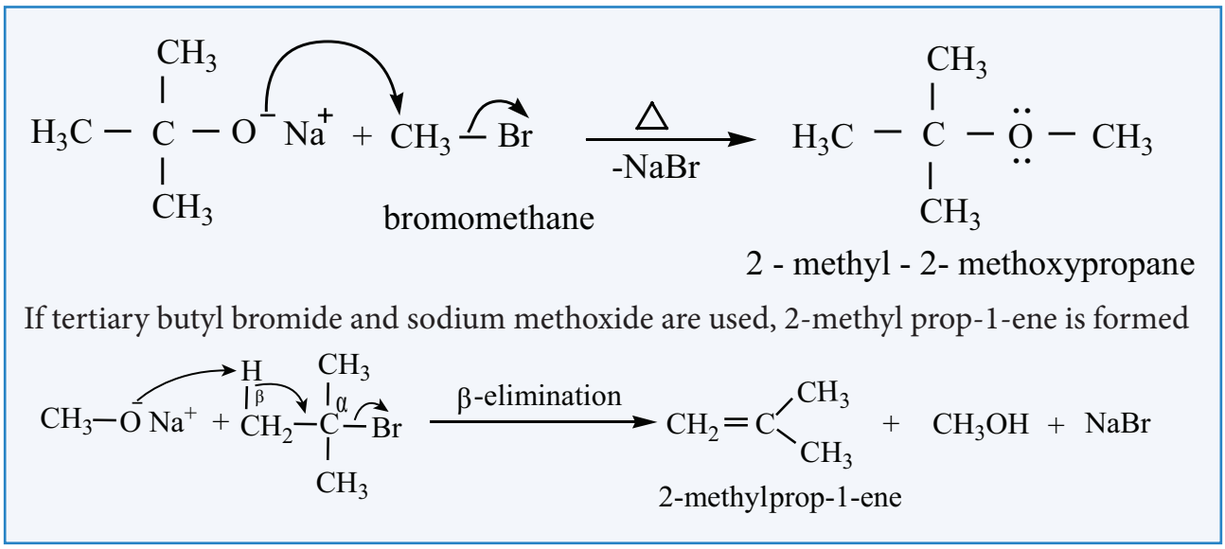
$$CH_3\text{-}ONa + Br\text{-}C_2H_5 \xrightarrow{\Delta} CH_3\text{-}O\text{-}C_2H_5 + NaBr$$

Mechanism:

$$CH_3 - O^-Na^+ + CH_3 - CH_2 - Br \xrightarrow[\Delta]{\text{-NaBr}} CH_3 - CH_2 - \ddot{O} - CH_3$$

methoxyethane

We know that primary alkyl halides are more susceptible for SN^2 reaction. Hence for the preparation of mixed ether having primary and tertiary alkyl group, primary alkyl halide and tertiary alkoxide are used. On the other hand, if we use tertiary alkyl halide and primary alkoxide, elimination dominates and succeeds over substitution to form an an alkene.



Methylation of alcohol

Methyl ethers can be prepared by treating an alcohol with diazomethane in presence of catalyst, fluoroboric acid.

$$CH_3\text{-}CH_2\text{-}OH + CH_2N_2 \xrightarrow[\Delta]{HBF_4} CH_3\text{-}CH_2\text{-}O\text{-}CH_3 + N_2$$

XII U11-Hydroxy compounds.indd 135 16-12-2022 19:42:18

Evaluate Yourself:

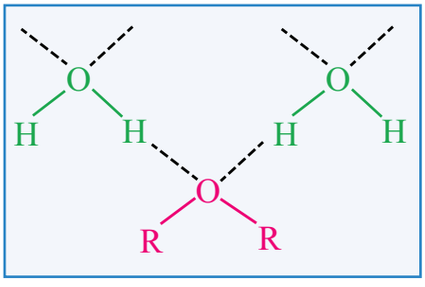
1. Which of the following reaction will give 1-methoxy-4-nitrobenzene.
   a) 4-nitro-1-bromobenzene + sodium methoxide.
   b) 4-nitrosodium phenoxide+bromomethane
2. Arrange the following compounds in the increasing order of their acid strength. propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Physical Properties:

Ethers are polar in nature. The dipolemoment of ether is the vector sum of two polar C-O bonds with significant contribution from two lone pairs of electrons. For example, the dipole moment of diethyl ether is 1.18D. Boiling point of ethers are slightly higher than that of alkanes and lower than that of alcohols of comparable masses.

Compound	Molar Mass	Boiling point
$CH_3-(CH_2)_5-CH_3$ n-heptane	100.21	371K
$CH_3-O-(CH_2)_4-CH_3$ 1-methoxypentane	102.17	373K
$CH_3-(CH_2)_5-OH$ hexan-1-ol	102.16	430K

Oxygen of ether can also form Hydrogen bond with water and hence they are miscible with water. Ethers dissolve wide range of polar and non-polar substances.



Chemical Properties of ethers:

1. Nucleophilic substitution reactions of ethers.

Ethers can undergo nucleophilic substitution reactions with HBr or HI . HI is more reactive than HBr .

$$CH_3\text{-}O\text{-}CH_2\text{-}CH_3 + HI \xrightarrow{\Delta} CH_3I + CH_3\text{-}CH_2\text{-}OH$$

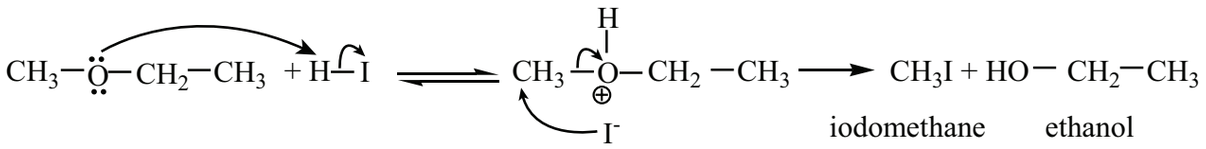
methoxy ethane — iodo methane — ethanol

$$C_6H_5\text{-}O\text{-}CH_3 + HI \longrightarrow C_6H_5\text{-}OH + CH_3I$$

methoxy benzene — Phenol — iodomethane

Mechanism:

Ethers having primary alkyl group undergo SN^2 reaction while tertiary alkyl ether undergo SN^1 reaction.Protonation of ether is followed by the attack of halide ion.The halide ion preferentially attacks the less sterically hindered of the two alkyl groups which are attached to etherial oxygen.



When excess HBr or HI is used, the alcohol formed will further react with HBr or HI to form alkyl halides.

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow{\text{excess HBr}} CH_3\text{-}CH_2\text{-}Br$$

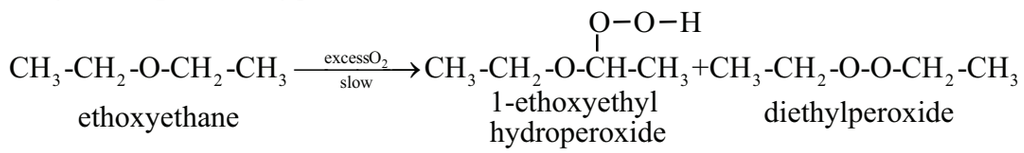
ethanol — bromoethane

Evaluate Yourself:

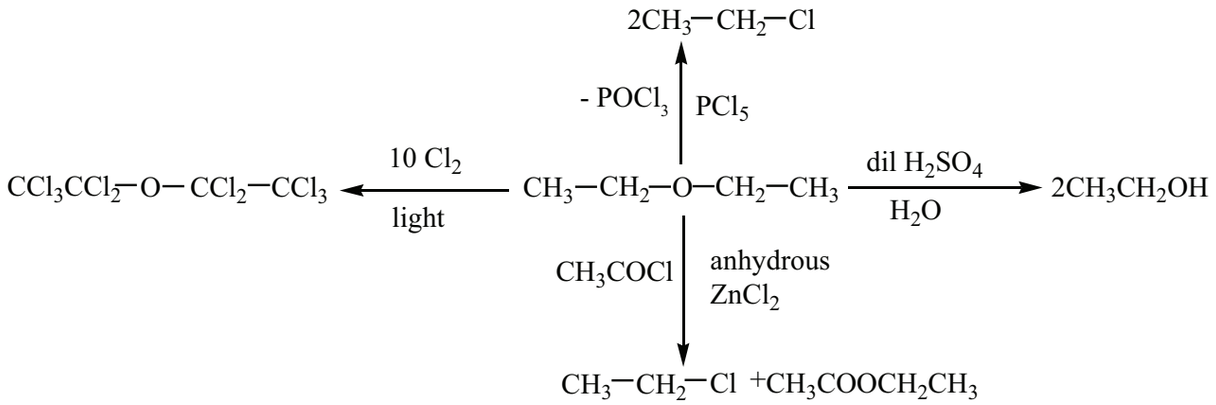
1mole of HI is allowed to react with t-butyl methylether. Identify the product and write down the mechanism of the reaction.

Autooxidation of ethers:

When ethers are stored in the presence of atmospheric oxygen, they slowly oxidise to form hydroperoxides and dialkylperoxides. These are explosive in nature. Such a spontaneous oxidation by atmospheric oxygen is called autooxidation.



Some of the reaction of diethyl ether.



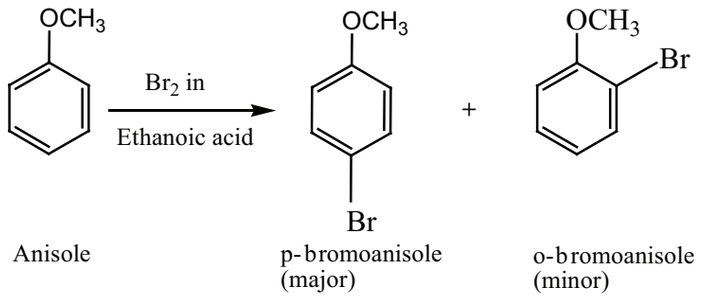
Aromatic electrophilic substitution reactions:

The alkoxy group (-OR) is an ortho, para directing group as well as activating group.It activates the aromatic ring towards electrophilic substitution.

XII U11-Hydroxy compounds.indd 137 16-12-2022 19:42:22

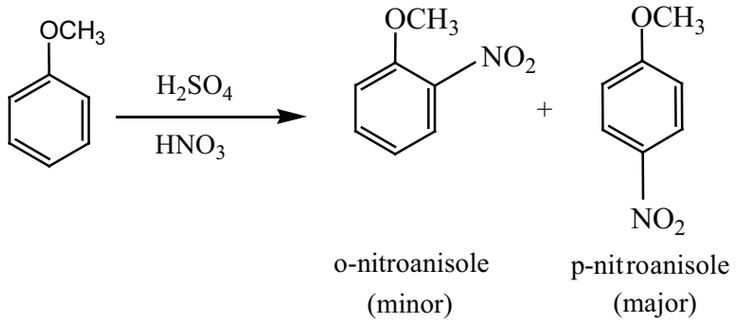
i) Halogenation:

Anisole undergoes bromination with bromine in acetic acid even in the absence of a catalyst, para isomer is obtained as the major product.



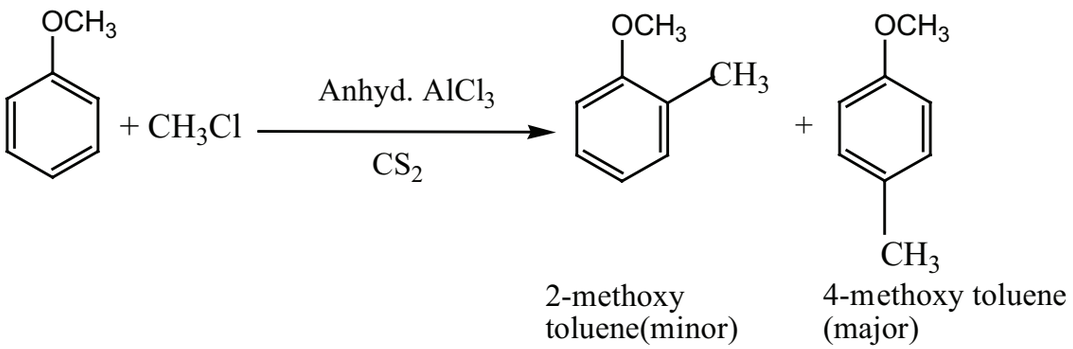
ii) Nitration:

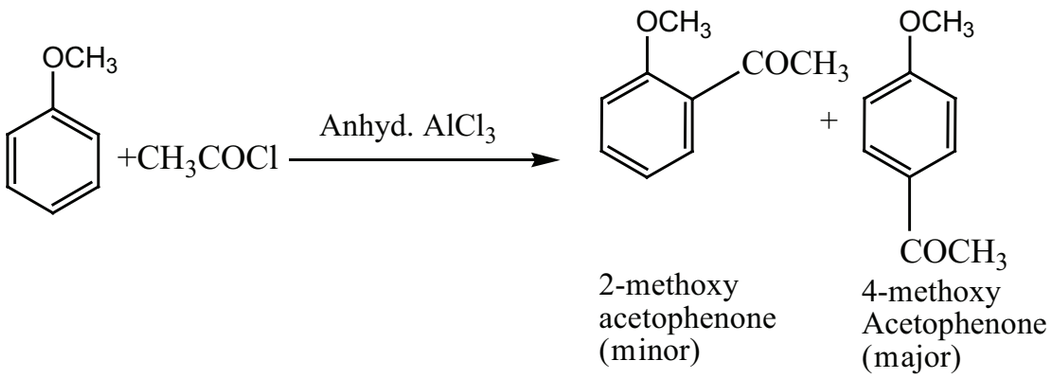
Anisole reacts with a mixture of conc. H_2SO_4/Conc.HNO_3 to yield a mixture of ortho nitro anisole and para nitro anisole.



iii) Friedel Craft's reaction:

Anisole undergoes Fridel Craft's reaction in presence of anhydrous $AlCl_3$ as a catalyst.





Uses of ethers

Uses of Diethyl ether

1. Diethyl ether is used as a surgical anaesthetic agent in surgery.
2. It is a good solvent for organic reactions and extraction.

XII U11-Hydroxy compounds.indd 138 16-12-2022 19:42:22

3. It is used as a volatile starting fluid for diesel and gasoline engine.
4. It is used as a refrigerant.

Uses of anisole

1. Anisole is a precursor to the synthesis of perfumes and insecticide pheromones,
2. It is used as a pharmaceutical agent .

EVALUATION

4NZEW

Choose the correct answer:

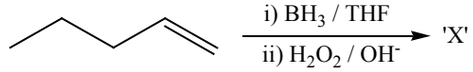
1. An alcohol (x) gives blue colour in Victormeyer's test and 3.7g of X when treated with metallic sodium liberates 560 mL of hydrogen at 273 K and 1 atm pressure what will be the possible structure of X?

   a) CH_3 CH (OH) CH_2CH_3 b) CH_3 – CH (OH) – CH_3

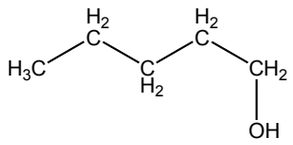
   b) CH_3 C (OH) $(CH_3)_2$ d) CH_3- CH_2 –CH (OH) – CH_2 – CH_3

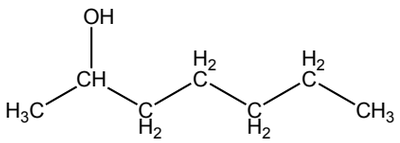
2. Which of the following compounds on reaction with methyl magnesium bromide will give tertiary alcohol.

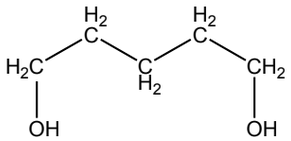
   a) benzaldehyde b) propanoic acid c) methyl propanoate d) acetaldehyde

3. 

   The X is

   a) 

   b) 

   c) 

   d) None of these

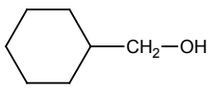
4. In the reaction sequence, Ethene $\xrightarrow{HOCl}$ A $\xrightarrow{X}$ ethan -1, 2 - diol . A and X respectively are

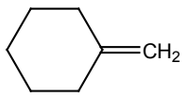
   a) Chloroethane and NaOH b) ethanol and H_2SO_4

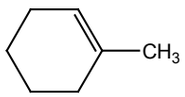
   c) 2 – chloroethan -1-ol and $NaHCO_3$ d) ethanol and H_2O

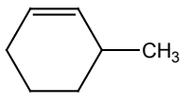
5. Which one of the following is the strongest acid

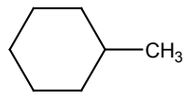
   a) 2 - nitrophenol b) 4 – chlorophenol c) 4 – nitrophenol d) 3 – nitrophenol

6.  on treatment with Con H_2SO_4, predominately gives

a) 

b) 

c) 

d) 

7. Carbolic acid is

   a) Phenol b) Picric acid d) benzoic acid d) phenylacetic acid

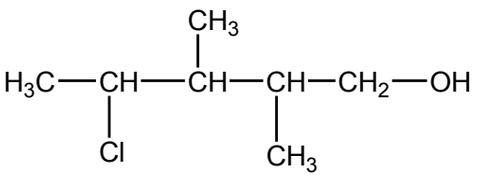
8. Which one of the following will react with phenol to give salicyladehyde after hydrolysis.

   a) Dichloro methane b) trichloroethane c) trichloro methane d) CO_2

9. $(CH_3)_3$- C - CH(OH) $CH_3 \xrightarrow{\text{Con } H_2SO_4}$ X (major product)

   a) $(CH_3)_3$ CCH = CH_2 b) $(CH_3)_2$ C = C $(CH_3)_2$

   c) CH_2 = C$(CH_3)CH_2$ - CH_2- CH_3 d) CH_2 = C (CH_3) - CH_2- CH_2- CH_3

10. The correct IUPAC name of the compound, 

    a) 4 – chloro – 2,3 – dimethyl pentan – 1-ol

    b) 2,3 – dimethyl – 4- chloropentan -1-ol

    c) 2,3,4 – trimethyl – 4- chlorobutan -1-ol

    d) 4 – chloro – 2,3,4 – trimethyl pentan – 1-ol

11. Assertion : Phenol is more acidic than ethanol

    Reason: Phenoxide ion is resonance stabilized

    a) both assertion and reason are true and reason is the correct explanation of assertion.

    b) both assertion and reason are true but reason is not the correct explanation of assertion.

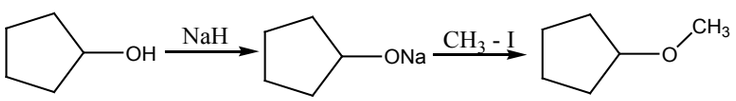
    c) assertion is true but reason is false

    d) both assertion and reason are false.

12. In the reaction Ethanol $\xrightarrow{PCl_5}$ X $\xrightarrow{\text{alc.KOH}}$ Y $\xrightarrow[298K]{H_2SO_4/H_2O}$ Z. The 'Z' is

    a) ethane b) ethoxyethane c) ethylbisulphite d) ethanol

13. The reaction



    Can be classified as

    a) dehydration b) Williamson alcoholsynthesis

    c) Williamson ether synthesis d) dehydrogenation of alcohol

14. Isopropylbenzene on air oxidation in the presence of dilute acid gives

a) C_6H_5COOH b) $C_6H_5COCH_3$ c) $C_6H_5COC_6H_5$ d) C_6H_5 - OH

15. Assertion : Phenol is more reactive than benzene towards electrophilic substitution reaction
Reason : In the case of phenol, the intermediate arenium ion is more stabilized by resonance.

a) if both assertion and reason are true and reason is the correct explanation of assertion.

b) if both assertion and reason are true but reason is not the correct explanation of assertion.

c) assertion is true but reason is false

d) both assertion and reason are false.

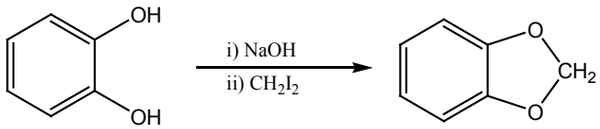
16. HO CH_2 CH_2 – OH on heating with periodic acid gives

a) methanoic acid b) Glyoxal c) methanal d) CO_2

17. Which of the following compound can be used as artifreeze in automobile radiators?

a) methanol b) ethanol c) Neopentyl alcohol d) ethan -1, 2-diol

18. The reactions



is an example of

a) Wurtz reaction b) cyclic reaction c) Williamson reaction d) Kolbe reactions

19. One mole of an organic compound (A) with the formula C_3H_8O reacts completely with two moles of HI to form X and Y. When Y is boiled with aqueous alkali it forms Z. Z answers the iodoform test. The compound (A) is

a) propan – 2-ol b) propan -1-ol c) ethoxy ethane d) methoxy ethane

20. Among the following ethers which one will produce methyl alcohol on treatment with hot HI?

a) $(H_3C)_3C-O-CH_3$ b) $(CH_3)_2-CH-CH_2-O-CH_3$

c) $CH_3(CH_2)_3-O-CH_3$ d) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_3$

21. Williamson synthesis of preparing dimethyl ether is a / an /

a) SN^1 reactions b) SN^2 reaction

c) electrophilic addition d) electrophilic substitution

22. On reacting with neutral ferric chloride, phenol gives

a) red colour b) violet colour c) dark green colour d) no colouration.

Short Answer Questions

1. Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction
2. Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI
3. Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.
4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.
5. Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.

   (i.) Acid catalysed hydration (ii.) Hydroboration

   (iii.) Hydroxylation using Baeyer's reagent
6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

   (i.) Butan – 2- ol, Butan -1-ol, 2 –methylpropan -2-ol

   (ii.) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol
7. Can we use nucelophiles such as NH_3,CH_3O^- for the Nucleophilic substitution of alcohols
8. Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound.
9. What happens when 1-phenyl ethanol is treated with acidified $KMnO_4$.
10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene.
11. How is phenol prepared from

    i) chloro benzene ii) isopropyl benzene
12. Explain Kolbe's reaction
13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol
14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent -2-en-1-ol.
15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methoxy propane
16. How are the following conversions effected

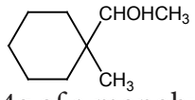
    i) benzylchloride to benzylalcohol ii) benzyl alcohol to benzoic acid
17. Complete the following reactions

XII U11-Hydroxy compounds.indd 142 16-12-2022 19:42:25

i) $CH_3 - CH_2 - OH \xrightarrow{P\,Br_3} A \xrightarrow{aq.NaOH} B \xrightarrow{Na} C$

ii) $C_6H_5 - OH \xrightarrow{Zn\ dust} A \xrightarrow[Anhydrs\ AlCl_3]{CH_3Cl} B \xrightarrow{acid\ KMnO_4} C$

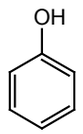
iii) Anisole $\xrightarrow[AlCl_3]{t\text{-butylchloride}} A \xrightarrow{Cl_2/FeCL_3} B \xrightarrow{HBr} C$

iv) 

$\xrightarrow{H^+}$ A $\xrightarrow[ii)\ H_2O]{i)\ O_3}$ B

18. 0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm^3 of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

19. Complete the following reactions

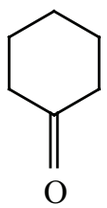
i) 

$\xrightarrow[OH^-]{C_6H_5COCl}$ A $\xrightarrow{Nitration}$ B

(major product)

ii) C_6H_5-CHCH(OH)CH$(CH_3)_2 \xrightarrow{ConH_2SO_4}$

20. Phenol is distilled with Zn dust followed by Friedel – Crafts alkylation with propyl chloride to give a compound A, A on oxidation gives (B) Identify A and B.

21. CH_3MgBr+  $\xrightarrow{H_3O^+}$ A $\xrightarrow{HBr}$ B $\xrightarrow{Mg\ /\ ether}$ C $\xrightarrow{HCHO\ /\ H_3O^+}$ D

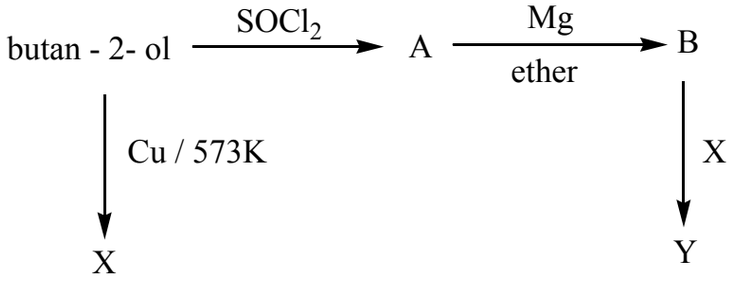
Identify A,B,C,D and write the complete equation

22. What will be the product (X and A)for the following reaction

acetylchloride $\xrightarrow[ii)\ H_3O^+]{i)\ CH_3MgBr}$ X $\xrightarrow{acid\ K_2Cr_2O_7}$ A

23. How will you convert acetylene into n-butyl alcohol.

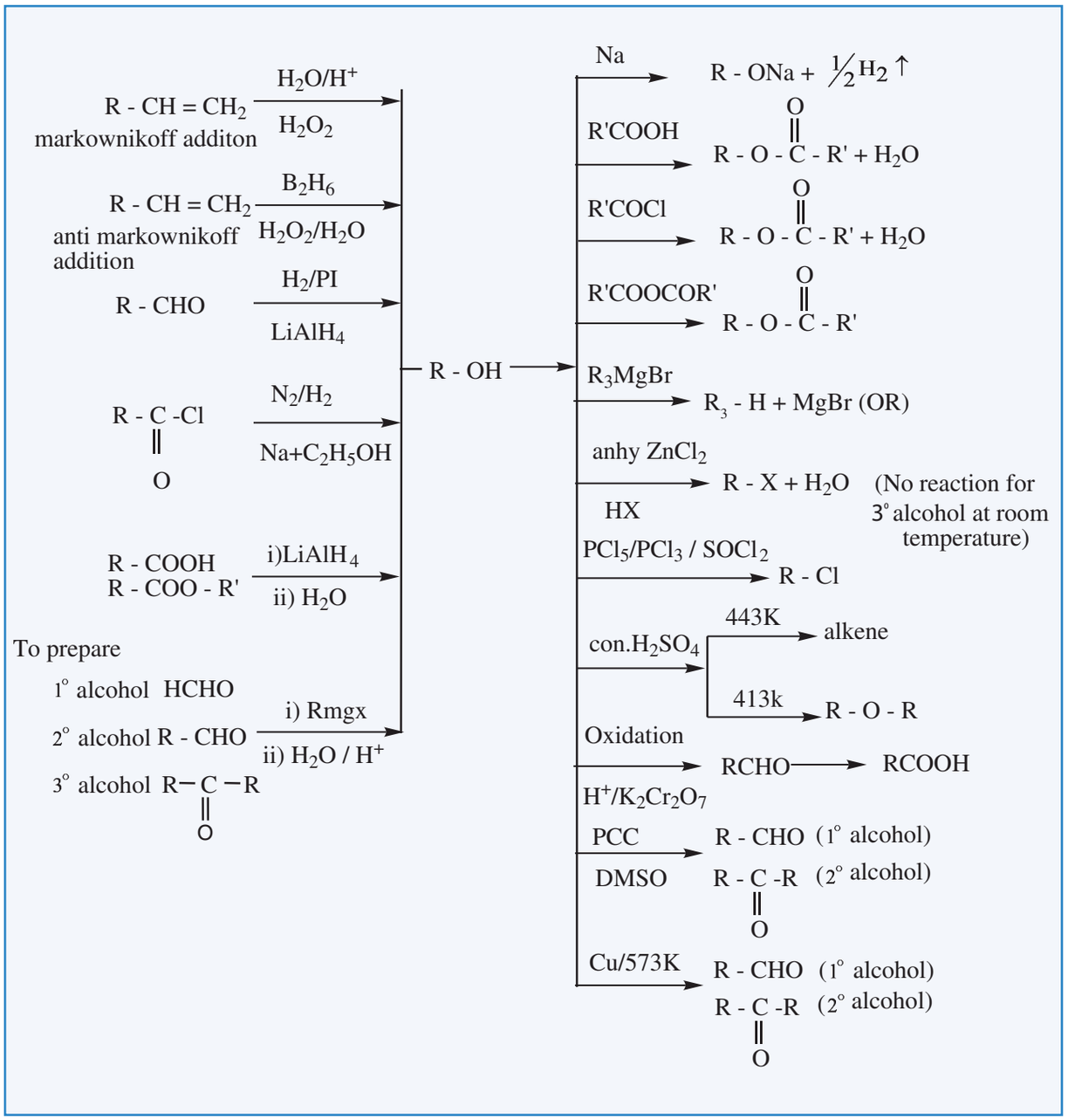
24. Predict the product A,B,X and Y in the following sequence of reaction



25. 3,3 – dimethylbutan -2-ol on treatment with conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism

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ALCOHOL



XII U11-Hydroxy compounds.indd 144 16-12-2022 19:42:26

UNIT 12

CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS



Adolf von Baeyer

Adolf Von Baeyer, German research chemist who synthesized indigo (1880) and formulated its structure (1883). He was awarded the Nobel Prize for Chemistry in 1905. Notable among Baeyer's many achievements were the discovery of the phthalein dyes and his investigations of uric acid derivatives, polyacetylenes, and oxonium salts. One derivative of uric acid that he discovered was barbituric acid, the parent compound of the sedative-hypnotic drugs known as barbiturates.

F23B4

Learning Objectives

After studying this unit the student will be able to

- describes the important methods of preparation and reactions of Carbonyl compounds
- explains the mechanism of Nucleophilic addition reaction of carbonyl compounds
- describes the preparation and chemical reactions of carboxylic acids and its derivatives
- list the uses of aldehydes, ketones and carboxylic acids

XII U12-Carbonyl Compounds.indd 145 08-12-2021 22:50:29

INTRODUCTION

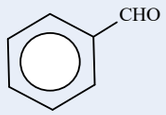
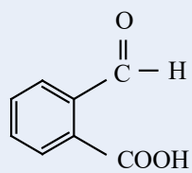
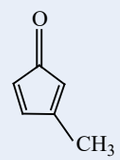
We come across many organic compounds containing a  group in our everyday Life. Biomolecules such as protein, carbohydrate etc… that makeup all plants and animals contains carbonyl group. They play an important role in the metabolic process. For example, pyridoxal, an aldehyde derived from vitamin B, function as a co –enzyme. Carbonyl compounds are important constituents of fabrics, plastis and drugs. For example, Formaldehyde is used for the manufacture of Bakelite and paracetamol, (p– acetylated aminophenol) a drug used to reduce fever, contains a carbonyl group. In this unit, we will learn the preparation, properties and uses of aldhydes, ketones and carboxylic acids.

12.1 Nomenclature of Aldehydes and ketones

We have already learnt the IUPAC system of nomenclature of organic compounds in XIth standard. Let us apply the rules to name the following compounds.

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Formaldehyde H – CHO methanal	–	meth	an$\not{e}$	al
Acetaldehyde CH_3 – CHO ethanal	–	eth	an$\not{e}$	al
Acrolein $CH_2 = CH – CHO$ prop – 2- enal	–	prop	2-en$\not{e}$	al
Crotonaldehyde $CH_3 – CH = CH – CHO$ but – 2 – enal	–	but	2-en$\not{e}$	al
Glyceraldehyde $HO — CH_2 — \underset{\displaystyle OH}{\underset{|}{CH}} — CHO$ 2, 3 – dihydroxy propanal	2, 3 dihydroxy	prop	an$\not{e}$	al

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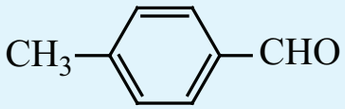
Benzaldehyde  phenyl methanal	phenyl	meth	ane	al
Acetone / Dimethyl ketone $CH_3 - CO - CH_3$ propanone	–	prop	ane	one
Mesityl oxide $(CH_3)_2C = CHCOCH_3$ 4 – methylpent-3-en-2-one	4 – methyl	pent	3-ene	2-one
Methyl Phenyl ketone $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$ Acetophenone (PIN)* 1-phenylethan-1-one	1-phenyl	eth	ane	1-one
Diphenyl ketone $C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$ Benzophenone (PIN)* Diphenylmethanone	Diphenyl	meth	ane	one
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CHO$ 3 - oxopentanal	3 - oxo	pent	ane	al
 2 – formylbenzoicacid	2 – formyl	benz	-	oicacid
 3 -methylcyclopent–2,4-dien-1-one	3 -methyl	cyclopent	2, 4 diene	1-one

* PIN– Preferred IUPAC name

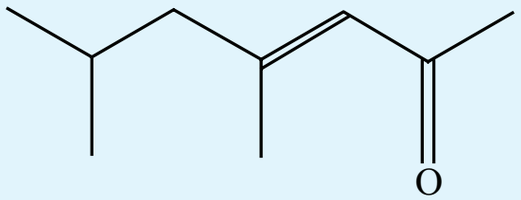
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Evaluate yourself

i) Write the IUPAC name for the following compound

i) 

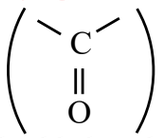
ii) $(CH_3)_2\,C = CHCOCH_3$

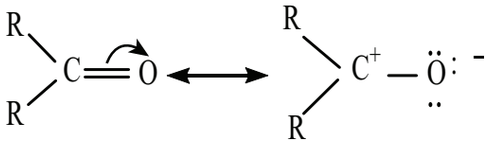
iii) 

iv) $(CH_3)_2\,C\,(OH)\,CH_2\,CHO$

ii) Wrtie all possible structural isomers and position isomers for the ketone represented by the molecular formula $C_5H_{10}O$.

12.2 Structure of carbonyl group

The carbonyl carbon  is sp^2 hybridised and the carbon – oxygen bond is similar to carbon – carbon double bond in alkenes. The carbonyl carbon forms three σ bonds using their three sp^2 hybridised orbital. One of the sigma bond is formed with oxygen and the other two with hydrogen and carbon (in aldehydes) or with two carbons (in ketones). All the three 'σ' bonded atoms are lying on the same plane as shown in the fig (12.1). The fourth valence electron of carbon remains in its unhybridised '2p' orbital which lies perpendicular to the plane and it overlaps with 2p orbital of oxygen to form a carbon – oxygen π bond. The oxygen atom has two nonbonding pairs of electrons, which occupy its remaining two p-orbitals. Oxygen, the second most electro negative atom attracts the shaired pair of electron between the carbon and oxygen towards itself and hence the bond is polar. This polarisation contributes to the reactivity of aldehydes and ketones.



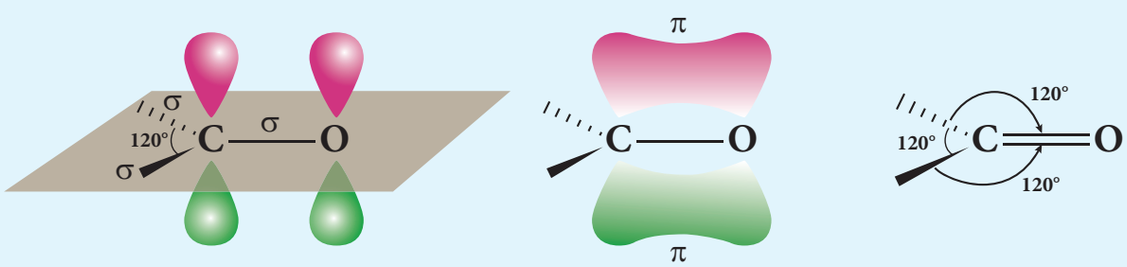


Fig 12.1 structure of carbonyl group

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12.3 General methods of preparation of aldehydes and ketones

A. Preparation of aldehydes and ketones

1.) Oxidation and catalytic dehydrogenation of alcohols

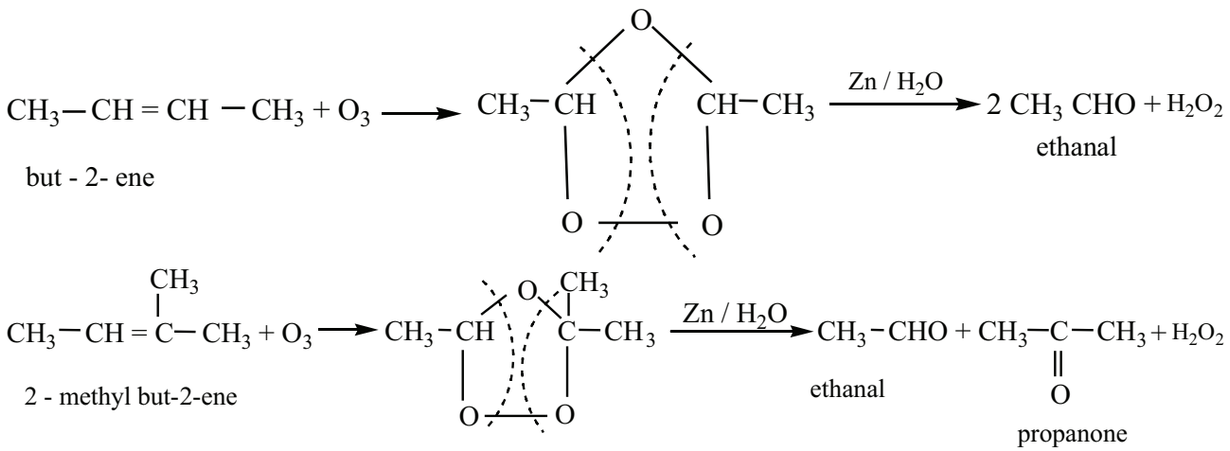
We have already learnt that the oxidation of primary alcohol gives aldehydes and secondary alcohol gives a ketone. Oxidising agents such as acidified $Na_2Cr_2O_7$, $KMnO_4$, PCC are used for oxidation. Oxidation using PCC yield aldehydes . Other oxidising agents further oxidise the aldhydes / ketones in to carboxylic acids (Refer Unit No. - 11 Oxidation of alcohols)

When vapours of alcohols are passed over heavy metal catalyst such as Cu, Ag, alcohols give aldehydes and ketons. (Refer Unit No. - 11 Catalytic dehydrogenation of alcohols

2.) Ozonolysis of alkenes

We have already learnt in XI th standard that the reductive ozonolysis of alkenes gives aldehydes and ketones.

Alkenes react with ozone to form ozonide which on subsequent cleavage with zinc and water gives aldehydes and ketones. Zinc dust removes H_2O_2 formed, which otherwise can oxidise aldehydes / ketones.



Terminal olefines give formaldehyde as one of the product.

Evaluate yourself - 1

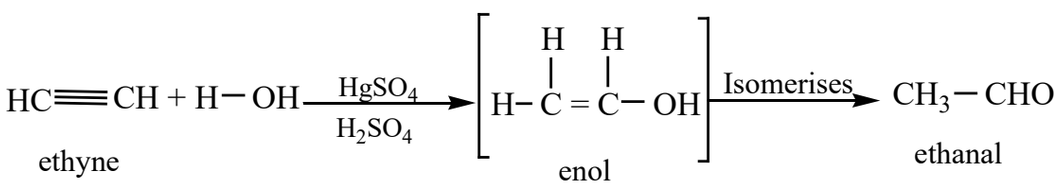
What happens when the following alkenes are subjected to reductive ozonolysis.

1) propene 2) 1 – Butene 3) Isobutylene

3. Hydration of alkynes

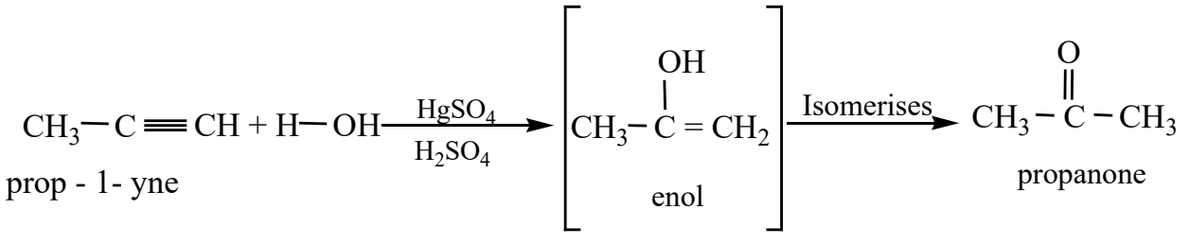
We have already learnt in XI standard that the hydration of alkynes in presence of 40% dilute sulpuric acid and 1% $HgSO_4$ to give the corresponding aldehydes / ketones.

a) Hydration of acetylene yields acetaldehyde



XII U12-Carbonyl Compounds.indd 149 08-12-2021 22:50:33

b) Hydration of alkynes, other than acetylene gives ketones



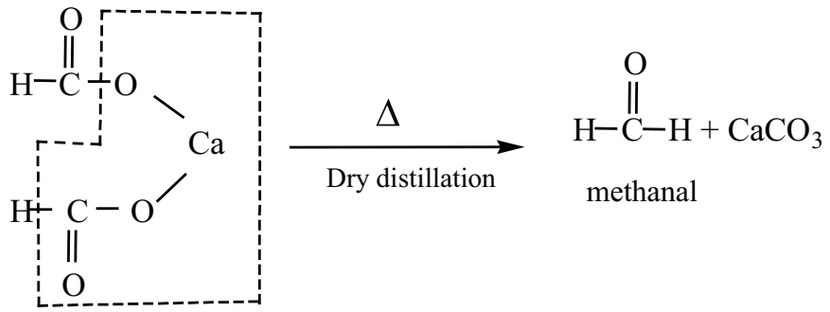
prop - 1- yne

propanone

4. From calcium salts of carboxylic acids

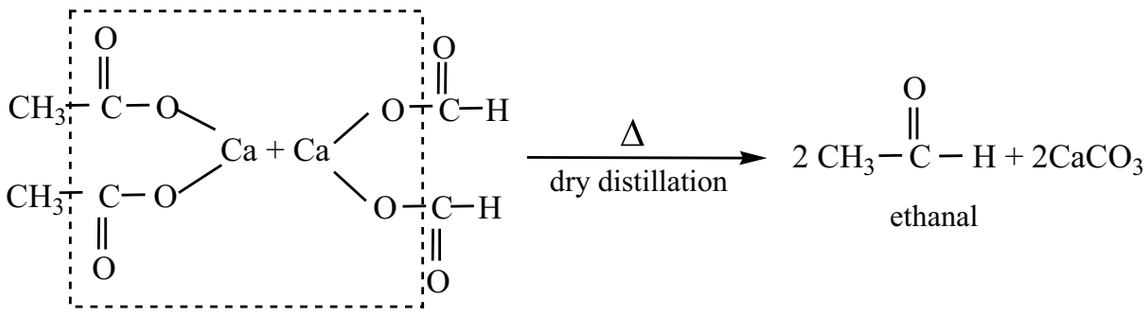
Aldehydes and ketones may be prepared by the dry distillation of calcium salts of carboxylic acids.

a) Aldehydes are obtained when the mixture of calcium salt of carboxylic acid and calcium formate is subjected to dry distillation.



Calcium methanoate

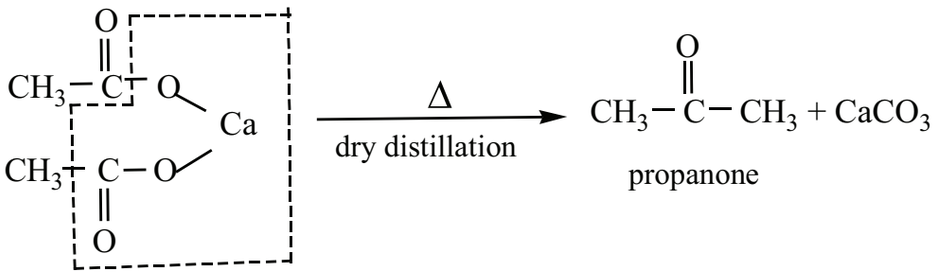
methanal



Calcium ethanoate Calcium methanoate

ethanal

b) Symmetrical ketones can be obtained by dry distillation of the calcium salt of carboxylic acid (except formic acid)



Calcium ethanoate

propanone

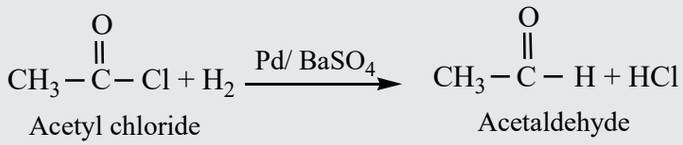
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B. Preparation of aldehydes

1) Rosenmund reduction

a) **Aldehydes** can be prepared by the hydrogenation of acid chloride, in the presence of palladium supported by barium sulphate. This reaction is called **Rosenmund reduction**.

Example



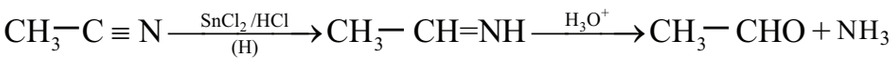
Acetyl chloride — Acetaldehyde

In this reaction, barium sulphate act as a catalytic poison to palladium catalyst, so that aldehyde cannot be further reduced to alcohol.

Formaldehyde and ketones cannot be prepared by this method.

2. Stephen's reaction

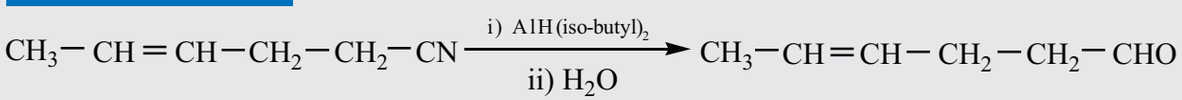
When alkylcyanides are reduced using $SnCl_2/HCl$, imines are formed, which on hydrolysis gives corresponding aldehyde.



3. Selective reduction of cyanides

Diisobutyl aluminium hydride (DIBAL –H) selectively reduces the alkyl cyanides to form imines which on hydrolysis gives aldehydes.

Example

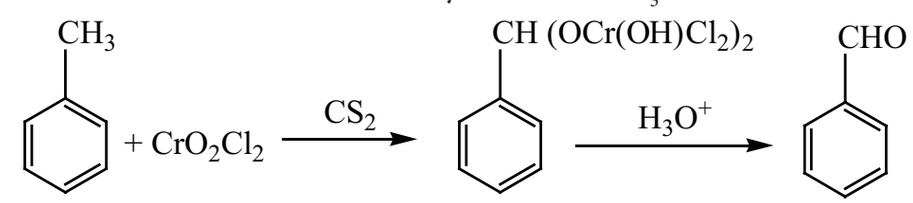


hex - 4- ennitrile — hex - 4- enal

C) Preparation of benzaldehyde

1. **Side chain oxidation of toluene and its derivatives** by strong oxidising agents such as $KMnO_4$ gives benzoic acid.

When chromylchloride is used as an oxidising agent, toluene gives benzaldehyde. This reaction is called **Etard reaction**. Acetic anhydride and CrO_3 can also be used for this reaction.



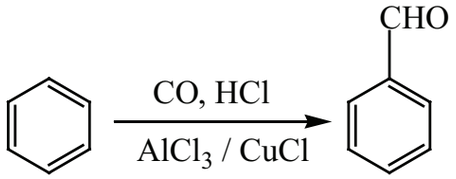
methylbenzene — benzaldehyde

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Oxidation of toluene by chromic oxide gives benzylidine diacetate which on hydrolysis gives benzaldehyde.

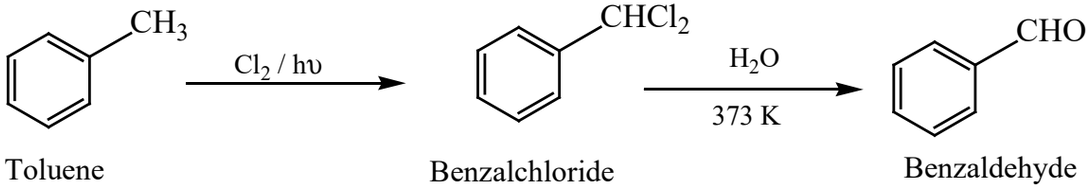
2) Gattermann – Koch reaction

This reaction is a variant of Friedel – Crafts acylation reaction. In this method, reaction of carbon monoxide and HCl generate an intermediate which reacts like formyl chloride.



3) Manufacture of benzaldehyde from toluene

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.

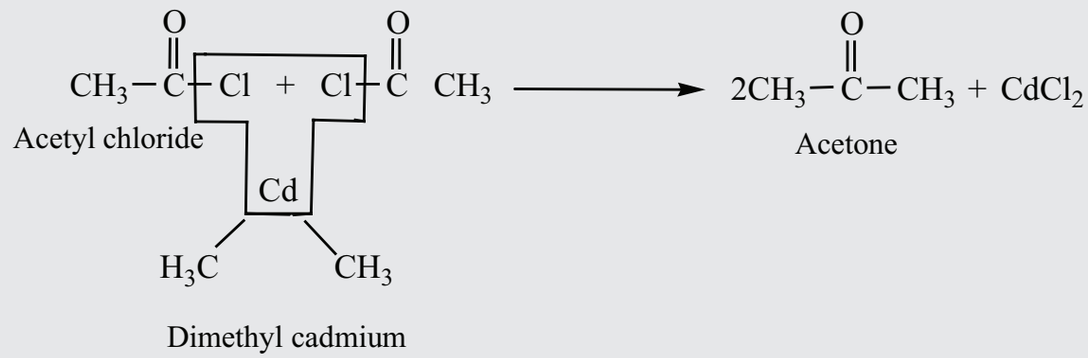


This is the commercial method for the manufacture of benzaldehye.

D) Preparation of ketones

1) Ketones can be prepared by the action of acid chloride with dialkyl cadmium.

Example



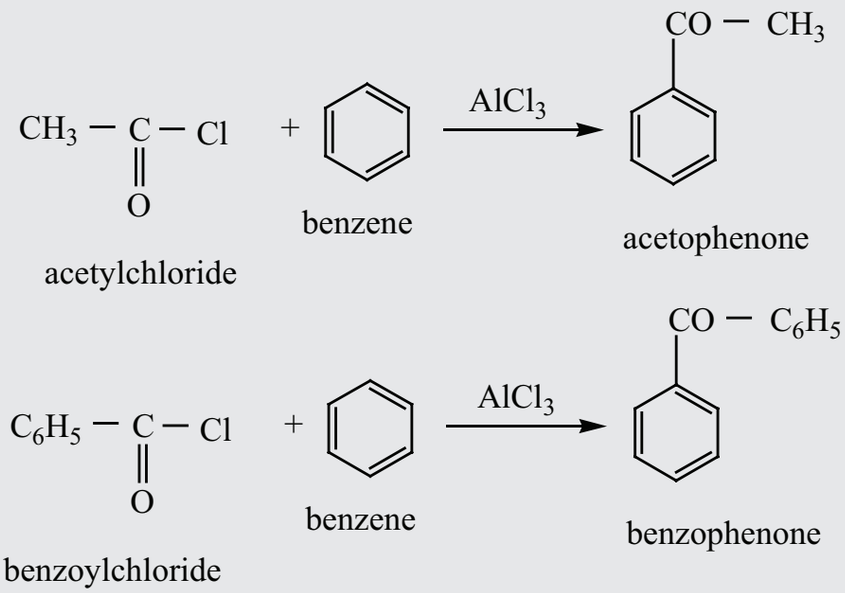
2) Preparation of phenyl ketones

Friedel – Crafts acylation

It is the best method for preparing alkyl aryl ketones or diaryl ketones. This reaction succeeds only with benzene and activated benzene derivatives.

XII U12-Carbonyl Compounds.indd 152 08-12-2021 22:50:34

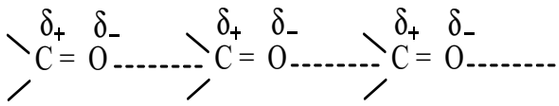
Example



12.4 Physical properties of aldehydes and ketones

1. **Physical State:** Formaldehyde is a gas at room temperature and acetaldehyde is a volatile liquid. All other aldehydes and ketones upto to C_{11} are colourless liquids while the higher ones are solids.
2. **Boiling points**

Aldehydes and ketones have relatively high boiling point as compared to hydrocarbons and ethers of comparable molecular mass. It is due to the weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.



These dipole-dipole interactions are weaker than intermolecular H-bonding. The boiling points of aldehydes and ketones are much lower than those of corresponding alcohols and carboxylic acids which possess inter molecular hydrogen bonding.

Compound	Molar mass	Boiling point (K)
$CH_3(CH_2)_3CH_3$ Pentane	72	309
$CH_3(CH_2)_2CHO$ butanal	72	349
$CH_3(CH_2)_3OH$ butanol	74	391

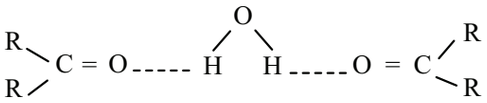
Compound	Molar mass	Boiling point (K)
$CH_3CH_2COCH_3$ butan - 2- one	72	353
CH_3CH_2COOH Propanoicacid	74	414

XII U12-Carbonyl Compounds.indd 153 08-12-2021 22:50:35

3. Solubility

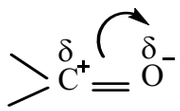
Lower members of aldehydes and ketones like formaldehyde, acetaldehyde and acetone are miscible with water in all proportions because they form hydrogen bond with water.

Solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.



4. Dipolemoment:

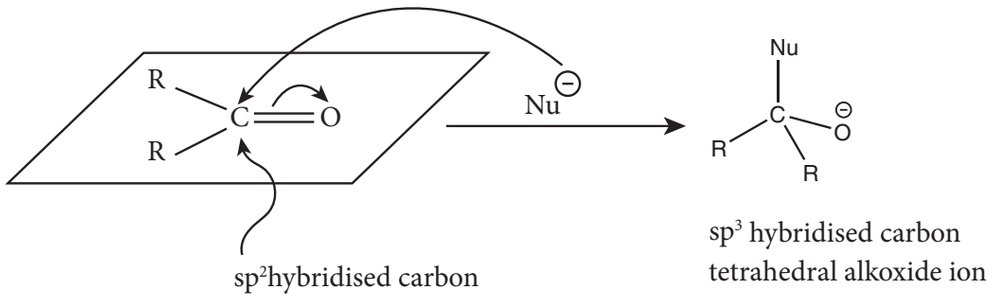
The carbonyl group of aldehydes and ketones contains a double bond between carbon and oxygen. Oxygen is more electronegative than carbon and it attracts the shared pair of electron which makes the carbonyl group as polar and hence aldehydes and ketones have high dipole moments.



12.5 Chemical properties of aldehydes and ketones

A) Nucleophilic addition reactions

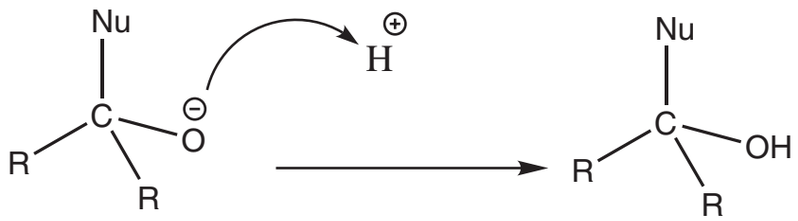
This reaction is the most common reactions of aldehydes and ketones. The carbonyl carbon carries a small degree of positive charge. Nucleophile such as CN^- can attack the carbonyl carbon and uses its lone pair to form a new carbon – nucleophile 'σ' bond, at the same time two electrons from the carbon – oxygen double bond move to the most electronegative oxygen atom. This results in the formation of an alkoxide ion. In this process, the hybridisation of carbon changes from sp^2 to sp^3.



sp^2hybridised carbon

sp^3 hybridised carbon
tetrahedral alkoxide ion

The tetrahedral intermediate can be protonated by water or an acid to form an alcohol.



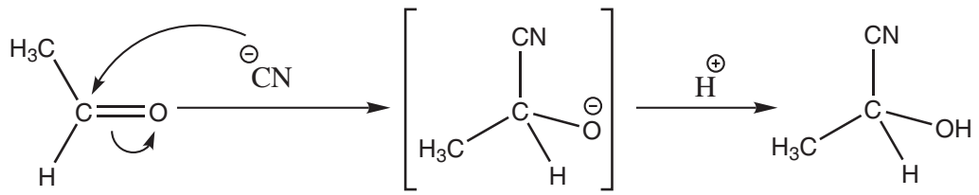
In general, aldehydes are more reactive than ketones towards nucleophilic addition reactions due to +I and steric effect of alkyl groups.

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Examples

1) Addition of HCN

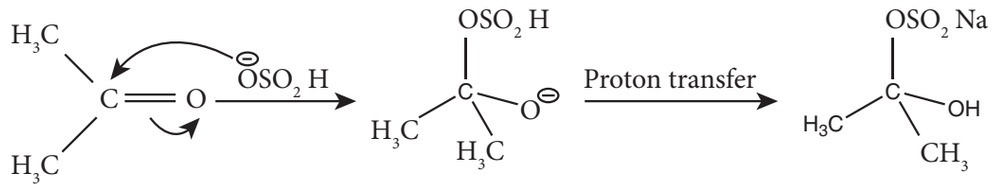
Attack of CN^- on carbonyl carbon followed by protonation gives cyanohydrins.



ethanal (acetaldehyde) | tetrahedral intermediate | 2-hydroxy propanenitrile (acetaldehyde cyano hydrin)

The cyanohydrins can be converted into hydroxy acid by acid hydrolysis. Reduction of cyanohydrins gives hydroxy amines

2) Addition of $NaHSO_3$



acetone (propanone) | bisulphite addition compound

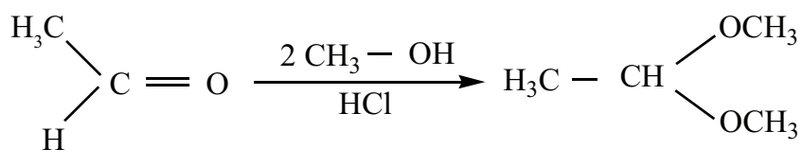
This reaction finds application in the separation and purification of carbonyl compound. The bisulphate addition compound is water soluble and the solution is treated with mineral acid to regenerate the carbonyl compounds .

3) Addition of alcohol

When aldehydes / ketones is treated with 2 equivalents of an alcohol in the presence of an acid catalyst to form acetals.

example

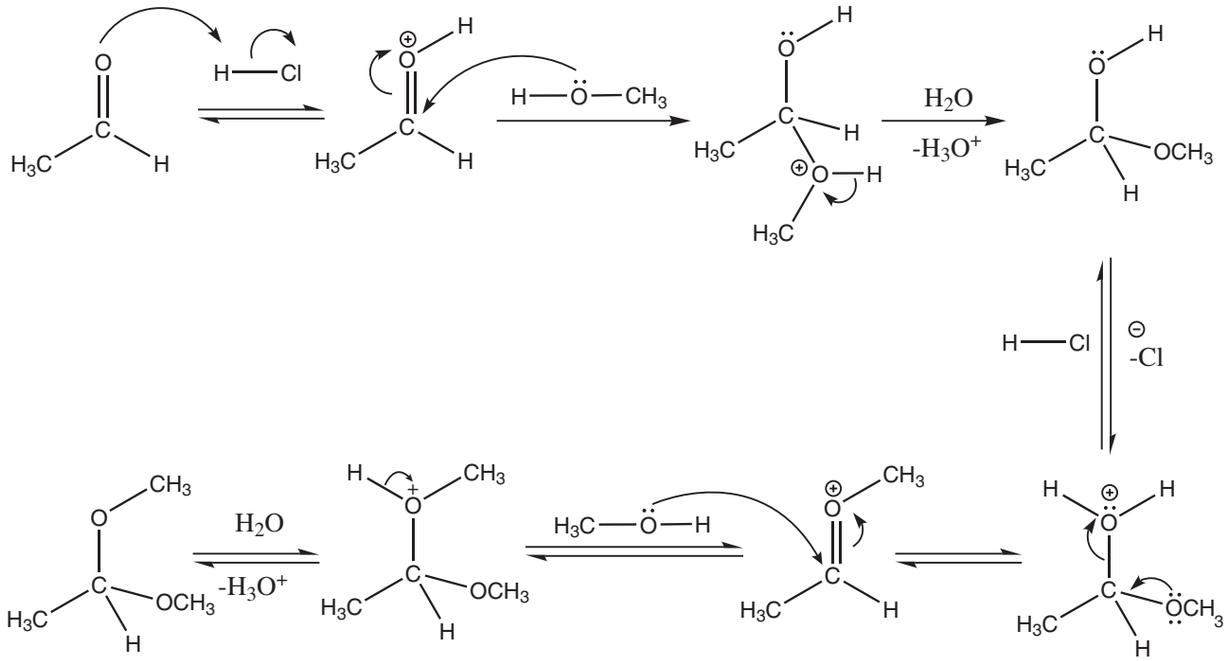
When acetaldehyde is treated with 2 equivalent of methanol in presence of HCl, 1,1, - dimethoxy ethane is obtained.



ethanal (acetaldehyde) | 1,1 - dimethoxyethane (acetaldehyde dimethyl acetal)

XII U12-Carbonyl Compounds.indd 155 08-12-2021 22:50:36

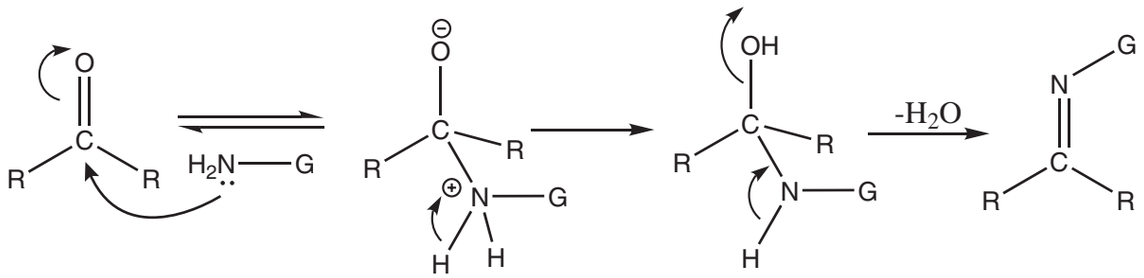
Mechanisum



4) Addition of ammonia and its derivatives

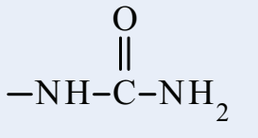
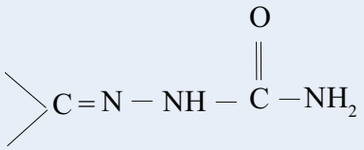
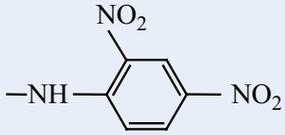
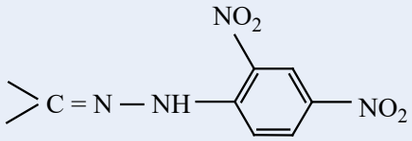
When the nucleophiles, such as ammonia and its derivative $H_2\ddot{N}$-G is treated with carbonyl compound, nuceophilic addition takes place, the carbonyl oxygen atom is protonated and then elimination takes place to form carbon – nitrogen double bond $\left(>C=N-G\right)$

When G – alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$ etc...



G	Ammonia derivatives	Carbonyl derivatives	Product name
— OH	Hydroxyl amine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
$-HN-C_6H_5$	Phenyl hydrazine	$>C=N-NH-C_6H_5$	Phenyl hydrazone

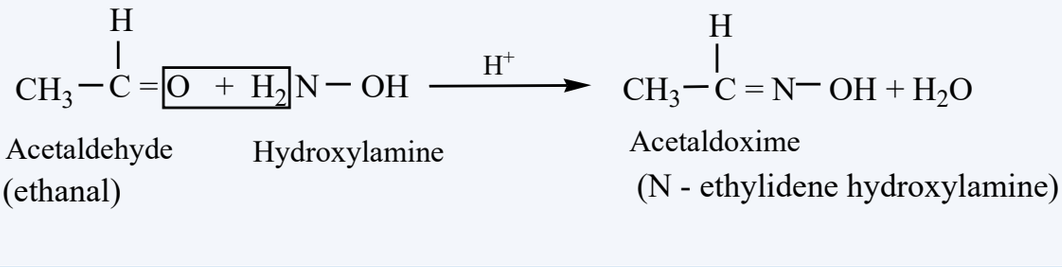
XII U12-Carbonyl Compounds.indd 156 08-12-2021 22:50:37

	Semi carbabazide		Semi carbazone
	2,4 – dinitrophenyl hydrazine		2,4 – dinitrophenyl hydrazone

i) Reaction with hydroxyl amine

Aldehyde and ketones react with hydroxylamine to form **oxime.**

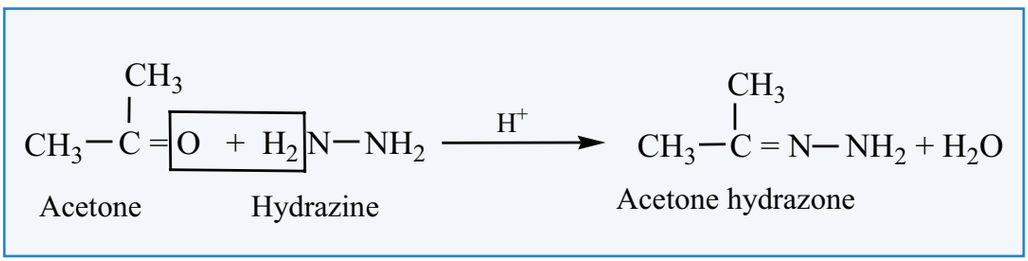
Example:



ii) Reaction with hydrazine

Aldehydes and ketones react with hydrazine to form **hydrazone.**

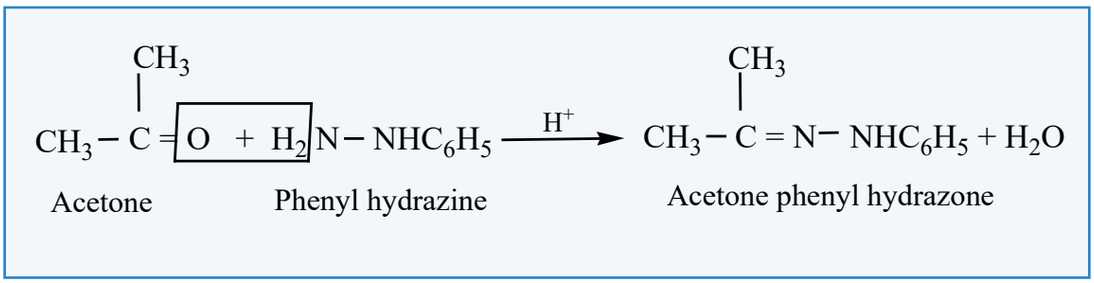
Example:



iii) Reaction with phenyl hydrazine

Aldehydes and ketones react with phenyl hydrazine to form **phenyl hydrazone**.

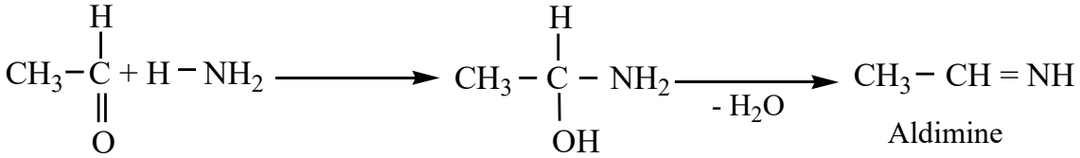
Example:



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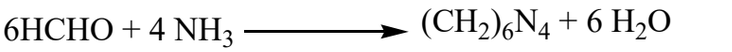
5) Reaction with NH_3

i) Aliphatic aldehydes (except formaldehyde) react with an ethereal solution of ammonia to form aldimines.



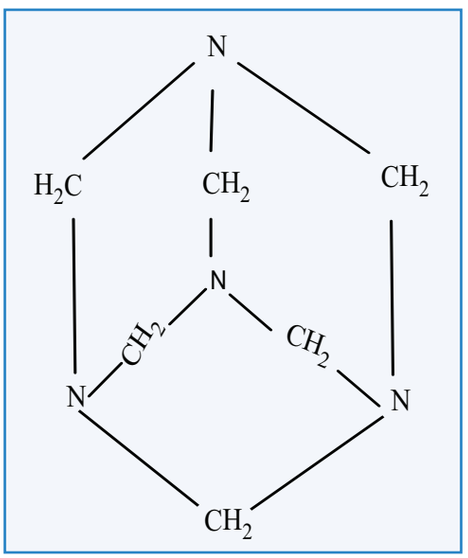
Acetaldehyde — Acetaldehyde ammonia — Aldimine

ii) Formaldehyde reacts with ammonia to form hexa methylene tetramine, which is also known as **Urotropine**.



Formaldehyde — Hexamethylene tetramine

Structure

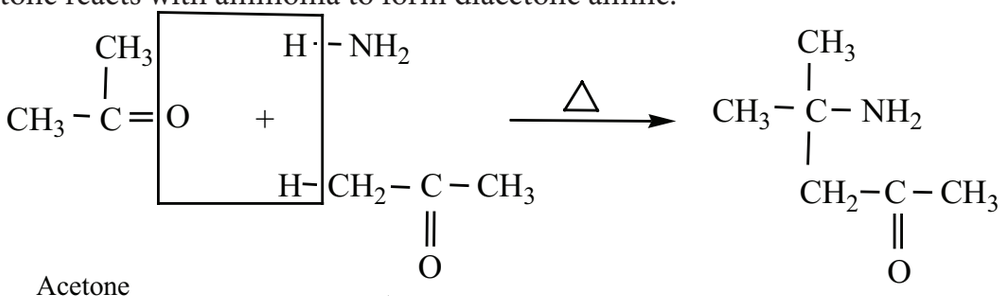


Uses

(i) Urotropine is used as a medicine to treat urinary infection.

(ii) Nitration of Urotropine under controlled condition gives an explosive RDX (Research and development explosive). It is also called cyclonite or cyclotri methylene trinitramine.

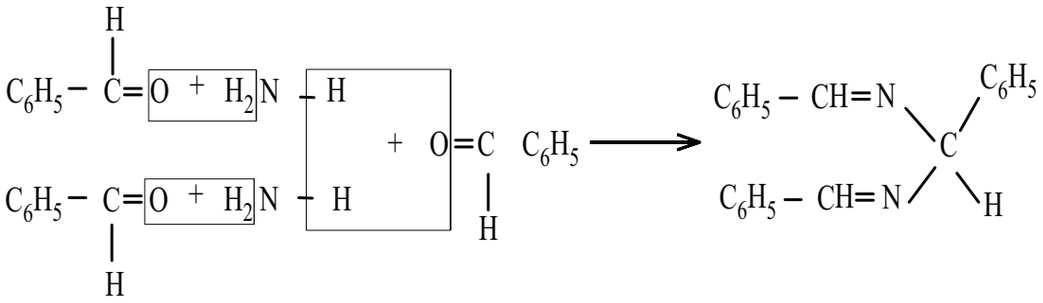
iii) Acetone reacts with ammonia to form diacetone amine.



Acetone — Acetone — Diacetone amine

XII U12-Carbonyl Compounds.indd 158 08-12-2021 22:50:38

iv) Benzaldehyde form a complex condensation product with ammonia.



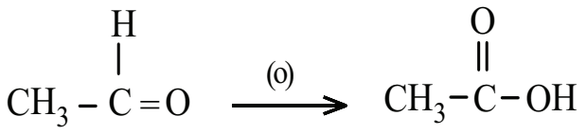
Benzaldehyde Ammonia Benzaldehyde Hydrobenzamide

B) Oxidation of aldehydes and ketones

a) Oxidation of aldehydes

Aldehydes are easily oxidised to carboxylic acid containing the same number of carbon atom, as in parent aldehyde. The common oxidising agents are acidified $K_2Cr_2O_7$, acidic or alkaline $KMnO_4$ or chromic oxide.

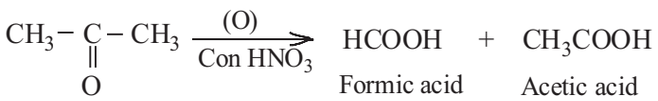
Example



Acetaldehyde Aceticacid

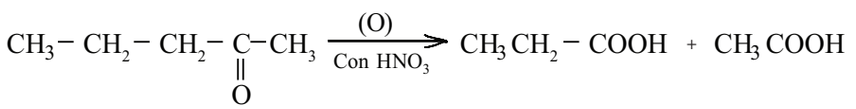
b) Oxidation of ketone

Ketones are not easily oxidised. Under drastic condition or with powerful oxidising agent like Con.HNO_3, $H^+/KMnO_4$, $H^+/K_2Cr_2O_7$, cleavage of carbon-carbon bond takes place to give a mixture of carboxylic acids having less number of carbon atom than the parent ketone.



Formic acid Acetic acid

The oxidation of unsymmetrical ketones is governed by **Popoff's rule**. It states that during the oxidation of an unsymmetrical ketone, a (C–CO) bond is cleaved in such a way that the keto group stays with the smaller alkyl group.



pentan – 2 – one Propanoic acid ethanoic acid

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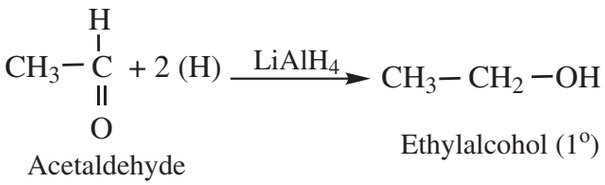
C) Reduction reactions

(i) Reduction to alcohols

We have already learnt that aldehydes and ketones can be easily reduced to primary and secondary alcohols respectively. The most commonly used reducing agents are Lithium Aluminium hydride ($LiAlH_4$), and Sodium borohydride ($NaBH_4$).

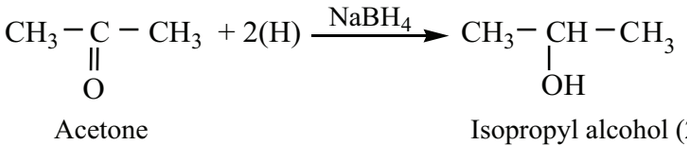
a) Aldehyde are reduced to primary alcohols.

Example



b) Ketone are reduced to Secondary alcohols.

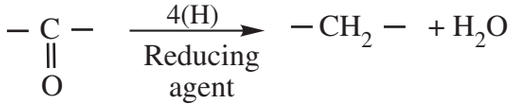
Example



The above reactions can also be carried out with hydrogen in the presence of metal catalyst like Pt, Pd, or Ni. $LiAlH_4$ and $NaBH_4$ do not reduce isolated carbon – carbon double bonds and double bond of benzene rings. In case of α, β unsaturated aldehyde and ketones, $LiAlH_4$ reduces only C = O group leaving C = C bond as such.

ii) Reduction to hydrocarbon

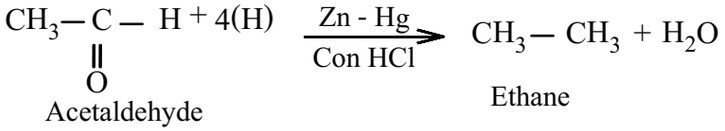
The carbonyl group of aldehydes and ketones can be reduced to methylene group using suitable reducing agents to give hydrocarbons.

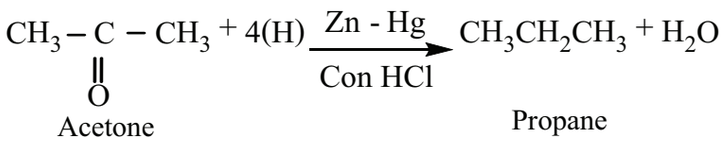


a) Clemmensen reduction

Aldehydes and Ketones when heated with zinc amalgam and concentrated hydrochloric acid gives hydrocarbons.

Example





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b) Wolf Kishner reduction Aldehydes and Ketones when heated with hydrazine (NH_2NH_2) and sodium ethoxide, hydrocarbons are formed Hydrazine acts as a reducing agent and sodium ethoxide as a catalyst.

Example

$$CH_3-\underset{\underset{O}{\|}}{C}-H + 4(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} CH_3-CH_3 + H_2O + N_2$$

Acetaldehyde — Ethane

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 4(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} CH_3CH_2CH_3 + H_2O + N_2$$

Acetone — Propane

Aldehyde (or) ketones is first converted to its hydrazone which on heating with strong base gives hydrocarbons.

(iii) Reduction to pinacols: Ketones, on reduction with magnesium amalgam and water, are reduced to symmetrical diols known as pinacol.

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O + O=\underset{\underset{CH_3}{|}}{C}-CH_3 + 2(H) \xrightarrow[H_2O]{Mg-Hg} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Acetone — Acetone — 2,3 dimethyl butane 2,3 - diol (pinacol)

D) Haloform reaction

Acetaldehyde and methyl ketones, containing $CH_3-\underset{\underset{O}{\|}}{C}-$ group, when treated with halogen and alkali give the corresponding haloform. This is known as Haloform reaction.

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{3Cl_2} CCl_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} CHCl_3 + CH_3-\underset{\underset{O}{\|}}{C}-ONa$$

E) Reaction involving alkylgroup

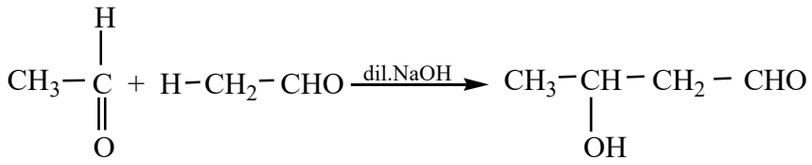
i) Aldol condensation

The carbon attached to carbonyl carbon is called α - **carbon** and the hydrogen atom attached to α - carbon is called α - hydrogen.

In presence of dilute base NaOH, or KOH, two molecules of an aldehyde or ketone having α - hydrogen add together to give β- hydroxyl aldehyde (aldol) or β - hydroxyl ketone (ketol). The reaction is called **aldol condensation reaction**. The aldol or ketol readily loses water to give α,β – unsaturated compounds which are aldol condensation products.

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a) Acetaldehyde when warmed with dil NaOH gives β - hydroxyl butyraldehyde (acetaldol)



Acetaldehyde

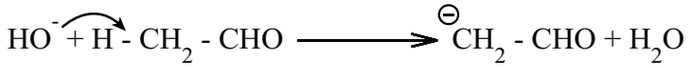
Acetaldol
(3 - Hydroxy butanal)

Mechanism

The mechanism of aldol condensation of acetaldehyde takes place in three steps.

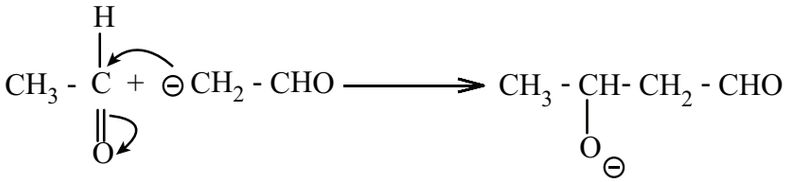
Step 1 :

The carbanion is formed as the α - **hydrogen atom** is removed as a proton by the base.



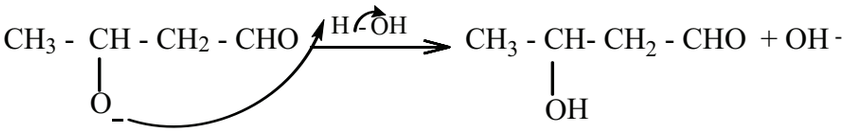
Step 2 :

The carbanion attacks the carbonyl carbon of another unionized aldehyde to form an alkoxide ion.



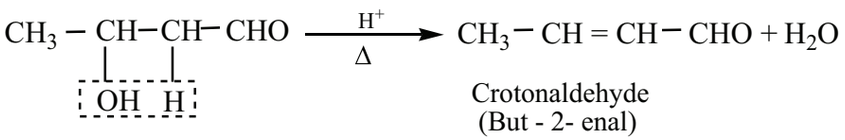
Step 3 :

The alkoxide ion formed is protonated by water to form aldol.



3-Hydroxy butanal

The aldol rapidly undergoes dehydration on heating with acid to form α - β unsaturated aldehyde.



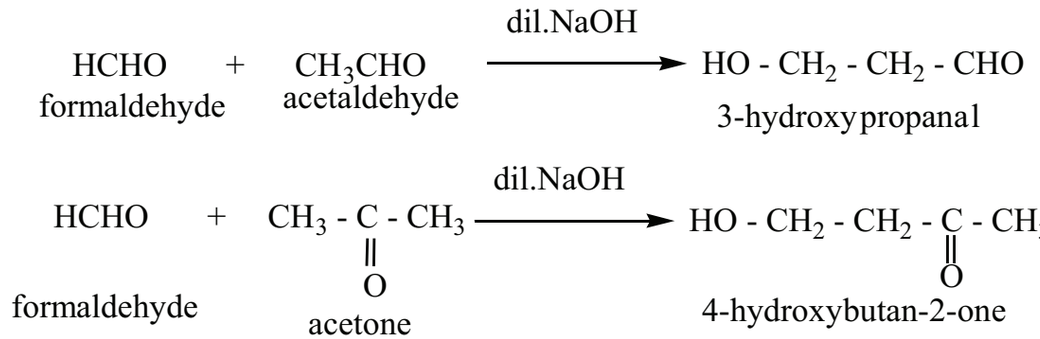
Crotonaldehyde
(But - 2- enal)

ii) Crossed aldol condensation

Aldol condensation can also take place between two different aldehydes or ketones or between one aldehyde and one ketone such an aldol condensation is called **crossed or mixed aldol condensation.** This reaction is not very useful as the product is usually a mixture of all possible condensation products and cannot be separated easily.

XII U12-Carbonyl Compounds.indd 162 08-12-2021 22:50:40

Example :

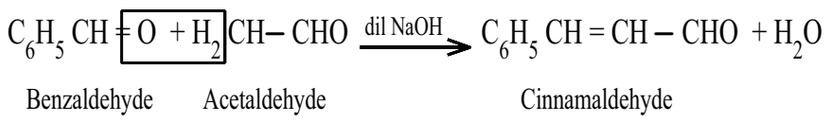


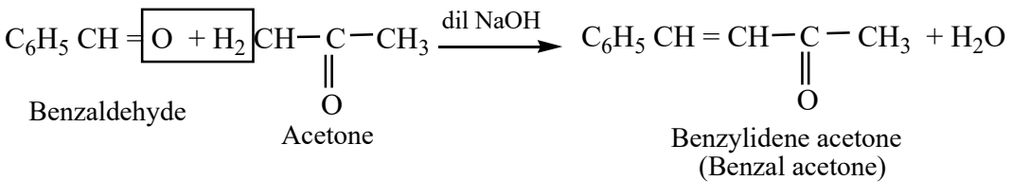
F) Some important reactions of benzaldehyde

i) Claisen – Schmidt Condensation

Benzaldehye condenses with aliphatic aldehyde or methyl ketone in the presence of dil. alkali at room temperature to form unsaturated aldehyde or ketone. This type of reaction is called Claisen – Schmidt condensation.

Example

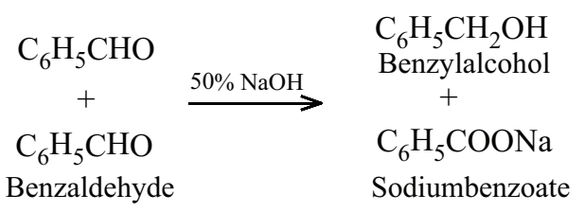




ii) Cannizaro reaction

In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have α - hydrogen atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid. This reaction is called **Cannizaro reaction**.

Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.



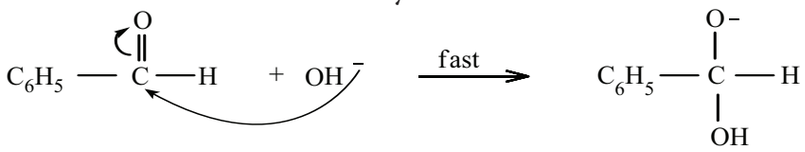
This reaction is an example disproportionation reaction

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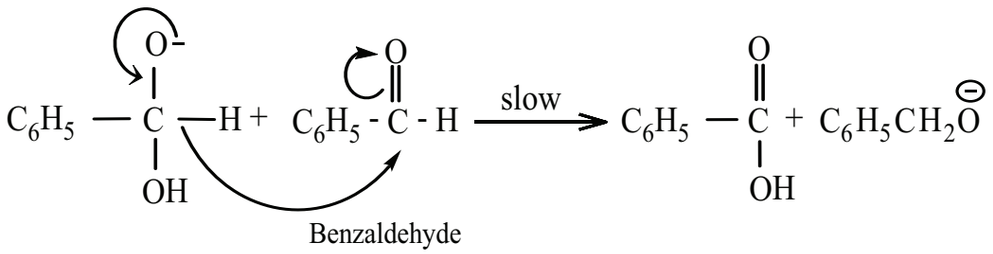
Mechanism of Cannizaro reaction

Cannizaro reaction involves three steps.

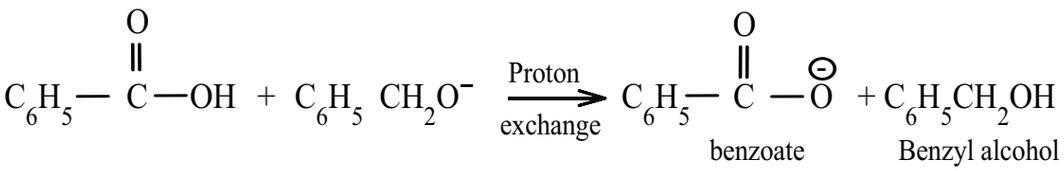
Step 1 : Attack of OH^- on the carbonyl carbon.



Step 2 : Hydride ion transfer



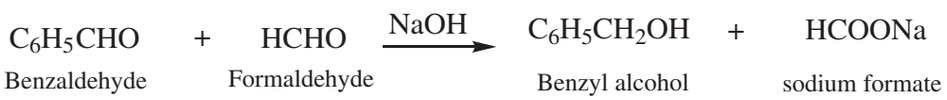
Step 3 : Acid – base reaction.



Cannizaro reaction is a characteristic reaction of aldehyde having no α – hydrogen.

Crossed Cannizaro reaction

When Cannizaro reaction takes place between two different aldehydes (neither containing an α hydrogen atom), the reaction is called as crossed cannizaro reaction.



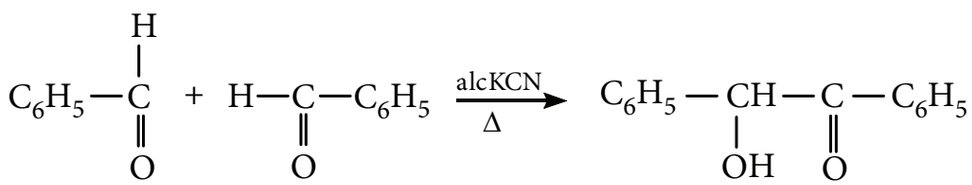
In crossed cannizaro reaction more reactive aldehyde is oxidized and less reactive aldehyde is reduced.

3) Benzoin condensation

The Benzoin condensation involves the treatment of an aromatic aldehyde with aqueous alcoholic KCN. The products are **α** hydroxy ketone.

Example

Benzaldehyde reacts with alcoholic KCN to form benzoin



Benzaldehyde

Benzoin

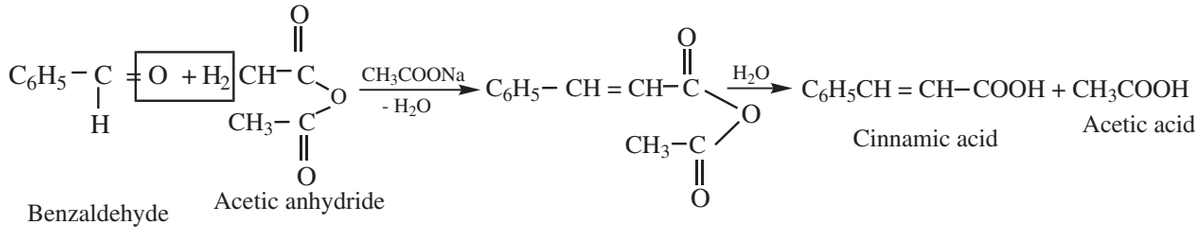
2-hydroxy – 1, 2 – diphenyl ethanone

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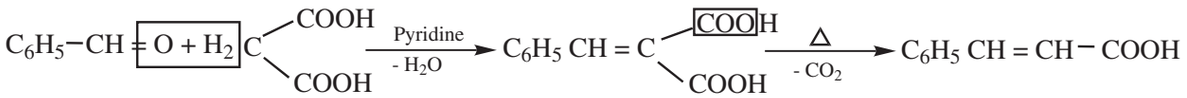
4) Perkins' reaction

When an aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the acid corresponding to the anhydride, condensation takes place and an α, β unsaturated acid is obtained. This reaction is known as **Perkin's reaction**.

Example:



5) Knoevenagal reaction

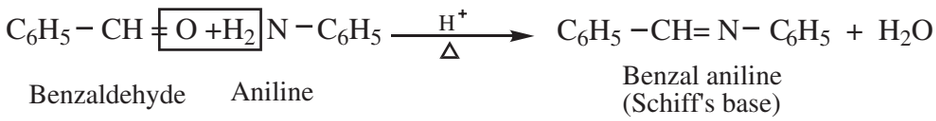


Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, Pyridine act as the basic catalyst.

6) Reaction with amine

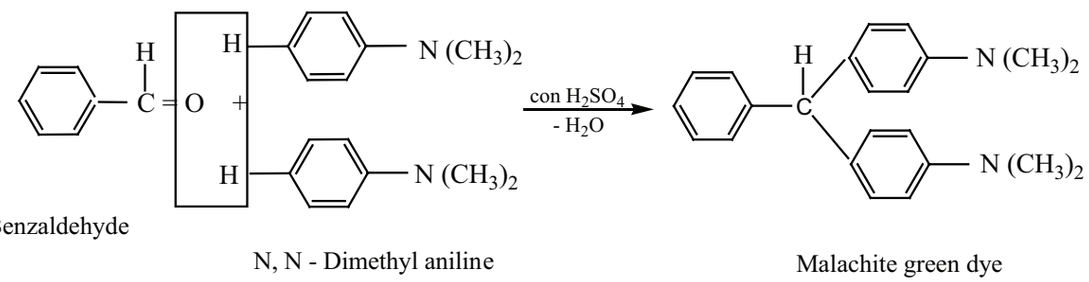
Aromatic aldehydes react with primary amines (aliphatic or aromatic) in the presence of an acid to form **schiff's base**.

Example



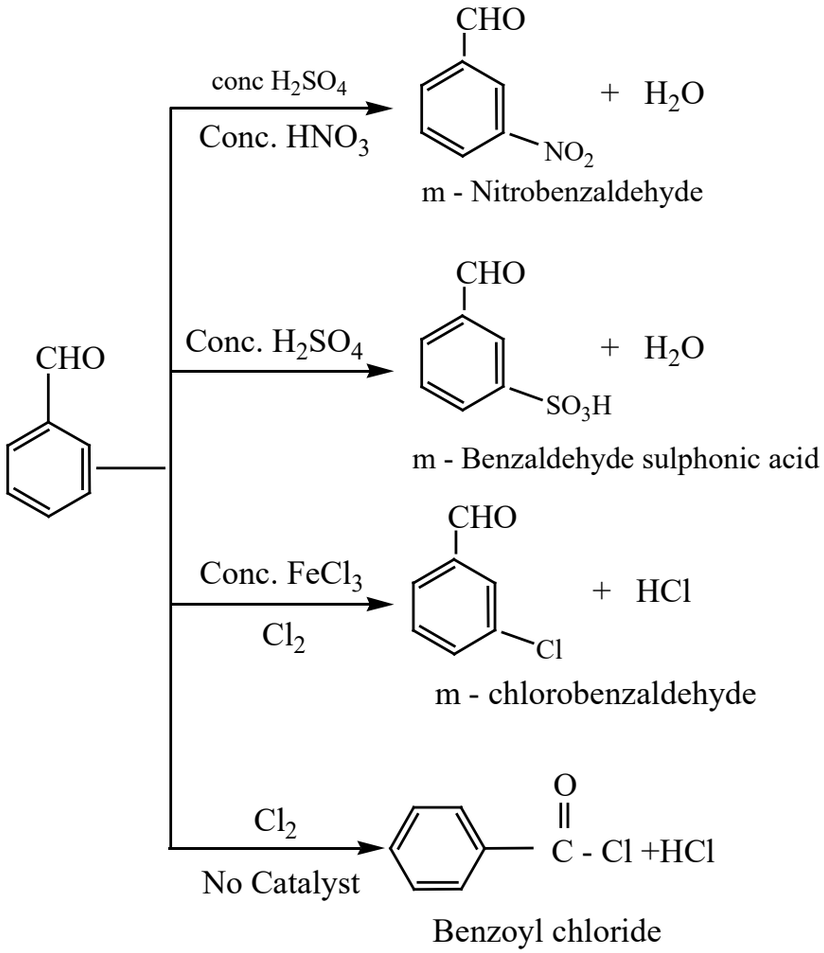
7) Condensation with tertiary aromatic amines

Benzaldehyde condenses with tertiary aromatic amines like N, N – dimethyl aniline in the presence of strong acids to form triphenyl methane dye.



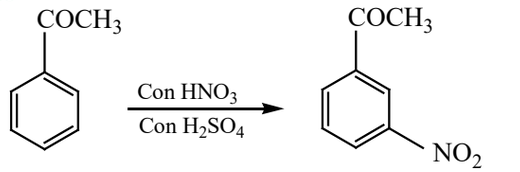
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8) Electrophilic substitution reactions of benzaldehyde



Electrophilic substitution reaction of acetophenone

Acetophenone reacts with Nitrating mixture to form m – nitroacetophenone.



12.6 Test for Aldehydes

i) Tollens Reagent Test

Tollens reagent is an ammonical silver nitrate solution. When an aldehyde is warmed with Tollens reagent a bright silver mirror is produced due to the formation of silver metal. This reaction is also called **silver mirror test** for aldehydes.

$$CH_3CHO + 2\,[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 4NH_3 + 2Ag + 2H_2O$$

Silver

ii) Fehling's solution Test

Fehling's solution is prepared by mixing equal volumes of Fehling's solution 'A' containing aqueous copper sulphate and Fehling's solution 'B' containing alkaline solution of sodium potassium tartarate (Rochelle salt)

When aldehyde is warmed with Fehling's solution deep blue colour solution is changed to red precipitate of cuprous oxide.

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$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + Cu_2O\downarrow + 3H_2O$$

(blue) (red)

iii) Benedict's solution Test:

Benedicts solution is a mixture of $CuSO_4$ + sodium citrate + NaOH. Cu^{2+} is reduced by aldehyde to give red precipitate of cuprous oxide.

$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + Cu_2O\downarrow + 3H_2O$$

(blue) (red)

iv) Schiffs' reagent Test

Dilute solution of aldehydes when added to schiffs' reagent (Rosaniline hydrochloride dissolved in water and its red colour decolourised by passing SO_2) yields its red colour. This is known as **Schiffs' test** for aldehydes . Ketones do not give this test. Acetone however gives a positive test but slowly.

12.7 Uses of Aldehydes and Ketones

Formaldehyde

(i) 40% aqueous solution of formaldehyde is called **formalin**. It is used for preserving biological specimens.

(ii) Formalin has hardening effect, hence it is used for tanning.

(iii) Formalin is used in the production of thermo setting plastic known as bakelite, which is obtained by heating phenol with formalin.

Acetaldehye

(i) Acetaldehyde is used for silvering of mirrors

(ii) Paraldehyde is used in medicine as a hypnotic.

(iii) Acetaldehyde is used in the commercial preparation of number of organic compounds like acetic acid, ethyl acetate etc.,

Acetone

(i) Acetone is used as a solvent, in the manufacture of smokeless gun powder (cordite)

(ii) It is used as a nail polish remover.

(iii) It is used in the preparation of sulphonal, a hypnotic.

(iv) It is used in the manufacture of thermosoftening plastic **Perspex.**

Benzaldehyde is used

(i) as a flavoring agent (ii) in perfumes (iii) in dye intermediates

(iv) as starting material for the synthesis of several other organic compounds like cinnamaldehyde, cinnamic acid, benzoyl chloride etc.

Aromatic Ketones

(i) Acetophenone has been used in perfumery and as a hypnotic under the name **hypnone.**

(ii) Benzophenone is used in perfumery and in the preparation of **benzhydrol eye drop.**

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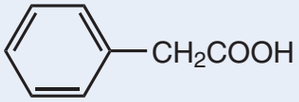
CARBOXYLIC ACIDS

Introduction

Carbon compounds containing a carboxyl function group, -COOH are called carboxylic acids. The Carboxyl group is the combination of carbonyl group $-\overset{\overset{O}{\|}}{C}-$ and the hydroxyl group (-OH).

However, carboxyl group has its own characteristic reaction. Carboxylic acids may be aliphatic (R – COOH) or aromatic (Ar – COOH) depending on the alkyl or aryl group attached to carboxylic carbon. Some higher members of aliphatic carboxylic acids (C_{12} to C_{18}) known as fatty acids occur in natural fats as esters of glycerol.

12.8 IUPAC nomenclature of Carboxylic acids

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Formic acid HCOOH methanoicacid	–	meth	ane	oicacid
Acetic acid CH_3COOH Ethanoic acid	–	eth	ane	oicacid
Isobutyric acid $(CH_3)_2CHCOOH$ 2 – methylpropanoic acid	2 – methyl	prop	ane	oicacid
Phenyl acetic acid  2-phenyl ethanoic acid	2-phenyl	eth	ane	oicacid
Oxalic acid HOOC - COOH ethane–1, 2 – dioicacid	–	eth	ane	1, 2 – dioicacid

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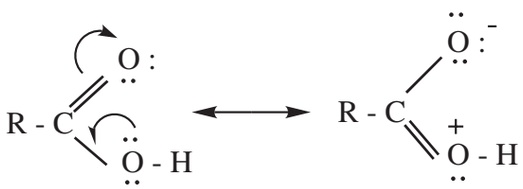
Malonic acid $HOOC-CH_2-COOH$ Propane-1,3-dioic acid	–	prop	ane	1, 3 – dioicacid
Succinic acid $HOOC-(CH_2)_2-COOH$ Butane-1,4-dioic acid	–	but	ane	1, 4 – dioicacid
Glutaric acid $HOOC-(CH_2)_3-COOH$ Pentane-1,5-dioic acid	–	pent	ane	1,5 – dioicacid
Adipic acid $HOOC-(CH_2)_4-COOH$ Hexane-1,6-dioic acid	–	hex	ane	1,6 – dioicacid

12.9 Structure of carboxyl group:

The carboxyl group represent a planar arrangement of atoms. In – COOH group, the centre carbon atom and both the oxygen atoms are in sp^2 hybridisation. The three sp^2 hybrid orbitals of the carbon atom overlap.

The two sp^2 – hybridised orbitals of the carboxyl carbon overlap with one sp^2 hybridised orbital of each oxygen atom while the third sp^2 hybridised orbital of carbon overlaps with either a s -orbital of H – atom or a sp^3 – hybridised orbital of C –atom of the alkyl group to form three σ- bonds. Each of the two oxygen atoms and the carbon atom are left with one unhybridised p – orbital which is perpendicular to the σ- bonding skeleton.

All these three p – orbitals being parallel overlap to form a π- bond which is partly delocalized between carbon and oxygen atom on one side, and carbon and oxygen of the OH group on the other side. In other words, RCOOH may be represented as a resonance hybrid of the following two canonical structures.



The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure. i.e., delocalisation of lone pair electrons from the oxygen in hydroxyl group.

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12.10 Methods of Preparation of carboxylic acids

Some important methods for the preparation of carboxylic acids are as follows :

1. From Primary alcohols and aldehydes

Primary alcohols and aldehydes can easily be oxidised to the corresponding carboxylic acids with oxidising agents such as potassium permanganate (in acidic or alkaline medium), potassium dichromate (in acidic medium)

Example

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[(O)]{H^+/\ K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{(O)} \underset{\text{Acetic acid}}{CH_3COOH}$$

2. Hydrolysis of Nitriles

Nitriles yield carboxylic acids when subjected to hydrolysis with an acid or alkali.

Example

$$\underset{\text{Methyl cyanide}}{CH_3 - C \equiv N} + 2H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

3. Acidic hydrolysis of esters

Esters on hydrolysis with dilute mineral acids yield corresponding carboxylic acid

Example

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

4. From Grignard reagent

Grignard reagent reacts with carbon di oxide (dry ice) to form salts of carboxylic acid which in turn give corresponding carboxylic acid after acidification with mineral acid.

Example

$$\overset{\overset{O}{\|}}{C}= O + \underset{\substack{\text{Methyl Magnesium}\\ \text{bromide}}}{CH_3MgBr} \xrightarrow[\text{ether}]{\text{dry}} CH_3-\overset{\overset{O}{\|}}{C}-OMgBr \xrightarrow[H^+]{H_2O} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + Mg\begin{matrix}OH\\ \\ Br\end{matrix}$$

$$\overset{\overset{O}{\|}}{C}= O + \underset{\substack{\text{Phenyl Magnesium}\\ \text{Bromide}}}{\text{C}_6\text{H}_5\text{MgBr}} \xrightarrow[\text{ether}]{\text{dry}} \text{C}_6\text{H}_5-\overset{\overset{O}{\|}}{C}-OMgBr \xrightarrow[H_2O]{H^+} \underset{\text{Benzoic acid}}{\text{C}_6\text{H}_5-\overset{\overset{O}{\|}}{C}-OH} + Mg\begin{matrix}OH\\ \\ X\end{matrix}$$

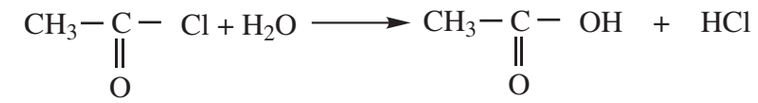
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Formic acid cannot be prepared by Grignard reagent since the acid contains only one carbon atom

5. Hydrolysis of acylhalides and anhydrides

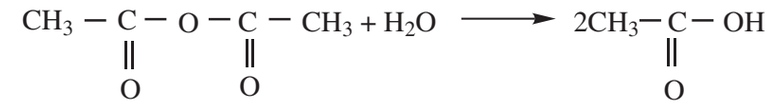
a) Acid chlorides when hydrolysed with water give Carboxylic acids.

Example

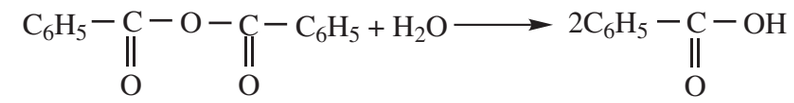


Acetyl chloride — Acetic acid

b) Acid anhydride when hydrolysed with water give corresponding carboxylic acids.



Acetic anhydride — Acetic Acid

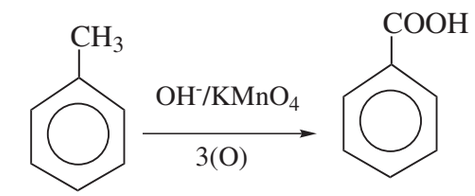


Benzoic anhydride — Benzoic acid

6. Oxidation of alkyl benzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzene with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidised to –COOH group irrespective of the length of the side chain.

Example



Toluene — Benzoic acid

Evaluate yourself

1) What happens when n-propyl benzene is oxidised using H^+ / $KMnO_4$?

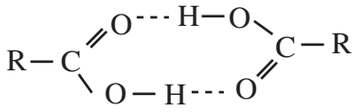
2) How will you prepare benzoic acid using Grignard reagent.

12.11 Physical Properties of carboxylic acids.

i) Aliphatic carboxylic acid upto nine carbon atoms are colour less liquids with pungent odour. The higher members are odourless wax like solids.

ii) Carboxylic acids have higher boiling point than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more association of carboxylic acid molecules through intermolecular hydrogen bonding.

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Inter molecular hydrogen bonding

In fact, most of the carboxylic acids exist as dimer in its vapour phase.

iii) Lower aliphatic carboxylic acids (up to four carbon) are miscible with water due to the formation of hydrogen bonds with water. Higher carboxylic acid are insoluble in water due to increased hydrophobic interaction of hydrocarbon part. The simplest aromatic carboxylic acid, benzoic acid is insoluble in water.

iv) Vinegar is 6 to 8% solution of acetic acid in water. Pure acetic acid is called **glacial acetic acid.** Because it forms ice like crystal when cooled. When aqueous acetic acid is cooled at 289.5 K, acetic acid solidifies and forms ice like crystals, where as water remains in liquid state and removed by filtration. This process is repeated to obtain glacial acetic acid.

12.12 Chemical properties of carboxylic acids.

Carboxylic acid do not give the characteristic reaction of carbonyl group $\diagdown C = O$ as given by the aldehydes and ketones. as the carbonyl group of carboxylic acid is involved in resonance:

The reactions of carboxylic acids can be classified as follows:

A) Reactions involving cleavage of O – H bond.

B) Reactions involving cleavage of C – OH bond.

C) Reactions involving – COOH group.

D) Substitution reactions involving hydrocarbon part.

A) Reactions involving cleavage of O – H bond.

1) Reactions with metals

Carboxylic acid react with active metals like Na, Mg, Zn etc to form corresponding salts with the liberation of hydrogen.

Example



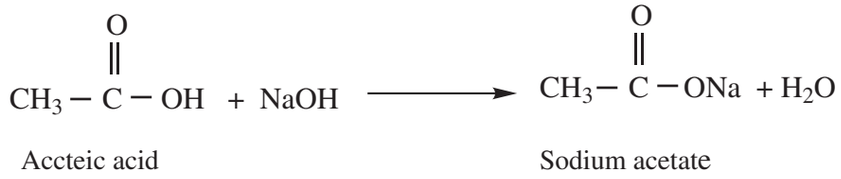
Acetic acid — Sodium acetate

2) Reaction with alkalies

Carboxylic acid reacts with alkalies to neutralise them and form salts.

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Example

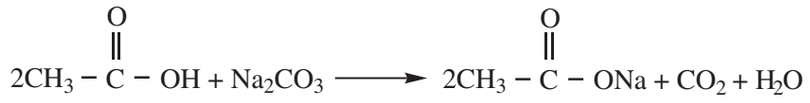


Accteic acid — Sodium acetate

3) Reaction with carbonates and bicarbonates (Test for carboxylic acid group)

Carboxylic acids decompose carbonates and bicarbonates evolving carbondioxide gas with effervescence.

Example



Acetic acid — Sodium acetate

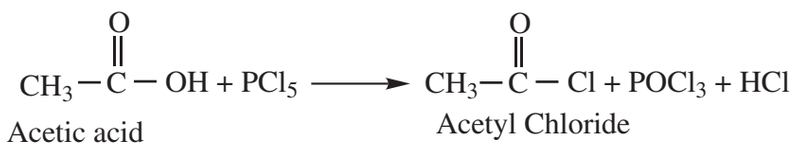
4) All Carboxylic acids turn blue litmus red

B) Reactions involving cleavage of C-OH bond

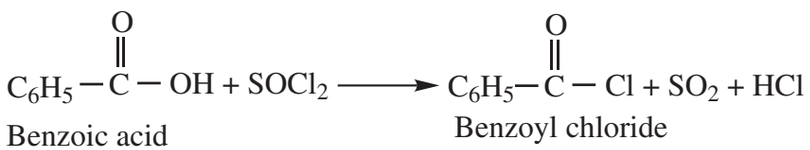
1) Reactions with PCl_5, PCl_3 and $SOCl_2$

The hydroxyl group of carboxylic acids behaves like that of an alcoholic group and is easily replaced by chlorine atom on treating with PCl_5, PCl_3 or $SOCl_2$.

Example



Acetic acid — Acetyl Chloride

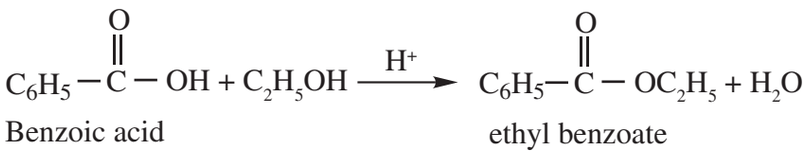


Benzoic acid — Benzoyl chloride

2) Reactions with alcohols (Esterification)

When carboxylic acids are heated with alcohols in the presence of conc. H_2SO_4 or dry HCl gas, esters are formed. The reaction is reversible and is called esterification.

Example

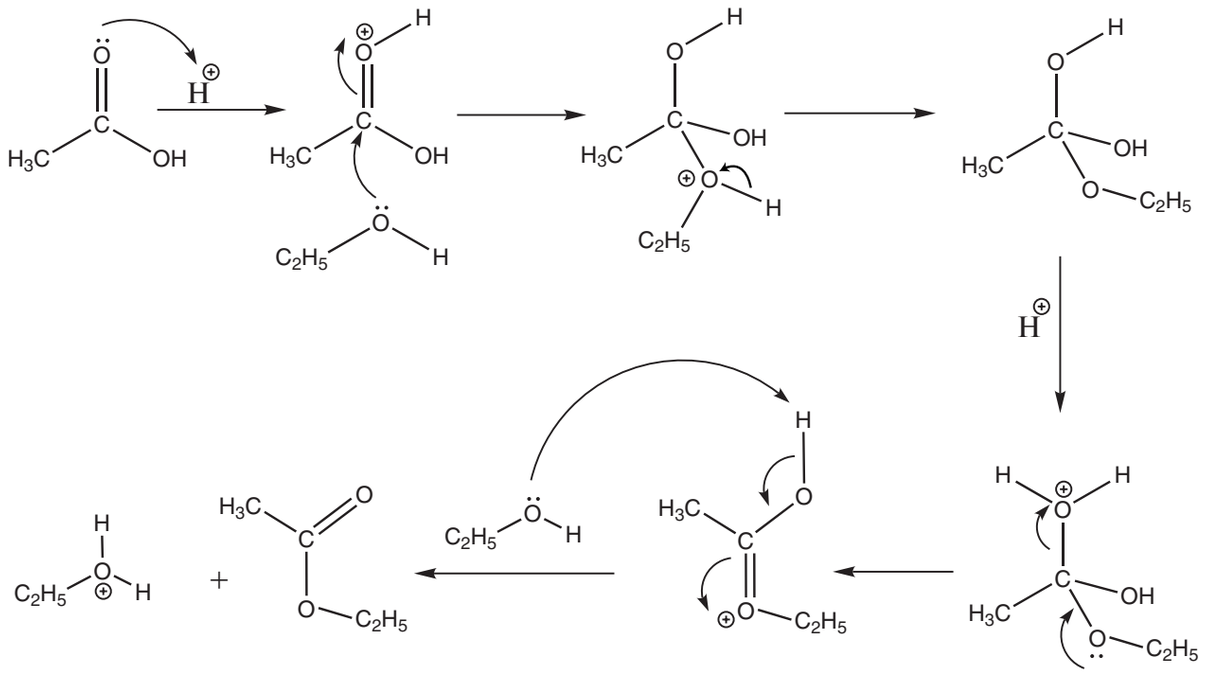


Benzoic acid — ethyl benzoate

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Mechanism of esterification:

The Mechanism of esterification involves the following steps.



C) Reactions involving – COOH group

1) Reduction

i) Partial reduction to alcohols

Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or with hydrogen in the presence of copper chromite as catalyst. Sodium borohydride does not reduce the – COOH group.

Example

$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[4(H)]{LiAlH_4} CH_3CH_2OH + H_2O$$

ethanoicacid — ethanol

ii) Complete reduction to alkanes

When treated with HI and red phosphorous, carboxylic acid undergoes complete reduction to yield alkanes containing the same number of carbon atoms.

Example

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + 6\,HI \xrightarrow[473\ K]{Red\ P} CH_3-CH_3 + 3I_2 + 2H_2O$$

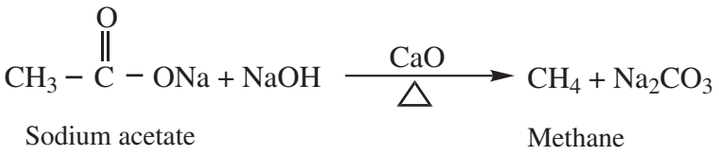
Acetic acid — Ethane

XII U12-Carbonyl Compounds.indd 174 08-12-2021 22:50:44

2) Decarboxylation

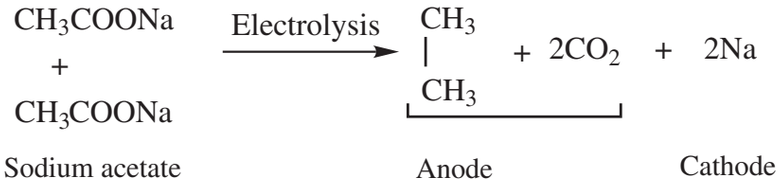
Removal of CO_2 from carboxyl group is called as **decarboxylation.** Carboxylic acids lose carbon di oxide to form hydrocarbon when their sodium salts are heated with soda lime (NaOH and CaO in the ratio 3: 1)

Example



3) Kolbe's electrolytic decarboxylation

The aqueous solutions of sodium or potassium salts of carboxylic acid on electrolysis gives alkanes at anode. This reaction is called kolbes electrolysis.

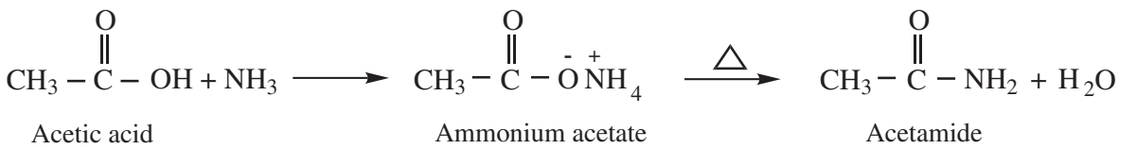


Sodium formate solution on electrolysis gives hydrogen

4) Reactions with ammonia

Carboxylic acids react with ammonia to form ammonium salt which on further heating at high temperature gives amides.

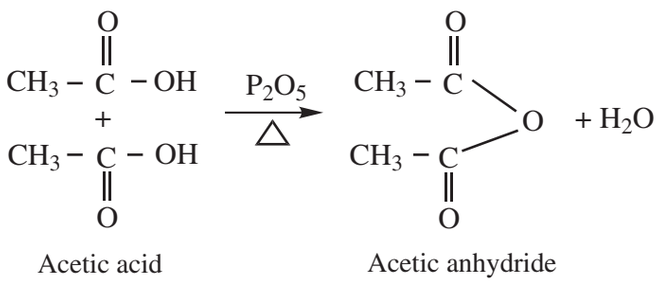
Example



5) Action of heat in the presence of P_2O_5

Carboxylic acid on heating in the presence of a strong dehydrating agent such as P_2O_5 forms acid anhydride.

Example

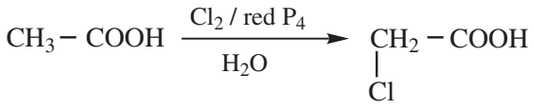


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D) Substitution reactions in the hydrocarbon part

1) α - Halogenation

Carboxylic acids having an α - hydrogen are halogenated at the α - position on treatment with chlorine or bromine in the presence of small amount of red posphorus to form α halo carboxylic acids. This reaction is known as **Hell – Volhard – Zelinsky reaction** (HVZ reaction) The α - Halogenated acids are convenient starting materials for preparing α - substituted acids.

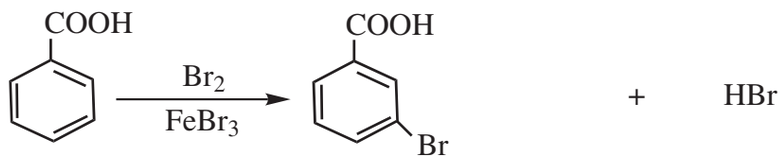


Acetic acid — Mono Chloro acetic acid

2) Electrophilic substitution in aromatic carboxylic acids

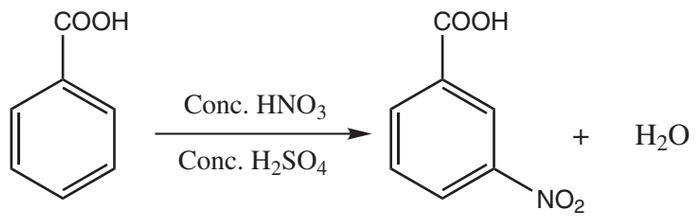
Aromatic carboxylic acid undergoes electrophilic substitution reactions. The carboxyl group is a deactivating and meta directing group. Some common electrophilic substitution reactions of benzoic acid are given below

i) Halogenation



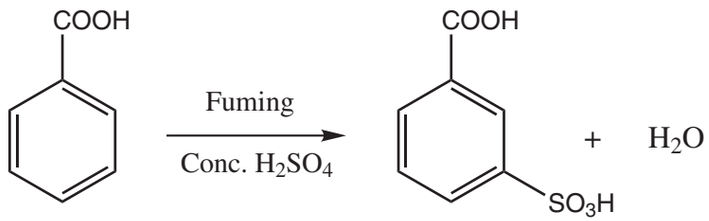
Benzoic acid — m - bromo benzoic acid

ii) Nitration



Benzoic acid — m-Nitrobenzoic acid

iii) Sulphonation



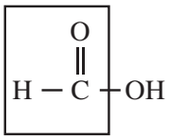
Benzoic acid — m-Sulphobenzoic acid

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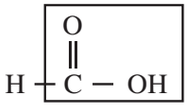
iv) Benzoic acid does not undergo friedal craft's reaction. This is due to the strong deactivating nature of the carboxyl group.

E) Reducing action of Formic acid

Formic acid contains both an aldehyde as well as an acid group. Hence, like other aldehydes, formic acid can easily be oxidised and therefore acts as a strong reducing agent



Aldehyde group



Carboxylic acid group

i) Formic acid reduces Tollens reagent (ammonical silver nitrate solution) to metallic silver.

$$HCOO^- + 2Ag^+ + 3OH^- \longrightarrow 2\,Ag + CO_3^{2-} + 2H_2O$$

(Tollens reagent) — Silver mirror

ii) Formic acid reduces Fehling's solution. It reduces blue coloured cupric ions to red coloured cuprous ions.

$$HCOO^- + 2Cu^{2+} + 5\,OH^- \longrightarrow Cu_2O + CO_3^{2-} + 3\,H_2O$$

(Fehlings solution) — red precipitate

Tests for carboxylic acid group

i) In aqueous solution carboxylic acid turn blue litmus red.

ii) Carboxylic acids give brisk effervescence with sodium bicarbonate due to the evolution of carbon-di -oxide.

iii) When carboxylic acid is warmed with alcohol and Con H_2SO_4 it forms an ester, which is detected by its fruity odour.

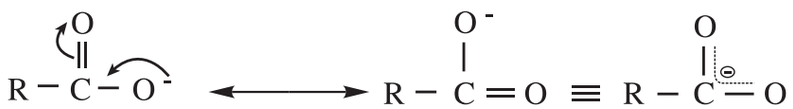
12.13 Acidity of Carboxylic acids

Carboxylic acids undergo ionisation to produce H^+ and carboxylate ions in aqueous solution. The carboxylate anion is stabilised by resonance which make the Carboxylic acid to donate the proton easily.



Carboxylic acid — Carboxylate ion

The resonance structure of carboxylate ion are given below.



The strength of carboxylic acid can be expressed in terms of the dissociation constant(Ka):

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$$R-COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$Ka = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

The dissociation constant is generally called acidity constant because it measures the relative strength of an acid. The stronger the acid, the higher will be its Ka value.

The dissociation constant of an acid can also be expressed in terms of pKa value.

$$pKa = - \log Ka$$

A stronger acid will have higher Ka value but smaller pKa value.

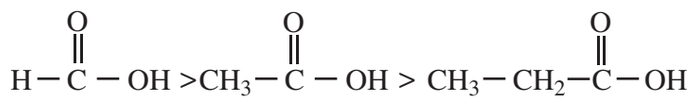
Ka and pKa values of some Carboxylic acids of 298 K

Carboxylic acid		pKa Value
Name of acid	Molecular formula	
Trichloroacetic acid	Cl_3CCOOH	0.64
Dichloroacetic acid	$Cl_2CHCOOH$	1.26
Fluoroacetic acid	FCH_2COOH	2.59
Chloroacetic acid	$ClCH_2COOH$	2.87
Bromoacetic acid	$BrCH_2COOH$	2.90
Iodoacetic acid	ICH_2COOH	3.17
Formic acid	$HCOOH$	3.75
Benzoic acid	C_6H_5COOH	4.20
Acetic acid	CH_3COOH	4.76
Propionic acid	CH_3CH_2COOH	4.88
o – nitrobenzoic acid	$o\text{-}NO_2C_6H_4COOH$	2.17
m-nitrobenzoic acid	$m\text{-}NO_2C_6H_4COOH$	3.49
p- nitrobenzoic acid	$p\text{-}NO_2C_6H_4COOH$	3.44

Effect of substituents on the acidity of carboxylic acid.

i) Electron releasing alkyl group decreases the acidity

The electron releasing groups (+I groups) increase the negative charge on the carboxylate ion and destabilise it and hence the loss of proton becomes difficult. For example, formic acid is more stronger than acetic acid.



Formic acid Acetic acid Propionic acid

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ii) Electron withdrawing substituents increases the acidity

The electron – withdrawing substituents decrease the negative charge on the carboxylate ion and stabilize it. In such cases, the loss of proton becomes relatively easy.

Acidity increases with increasing electronegativity of the substituents. For example, the acidity of various halo acetic acids follows the order

$$F-CH_2-COOH > Cl-CH_2-COOH > Br-CH_2-COOH > I-CH_2-COOH$$

Acidity increases with increasing number of electron – withdrawing substituents on the α - carbon. For example

$$Cl_3C-COOH > Cl_2CH-COOH > ClCH_2COOH > CH_3COOH$$

The effect of various, electron withdrawing groups on the acidity of a carboxylic acid follows the order,

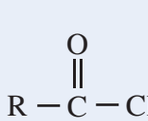
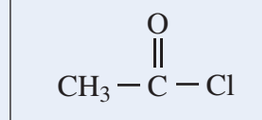
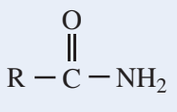
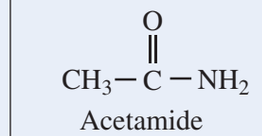
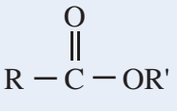
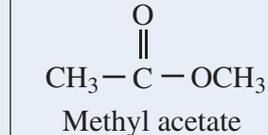
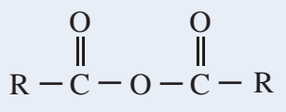
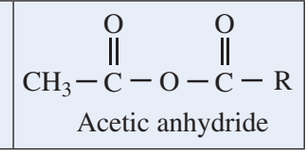
$$-NO_2 > -CN > -F > -Cl > -Br > -I > -Ph$$

The relative acidities of various organic compounds are

$$RCOOH > ArOH > H_2O > ROH > RC \equiv CH$$

12.14 Functional derivatives of carboxylic acids

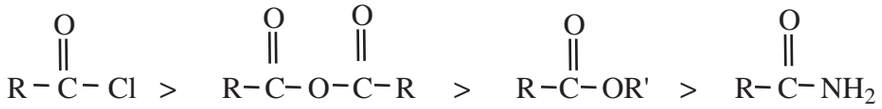
Compounds such as acid chlorides, amides, esters etc., are called carboxylic acid derivatives because they differ from a carboxylic acid only in the nature of the group or atom that has replaced the -OH group of carboxylic acid.

Group replacing - OH	Name	Structure	Example
–Cl	Acid chloride		 Acetyl chloride
$-NH_2$	Acid amide		 Acetamide
–OR'	ester		 Methyl acetate
–OOCR	Acid anhydride		 Acetic anhydride

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Relative reactivity of Acid derivatives

The reactivity of the acid derivatives follows the order



The above order of reactivity can be explained in terms of

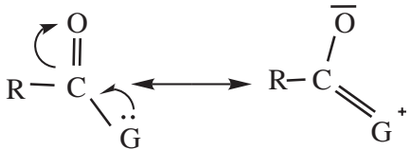
i) Basicity of the leaving group ii) Resonance effect

(i) Basicity of the leaving group

Weaker bases are good leaving groups. Hence acyl derivatives with weaker bases as leaving groups (L) can easily rupture the bond and are more reactive. The correct order of the basicity of the leaving group is $H_2\bar{N}$: > : $\bar{O}R$ > $RCO\bar{O}$: > : $\bar{Cl}$ Hence the reverse is the order of reactivity.

(ii) Resonance effect

Lesser the electronegativity of the group, greater would be the resonance stabilization as shown below.

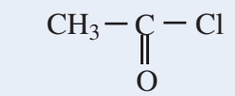
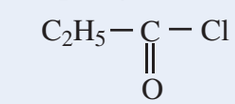
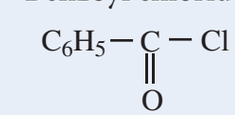


This effect makes the molecule more stable and reduces the reactivity of the acyl compound. The order of electronegativity of the leaving groups follows the order – Cl > - OCOR > - OR > - NH_2

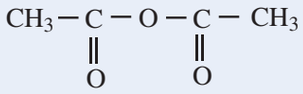
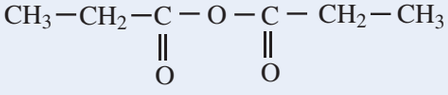
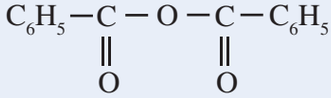
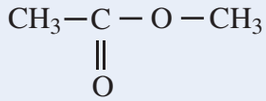
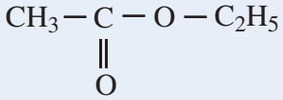
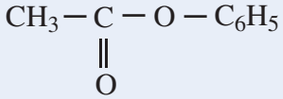
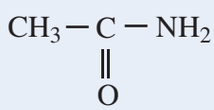
Hence the order of reactivity of the acid derivatives with nucleophilic reagent follows the order

acid halide > acid anhydride > esters > acid amides

12.14.1 Nomenclature

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Acetyl chloride  Ethanoylchloride	–	eth	ane	oyl chloride
Propionyl chloride  Propanoylchloride	–	prop	ane	oyl chloride
Benzoyl chloride  Benzoylchloride	–	Benz	ane	oyl chloride

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Acetic anhydride  Ethanoic anhydride	–	eth	ane	oic anhydride
Propionic anhydride  Propanoic anhydride	–	prop	ane	oic anhydride
Benzoic anhydride  Benzoic anhydride	–	Benz		oic anhydride
Esters				
Methyl acetate  Methyl ethanoate	Methyl	eth	ane	oate
Ethyl acetate  Ethyl ethanoate	Ethyl	eth	ane	oate
Phenyl acetate  Phenyl ethanoate	Phenyl	eth	ane	oate
Acid Amides				
Acetamide  Ethanamide	–	eth	ane	amide

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Propionamide $C_2H_5-\underset{\underset{O}{\|}}{C}-NH_2$ Propanamide	–	prop	ane	amide
Benzamide $C_6H_5-\underset{\underset{O}{\|}}{C}-NH_2$ Benzamide	–	benz	_	amide

12. 14. 2. Acid Halides:

Methods of Preparation of acid chloride:

Acid chlorides are prepared from carboxylic acid by treating it with anyone of the chlorinating agent such as $SOCl_2$, PCl_5, or PCl_3

1) By reaction with thionyl Chloride ($SOCl_2$)

$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + HCl + SO_2$$

This method is superior to others as the by products being gases escape leaving the acid chloride in the pure state.

Physical properties:

- They emit pale fumes of hydrogen chloride when exposed to air on account of their reaction with water vapour.
- They are insoluble in water but slowly begins to dissolve due to hydrolysis.

Chemical properties:

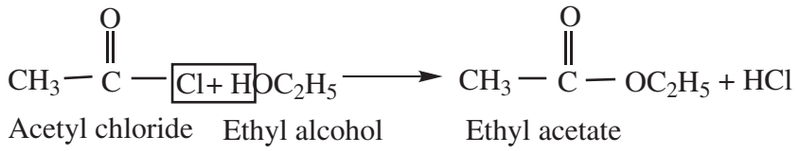
They react with weak nucleophiles such as water, alcohols, ammonia and amines to produce the corresponding acid, ester, amide or substituted amides.

1) Hydrolysis. Acyl halides undergo hydrolysis to form corresponding carboxylic acids

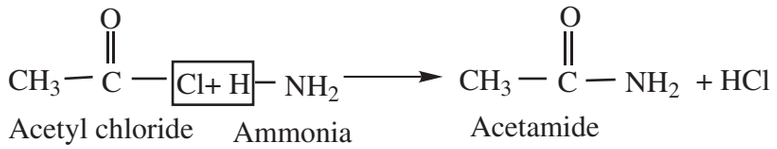
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl + HOH}} \longrightarrow \underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + HCl$$

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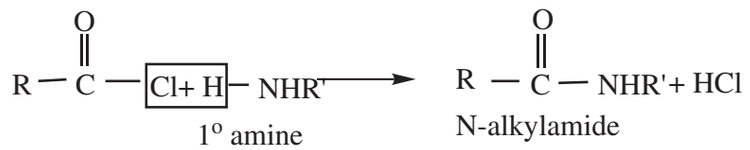
2) Reaction with Alcohols (*Alcoholysis*) gives esters.

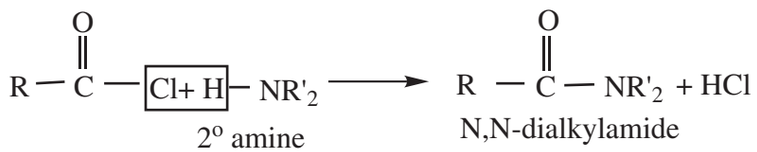


3) Reaction with Ammonia (*Ammonolysis*) gives acid amides.



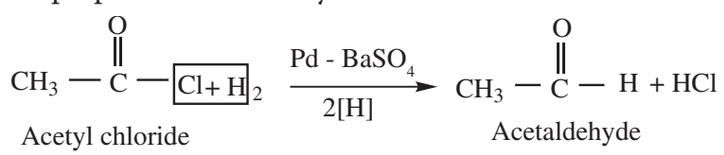
4) Reaction with 1° and 2° Amines gives N-alkyl amides.



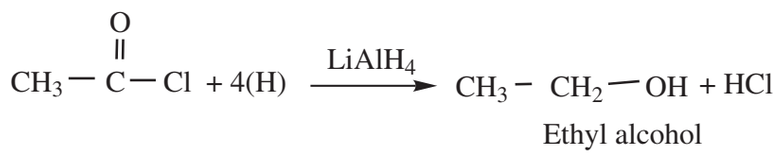


(5) Reduction.

(a) When reduced with hydrogen in the presence of 'poisoned' palladium catalyst, they form aldehydes. This reaction is called Rosenmund reduction. We have already learnt this reaction under the preparation of aldehydes



(b) When reduced with $LiAlH_4$ gives primary alcohols.



12.14.3 Acid anhydride

Methods of preparation

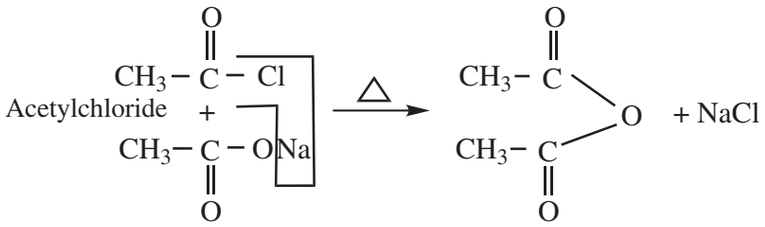
1. Heating carboxylic acid with P_2O_5

We have already learnt that when carboxylic acids are heated with P_2O_5 dehydration takes place to form acid anhydride.

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2. By reaction of acid halide with a salt of carboxylic acids.

Acid chlorides on heating with sodium salt of carboxylic acids gives corresponding anhydride.

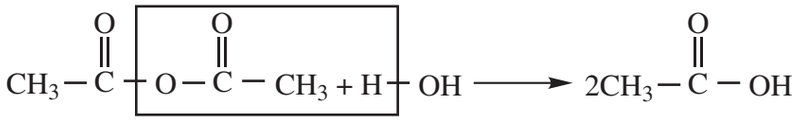


Sodium acetate Acetic anhydride

Chemical properties

1. Hydrolysis

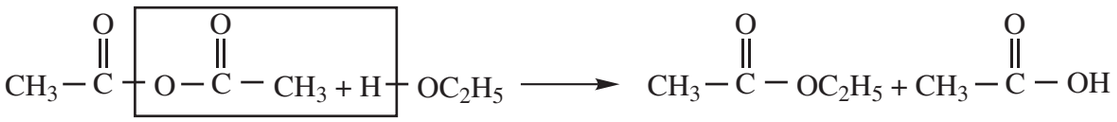
Acid anhydride are slowly hydrolysed, by water to form corresponding carboxylic acids.



Acetic anhydride Acetic acid

2. Reaction with alcohol

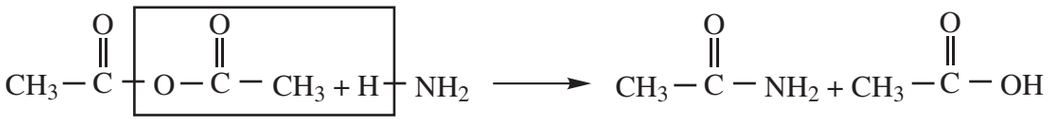
Acid anhydride reacts with alcohols to form esters.



Acetic anhydride Ethylalcohol Ethyl acetate Acetic acid

3. Reaction with ammonia

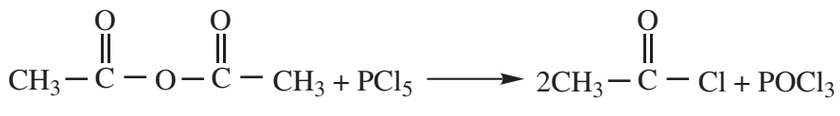
Acid anhydride reacts with ammonia to form amides.



Acetic anhydride Ammonia Acetamide Acetic acid

4. Reaction with PCl_5

Acid anhydride reacts with PCl_5 to form acyl chlorides.



Acetic anhydride Acetyl chloride

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12.14.4 Esters

Methods of preparation

1. Esterification

We have already learnt that treatment of alcohols with carboxylic acids in presence of mineral acid gives esters. The reaction is carried to completion by using an excess of reactant or by removing the water from the reaction mixture.

2. Alcoholysis of Acid chloride or Acid anhydrides

ii) Treatment of acid chloride or acid anhydride with alcohol also gives esters

Physical Properties

Esters are colour less liquids or solids with characteristic fruity smell. Flavours of some of the esters are given below.

S.No	Ester	Flavour
1	Amyl acetate	Banana
2	Ethyl butyrate	Pineapple
3	Octyl acetate	Orange
4	Isobutyl formate	Raspberry
5	Amyl butyrate	Apricot

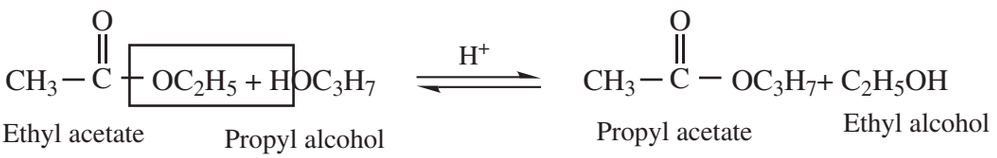
Chemical Properties

1. Hydrolysis

We have already learnt that hydrolysis of esters gives alcohol and carboxylic acid.

2. Reaction with alcohol (Transesterification)

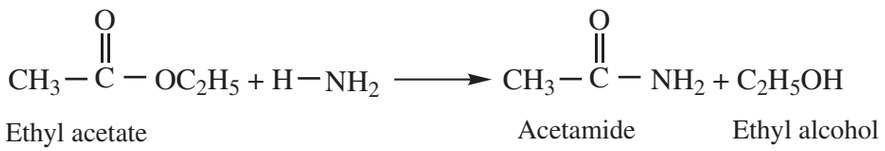
Esters of an alcohol can react with another alcohol in the presence of a mineral acid to give the ester of second alcohol. The interchange of alcohol portions of the esters is termed **transesterification**



The reaction is generally used for the preparation of the esters of a higher alcohol from that of a lower alcohol.

3. Reaction with ammonia (Ammonolysis)

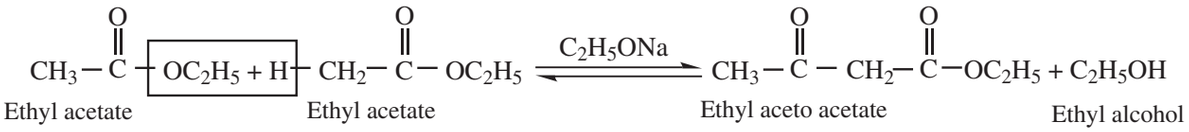
Esters react slowly with ammonia to form amides and alcohol.



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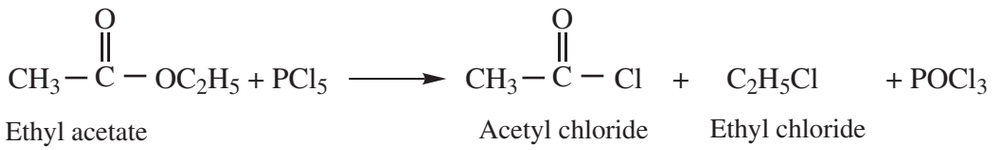
4. Claisen Condensation

Esters containing at least one ∝- hydrogen atom undergo self condensation in the presence of a strong base such as sodium ethoxide to form **β- keto ester.**



5. Reaction with PCl_5

Esters react with PCl_5 to give a mixture of acyl and alkyl chloride

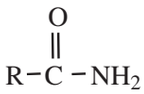


Evaluate yourself

Why is acid anhydride preferred to acyl chloride for carrying out acylation reactions ?

12.14.5 Acid Amides

Acid amides are derivatives of carboxylic acid in which the – OH part of carboxyl group has been replaced by – NH_2 group. The general formula of amides are given as follows.

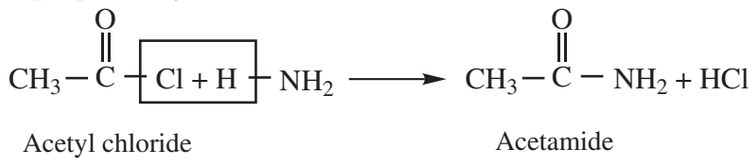


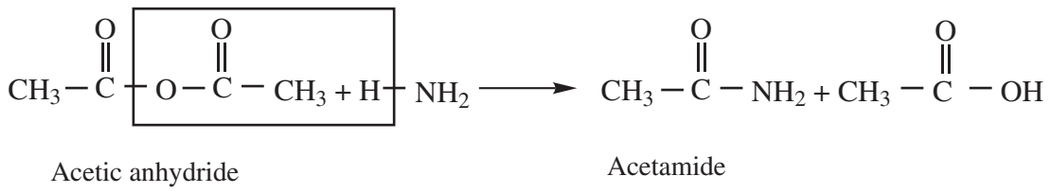
Now, we shall focus our attention mainly on the study of chemistry of acetamide.

Methods of Preparation

1. Ammonolysis of acid derivatives

Acid amides are prepared by the action of ammonia with acid chlorides or acid anhydrides.





2) Heating ammonium carboxylates

Ammonium salts of carboxylic acids (ammonium carboxylates) on heating, lose a molecule of water to form amides.



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3) Partial hydrolysis of alkyl cyanides (Nitriles)

Partial hydrolysis of alkyl cyanides with cold con HCl gives amides

$$CH_3-C\equiv N \xrightarrow[H_2O\,/\,OH^-]{\text{Conc HCl}} CH_3-\underset{\underset{O}{\|}}{C}-NH_2$$

Methyl cyanide — Acetamide

Chemical Properties

1. Amphoteric character

Amides behave both as weak acid as well as weak base and thus show amphoteric character. This can be proved by the following reactions.

Acetamide (as base) reacts with hydrochloric acid to form salt

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + HCl \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-\overset{+}{N}H_3\,Cl^-$$

Acetamide — Acetamide hydrochloride

Acetamide (as acid) reacts with sodium to form sodium salt and hydrogen gas is liberated.

$$2CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + 2Na \longrightarrow 2CH_3-\underset{\underset{O}{\|}}{C}-NHNa + H_2$$

Acetamide — Sodium acetamide

2) Hydrolysis

Amides can be hydrolysed in acid or in alkaline solution on prolonged heating

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{\text{dil HCl}} CH_3-\underset{\underset{O}{\|}}{C}-OH + NH_4Cl$$

Acetamide — Acetic acid

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{NaOH} CH_3-\underset{\underset{O}{\|}}{C}-ONa + NH_3$$

Acetamide — Sodium acetate

3) Dehydration

Amides on heating with strong dehydrating agents like P_2O_5 get dehydrated to form cyanides.

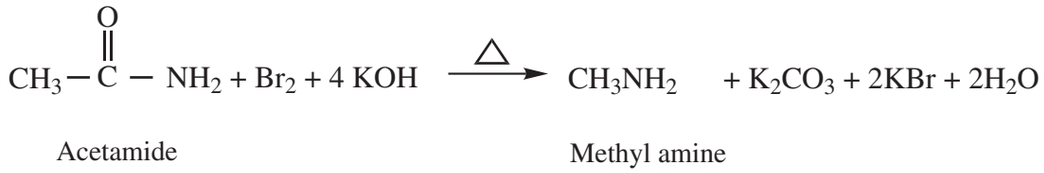
$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[\triangle]{P_2O_5} CH_3-C\equiv N + H_2O$$

Acetamide — Methyl cyanide (aceto nitrile)

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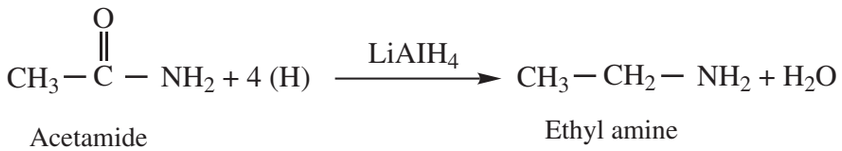
4) Hoff mann's degradation

Amides reacts with bromine in the presence of caustic alkali to form a primary amine carrying one carbon less than the parent amide.



5) Reduction

Amides on reduction with $LiAlH_4$ or Sodium and ethyl alcohol to form corresponding amines.



12.15 Uses of carboxylic acids and its derivatives

Formic acid

It is used

i) for the dehydration of hides.
ii) as a coagulating agent for rubber latex
iii) in medicine for treatment of gout
iv) as an antiseptic in the preservation of fruit juice.

Acetic acid

It is used

i) as table vinegar
ii) for coagulating rubber latex
iii) for manufacture of cellulose acetate and poly vinylacetate

Benzoic acid

It is used

i) as food preservative either in the pure form or in the form of sodium benzoate
ii) in medicine as an urinary antiseptic
iii) for manufacture of dyes

Acetyl Chloride

It is used

i) as acetylating agent in organic synthesis
ii) in detection and estimation of – OH, - NH_2 groups in organic compounds

Acetic anhydride

It is used

i) acetylating agent
ii) in the preparation of medicine like asprin and phenacetin
iii) for the manufacture plastics like cellulose acetate and poly vinyl acetate.

Ethyl acetate is used

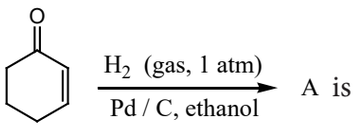
i) in the preparation of artificial fruit essences.
ii) as a solvent for lacquers.
iii) in the preparation of organic synthetic reagent like ethyl acetoacetate.

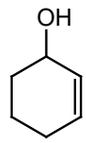
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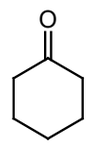
EVALUATION

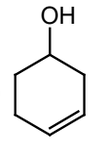
Choose the correct answer:

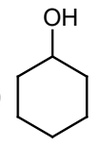
1. The correct structure of the product 'A' formed in the reaction (NEET)



a) 

b) 

c) 

d) 

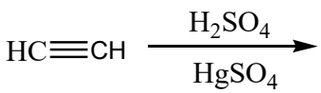
2. The formation of cyanohydrin from acetone is an example of

   a) nucleophilic substitution
   b) electrophilic substitution
   c) electrophilic addition
   d) Nucleophilic addition

3. Reaction of acetone with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

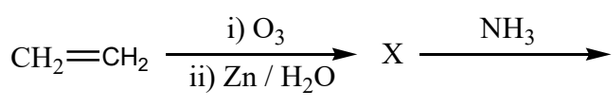
   a) Grignard reagent
   b) Sn / HCl
   c) hydrazine in presence of slightly acidic solution
   d) hydrocyanic acid

4. In the following reaction,



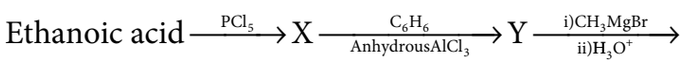
X Product 'X' will not give

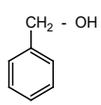
   a) Tollen's test
   b) Victor meyer test
   c) Iodoform test
   d) Fehling solution test

5. 

   a) Formaldelyde
   b) di acetone ammonia
   c) hexamethylene tetraamine
   d) oxime

6. Predict the product Z in the following series of reactions



   a) $(CH_3)_2C(OH)C_6H_5$
   b) $CH_3CH(OH)C_6H_5$
   c) $CH_3CH(OH)CH_2 - CH_3$
   d) 

7. Assertion: 2,2 – dimethyl propanoic acid does not give HVZ reaction.

   Reason: 2 – 2, dimethyl propanoic acid does not have α - hydrogen atom

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a) if both assertion and reason are true and reason is the correct explanation of assertion.

b) if both assertion and reason are true but reason is not the correct explanation of assertion.

c) assertion is true but reason is false

d) both assertion and reason are false.

8. Which of the following represents the correct order of acidity in the given compounds

a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

b) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

c) $CH_3COOH > ClCH_2COOH > FCH_2COOH >$ Br-CH_2COOH

d) Cl $CH_2COOH > CH_3COOH > BrCH_2COOH > ICH_2COOH$

9. Benzoic acid $\xrightarrow[\text{ii) }\Delta]{\text{i) }NH_3}$ A $\xrightarrow{NaOBr}$ B $\xrightarrow{NaNO_2/HCl}$ C 'C' is

a) anilinium chloride
b) O – nitro aniline
c) benzene diazonium chloride
d) m – nitro benzoic acid

10. Ethanoic acid $\xrightarrow{P/Br_2}$ 2 – bromoethanoic acid. This reaction is called

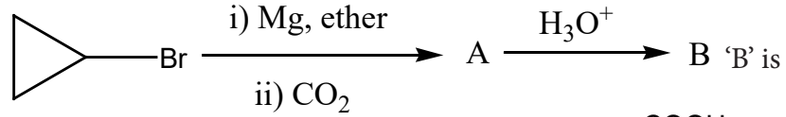
a) Finkelstein reaction
b) Haloform reaction
c) Hell – Volhard – Zelinsky reaction
d) none of these

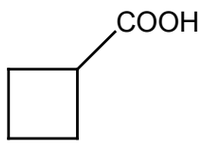
11. $CH_3Br \xrightarrow{KCN}$ (A) $\xrightarrow{H_3O^+}$ (B) $\xrightarrow{PCl_5}$ (C) product (C) is

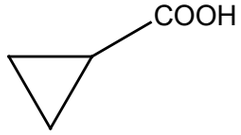
a) acetylchloride
b) chloro acetic acid
c) α- chlorocyano ethanoic acid
d) none of these

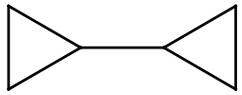
12. Which one of the following reduces tollens reagent

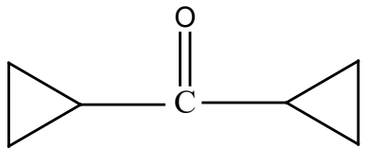
a) formic acid
b) acetic acid
c) benzophenone
d) none of these

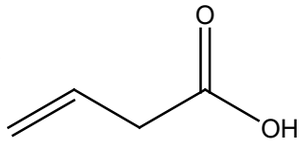
13. 

a) 

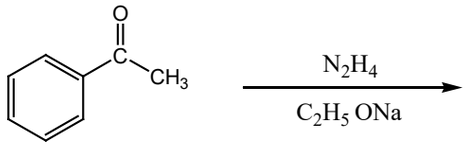
b) 

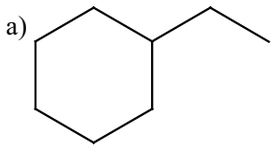
c) 

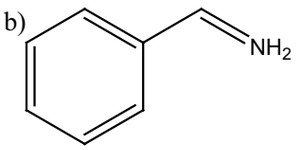
d) 

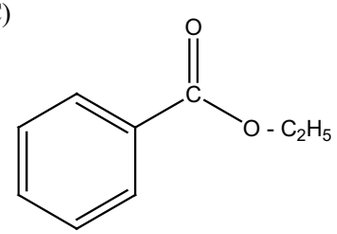
14. The IUPAC name of 

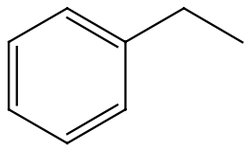
a) but – 3- enoicacid
b) but – 1- ene-4-oicacid
c) but – 2- ene-1-oic acid
d) but -3-ene-1-oicacid

15. Identify the product formed in the reaction 

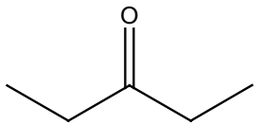
a) 

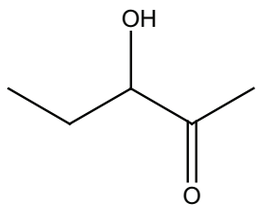
b) 

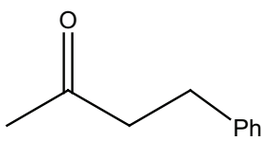
C) 

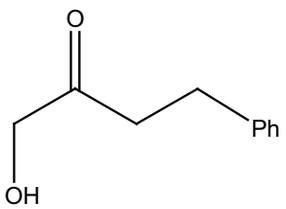
d) 

16. In which case chiral carbon is not generated by reaction with HCN

a) 

b) 

C) 

d) 

17. Assertion : p – N, N – dimethyl aminobenzaldehyde undergoes benzoin condensation
Reason : The aldehydic (-CHO) group is meta directing
a) if both assertion and reason are true and reason is the correct explanation of assertion.
b) if both assertion and reason are true but reason is not the correct explanation of assertion.
c) assertion is true but reason is false
d) both assertion and reason are false.

18. Which one of the following reaction is an example of disproportionation reaction
a) Aldol condensation
b) cannizaro reaction
c) Benzoin condensation
d) none of these

19. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid
a) Phenylmethanal
b) ethanal
c) ethanol
d) methanol

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20. The reagent used to distinguish between acetaldehyde and benzaldehyde is

a) Tollens reagent b) Fehling's solution

c) 2,4 – dinitrophenyl hydrazine d) semicarbazide

21. Phenyl methanal is reacted with concentrated NaOH to give two products X and Y. X reacts with metallic sodium to liberate hydrogen X and Y are

a) sodiumbenzoate and phenol b) Sodium benzoate and phenyl methanol

c) phenyl methanol and sodium benzoate d) none of these

22. In which of the following reactions new carbon – carbon bond is not formed?

a) Aldol condensation b) Friedel craft reaction

c) Kolbe's reaction d) Wolf kishner reduction

23. An alkene "A" on reaction with O_3 and $Zn - H_2O$ gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene "A" gives "B" as the major product. The structure of product "B" is

a) $Cl-CH_2-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{CH}}}}$

b) $H_3C-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2Cl}{\overset{|}{\underset{|}{CH}}}}$

c) $H_3C-CH_2-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

d) $H_3C-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{CH}}}}-CH$

24. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their (NEET)

a) more extensive association of carboxylic acid via van der Waals force of attraction

b) formation of carboxylate ion

c) formation of intramolecular H-bonding

d) formation of intermolecular H – bonding

Short Answer Questions

1. How is propanoic acid is prepared starting from

(a) an alcohol (b) an alkylhalide (c) an alkene

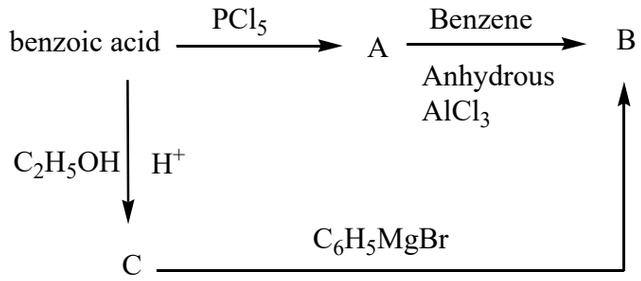
2. A Compound (A) with molecular formula C_2H_3N on acid hydrolysis gives(B) which reacts with thionylchloride to give compound(C). Benzene reacts with compound (C) in presence of anhydrous $AlCl_3$ to give compound(D). Compound (D) on reduction with Zn/Hg and Conc.HCl gives (E). Identify (A), (B), (C), (D) and (E). Write the equations.

3. Identify X and Y.

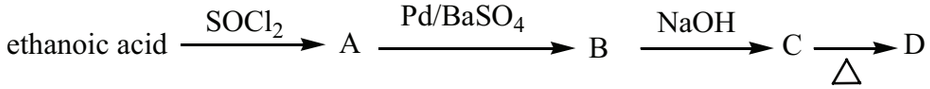
$$CH_3COCH_2CH_2COOC_2H_5 \xrightarrow{CH_3MgBr} X \xrightarrow{H_3O^+} Y$$

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4. Identify A, B and C



5. Identify A, B, C and D



6. An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidised (C) is obtained. (C) is treated with Br_2/P gives (D) which on hydrolysis gives (E). When propanone is treated with HCN followed by hydrolysis gives (E). Identify A, B, C, D and E.
7. How will you convert benzaldehyde into the following compounds?

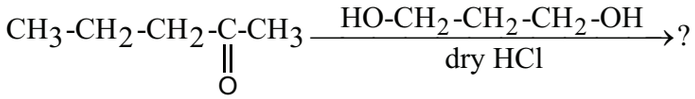
   (i) benzophenone (ii) benzoic acid

   (iii) α-hydroxyphenylaceticacid.
8. What is the action of HCN on

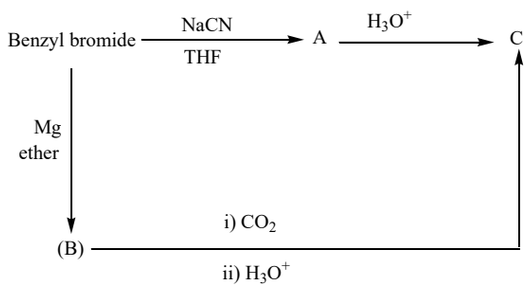
   (i) propanone (ii) 2,4-dichlorobenzaldehyde. iii) ethanal
9. A carbonyl compound A having molecular formula $C_5H_{10}O$ forms crystalline precipitate with sodium bisulphite and gives positive iodoform test. A does not reduce Fehling solution. Identify A.
10. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.
11. How are the following conversions effected

    (a) propanal into butanone (b) Hex-3-yne into hexan-3-one.

    (c) phenylmethanal into benzoic acid (d) phenylmethanal into benzoin
12. Complete the following reaction.



13. Identify A, B and C



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14. Oxidation of ketones involves carbon – carbon bond cleavage. Name the product (s) is / are formed on oxidising 2,5 – dimethyhexan – 3- one using strong oxidising agent.

15. How will you prepare

    i. Acetic anhydride from acetic acid

    ii. Ethylacetate from methylacetate

    iii. Acetamide from methylcyanide

    iv. Lactic acid from ethanal

    v. Acetophenone from acetylchloride

    vi. Ethane from sodium acetate

    vii. Benzoic acid from toluene

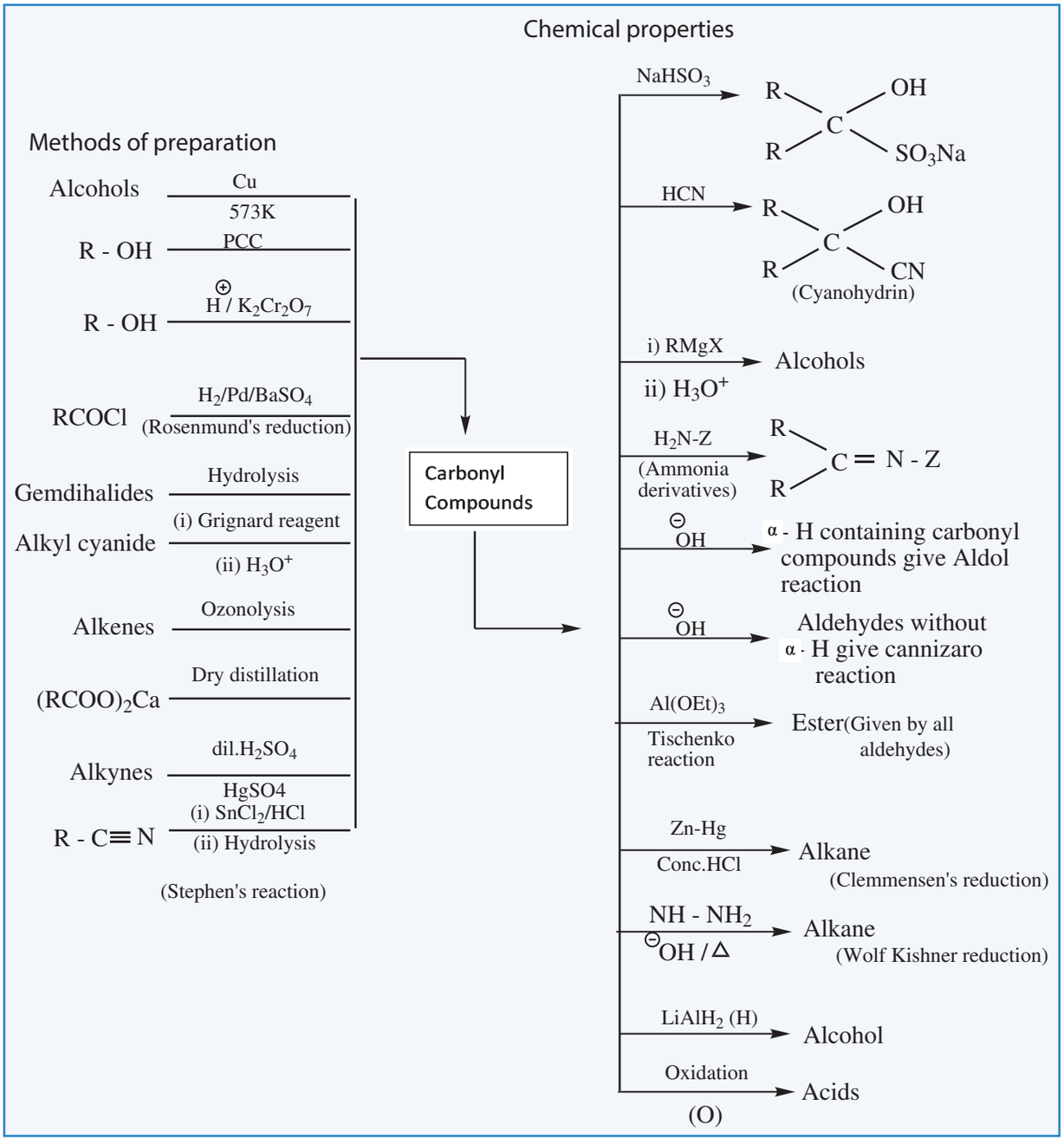
    viii. Malachitegreen from benzaldehyde

    ix. Cinnamic acid from benzaldehyde

    x. Acetaldehyde from ethyne

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CARBONYL COMPOUNDS

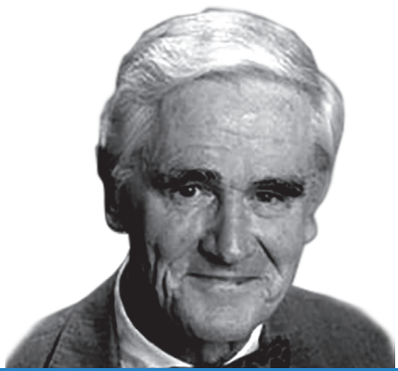


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UNIT 13

ORGANIC NITROGEN COMPOUNDS



Donald James Cram

Donald James Cram was an American chemist who shared the 1987 Nobel Prize in Chemistry with Jean-Marie Lehn and Charles J. Pedersen "for their development and use of molecules with structure-specific interactions of high selectivity." They were the founders of the field of host–guest chemistry Cram expanded upon Charles Pedersen's ground-breaking synthesis of crown ethers, two-dimensional organic compounds that are able to recognize and selectively combine with the ions of certain metal elements. He also did work in stereochemistry and Cram's rule of asymmetric induction is named after him.

GQUAV

Learning Objectives

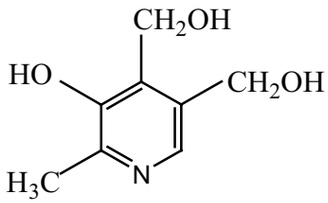
After studying this unit the student will be able to

- understand isomerism in organic nitro compounds
- describe the preparation and properties of nitro compounds
- classify amines as primary, secondary and tertiary
- describe the methods of preparation of amines
- explain the properties of amines
- distinguish between primary, secondary and tertiary amines
- describe the method of preparation of diazonium salts
- explain the preparation and properties of cyanides

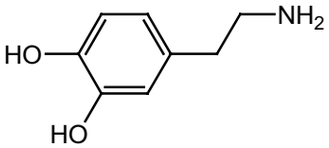
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INTRODUCTION

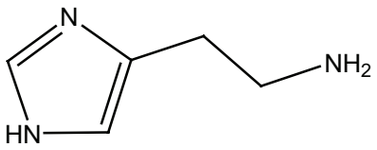
Organic compounds containing nitrogen are essential to life. For example; amines, the organic derivatives of ammonia play an important role in bioregulation, neurotransmission,etc., Pyridoxine, Vitamin B_6 is an organic nitrogen compound which is needed to maintain the health of nerves, skin and red blood cells. Plants synthesise alkaloids, and biologically active amines to protect them from being eaten away by insects and other animals. Diazonium salts finds important applications in synthetic organic chemistry. Nitrogen compounds are the important constituents of explosives, drugs, dyes, fuels, polymers, synthetic rubbers, etc.,



Vitamin B_6



dopamine
neurotransmitter



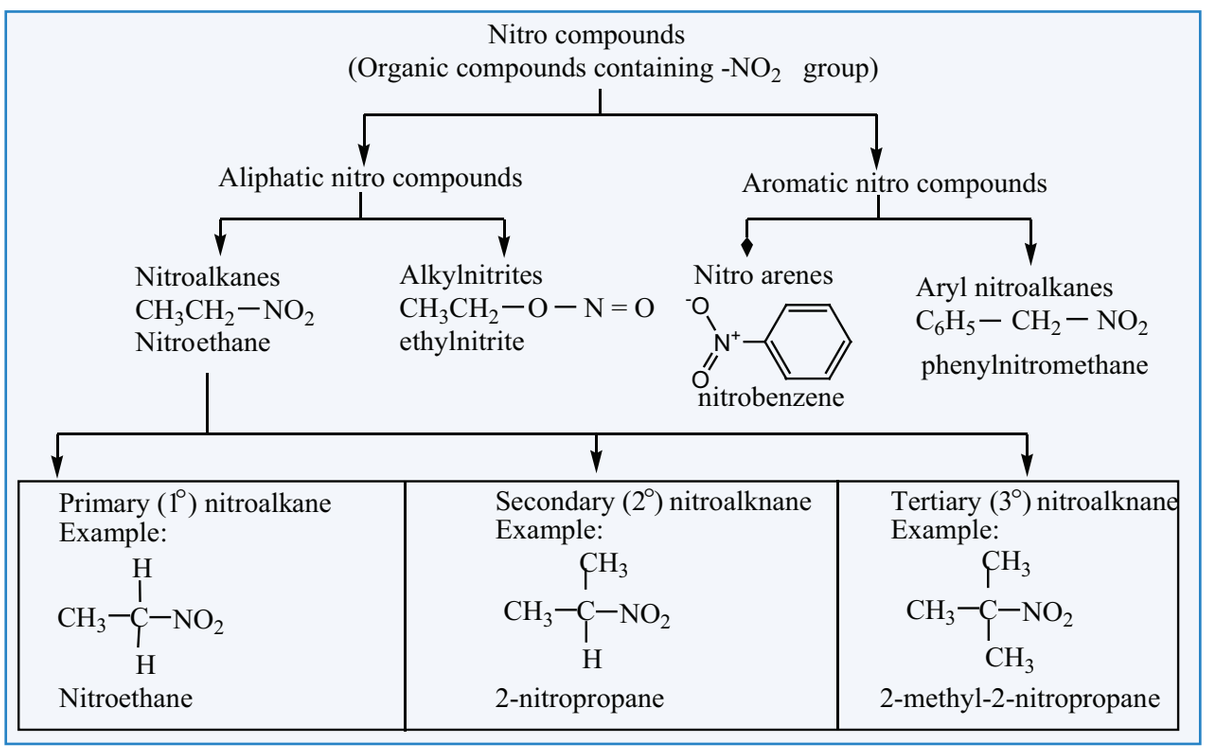
Histamine
dilates blood vessels

In this unit, we will learn the preparation, properties and uses of nitrocompounds and amines.

13.1 NITRO COMPOUNDS

Nitro compounds are considered as the derivaties of hydrocarbons. If one of the hydrogen atom of hydrocarbon is replaced by the $-NO_2$ group, the resultant organic compound is called a nitrocompound.

13.1.1 Classification of nitrocompounds

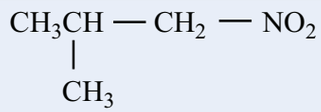
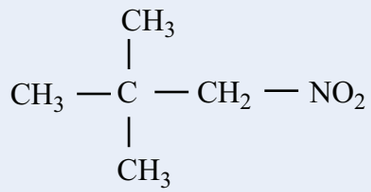
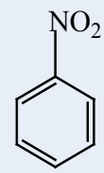
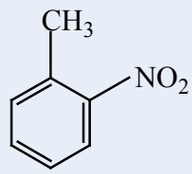
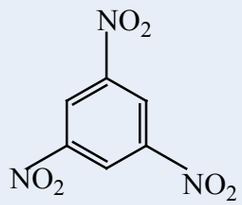
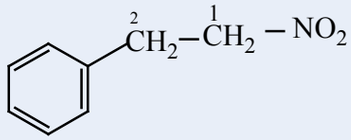


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Nitroalkanes are represented by the formula, R-NO_2 where R is an alkyl group (C_nH_{2n+1}-). Nitroalkanes are further classified into primary, secondary, tertiary nitroalkanes on the basis of type of carbon atom to which the nitro (-NO_2) group is attached.

13.1.2 Nomenclature of nitroalkanes

In the IUPAC nomenclature, the nitroalkanes are named by adding prefix nitro before the name of alkane, the position of the nitro group is indicated by number.

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
 2- Methyl – 1- nitropropane	2- Methyl – 1- nitro	prop	ane	–
 2,2 – dimethyl – 1- nitro propane	2,2 – dimethyl – 1- nitro	prop	ane	–
 Nitrobenzene	nitro	benzene	–	–
 2-nitro -1-methyl benzene	2-nitro-1-methyl	benzene	–	–
 1,3,5 – trinitrobenzene	1,3,5 – trinitro	benzene	–	–
 2 – phenyl – 1- nitroethane	2 – phenyl – 1- nitro	eth	ane	

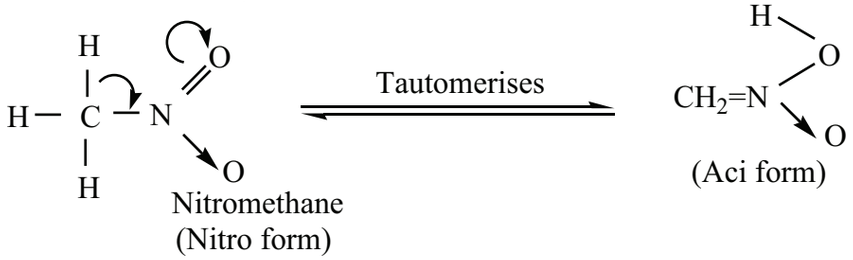
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13.1.3 ISOMERISM

Nitroalkanes exhibit chain and position isomerism among their own class and functional isomerism with alkyl nitrites and special type tautomerism can also exist in nitro alkanes having an α-H atom. For example, nitro compounds having the molecular formula $C_4H_9NO_2$ exhibit the following isomerisms.

Isomerism	Structural formula of isomers
Chain isomerism: They differ in the length of carbon chain.	$CH_3CH_2CH_2CH_2 - NO_2$ and $CH_3CHCH_2 - NO_2$ (with CH_3 branch) 1 - nitrobutane 2 - methyl - 1-nitropropane
Position isomerism: They differ in the position of nitro group.	$CH_3CH_2CH_2CH_2-NO_2$ and $CH_3CH(NO_2)CH_2CH_3$ 1 - nitrobutane 2 - nitrobutane
Functional isomerism: Nitroalkanes exhibit functional isomerism with alkylnitrites	$CH_3CH_2CH_2CH_2 - NO_2$ and $CH_3CH_2CH_2CH_2 - O - N = O$ 1 - nitrobutane butyl nitrite

Tautomerism: Primary and secondary nitroalkanes, having α-H , also show an equilibrium mixture of two tautomers namely nitro – and aci – form



Nitromethane (Nitro form) (Aci form)

Tertiary nitro alkanes donot exhibit tautomerism due to absence of α-H atom.

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly
3.	Decolourises $FeCl_3$ solution	With $FeCl_3$ gives reddish brown colour
4.	Electrical conductivity is low	Electrical conductivity is high

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13.1.4 Acidic nature of nitro alkanes

The α-H atom of 1° & 2° nitroalkanes show acidic character because of the electron with drawing effect of NO_2 group. These are more acidic than aldehydes, ketones, ester and cyanides. Nitroalkanes dissolve in NaOH solution to form a salt. Aci – nitro derivatives are more acidic than nitro form. When the number of alkyl group attached to α carbon increases, acidity decreases. due to +I effect of alkyl groups.

$$CH_3 - NO_2 > CH_3CH_2 - NO_2 > \begin{matrix} CH_3 \\ \diagdown \\ CH - NO_2 \\ \diagup \\ CH_3 \end{matrix}$$

Evaluate yourself

Write all possible isomers for the following compounds.

i) C_2H_5-NO_2 ii) C_3H_7-NO_2

13.1.5 Preparation of nitroalkanes

1) From alkyl halides: (Laboratory method)

a) Alkyl bromides (or) iodides on heating with ethanolic solution of potassium nitrite gives nitroethane.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2\text{-Br}} + KNO_2 \xrightarrow[SN^2]{\text{ethanol}/\Delta} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2} + KBr$$

The reaction follows SN2 mechanism.

This method is not suitable for preparing nitrobenzene because the bromine directly attached to the benzene ring cannot be cleaved easily.

2) Vapour phase nitration of alkanes: (Industrial method)

Gaseous mixture of methane and nitric acid passed through a red hot metal tube to give nitromethane.

$$\underset{\text{Methane}}{CH_{4(g)}} + HNO_{3\,(g)} \xrightarrow[\text{Red hot Si tube}]{675\ K} \underset{\text{nitro methane}}{CH_3\text{-}NO_2} + H_2O$$

Except methane, other alkanes (upto n – hexane) give a mixture of nitroalkanes due to C-C cleavage. The individual nitro alkanes can be separated by fractional distillation.

$$\underset{\text{Ethane}}{CH_3\text{-}CH_3} + HNO_3 \xrightarrow{675\ K} \underset{\text{Nitroethane(73\%)}}{CH_3CH_2\text{-}NO_2} + \underset{\text{Nitromethane (27\%)}}{CH_3NO_2}$$

3) From α- halocarboxylic acid

α-choloroacetic acid when boiled with aqueous solution of sodium nitrite gives nitromethane.

$$\underset{\alpha\text{ - chloro acetic acid}}{Cl\text{ - }CH_2\text{-COOH}} + NaNO_2 \xrightarrow[SN^2]{H_2O/Heat} \underset{\text{Nitromethane}}{CH_3\text{-}NO_2} + CO_2 + NaCl$$

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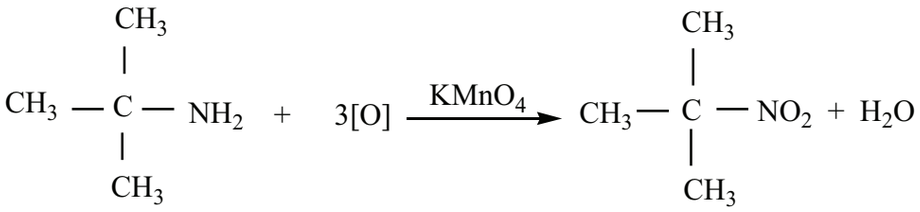
Evaluate yourself

4) Find out the product of the following reactions.

i) $CH_3CH(Cl)COOH \xrightarrow[ii)\ H_2O/\Delta]{i)\ NaNO_2} ?[X]$ ii) $CH_3CH_2\text{-}Br + NaNO_2 \xrightarrow{\text{alcohol }/\Delta} [Y]$

4) Oxidation of tert – alkyl amines

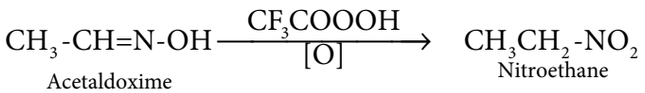
tert – butyl amine is oxidised with aqueous $KMnO_4$ to give tert – nitro alkanes.



tert-butylamine — 2 - methyl - 2 - nitro propane

5) Oxidation of Oximes

Oxidation of acetaldoxime and acetoneoxime with trifluoroperoxy acetic acid gives nitroethane (1^0) and 2 – nitropropane (2^0) respectively.

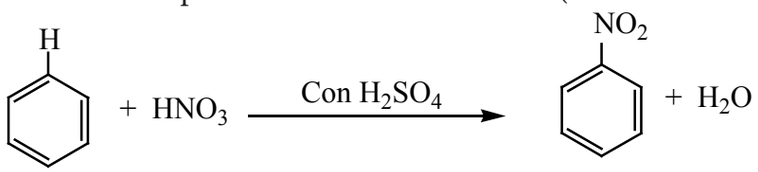


Acetaldoxime — Nitroethane

13.1.6 Preparation of Nitroarenes

1) By Direct nitration

When benzene is heated at 330K with a nitrating mixture $(Con.HNO_3 + Con.H_2SO_4)$, electrophilic substitution takes place to form nitro benzene. (Oil of mirbane)

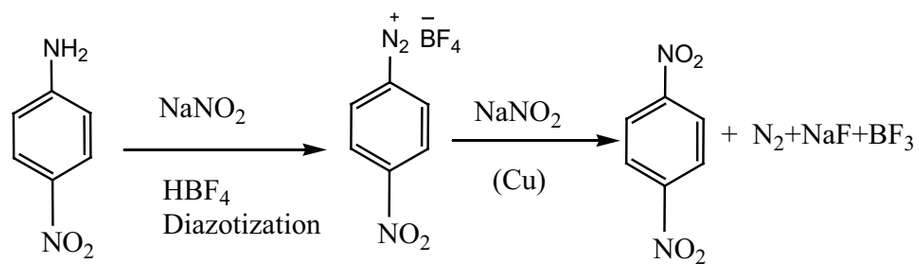


On direct nitration of nitrobenzene m- dinitrobenzene is obtained

2) Indirect method

Nitration of nitro benzene gives m-dinitrobenzene. The following method is adopted for the preparation of p-dinitrobenzene.

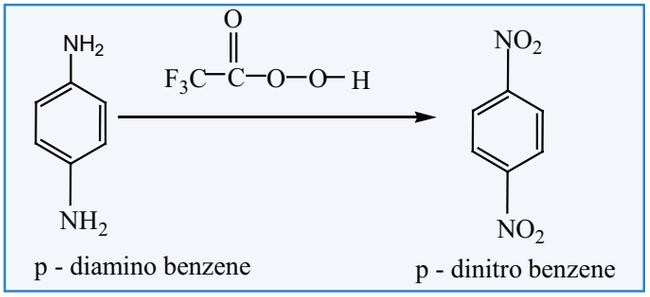
For example



p - nitroaniline — p - nitrodiazo fluoroborate — p - dinitro benzene

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Amino group can be directly converted into nitro group, using caro's acid (H_2SO_5) (or) persulphuric acid ($H_2S_2O_8$) (or) peroxytrifluro acetic acid ($F_3C.CO_3H$) as oxidising agent.



13.1.7 Physical properties of nitro alkane

The lower nitroalkanes are colourless pleasant smelling liquids, sparingly soluble in water, but readily soluble in organic solvents like benzene, acetone etc… They have high boiling points because of their highly polar nature. Alkylnitrites have lower boiling points than nitro alkanes.

13.1.8 Chemical properties of nitroalkanes

Nitroalkanes undergo the following common reactions.

i. Reduction ii. Hydrolysis iii. Halogenations

i. Reduction of nitroalkanes

Reduction of nitroalkanes has important synthetic applications. The various reduction stages of nitro group are given below.

$$CH_3 - NO_2 \xrightarrow[-H_2O]{+2[H]} CH_3 - N = O \xrightarrow{+2[H]} CH_3 - NHOH \xrightarrow[-H_2O]{+2[H]} CH_3 - NH_2$$

nitromethane — nitroso methane — N - methyl hydroxylamine — methylamine

The final product depends upon the nature of reducing agent as well as the pH of the medium.

$$CH_3 - NO_2 \xrightarrow[6[H]]{Sn/HCl} CH_3 - NH_2 + 2H_2O \quad \text{(acid medium)}$$

Nitromethane — Methyl amine

$$CH_3 - NO_2 \xrightarrow[4[H]]{Zn / NH_4Cl} CH_3 - NHOH + H_2O \quad \text{(neutral medium)}$$

Nitromethane — N - methyl hydroxylamine

Reduction of alkyl nitrites

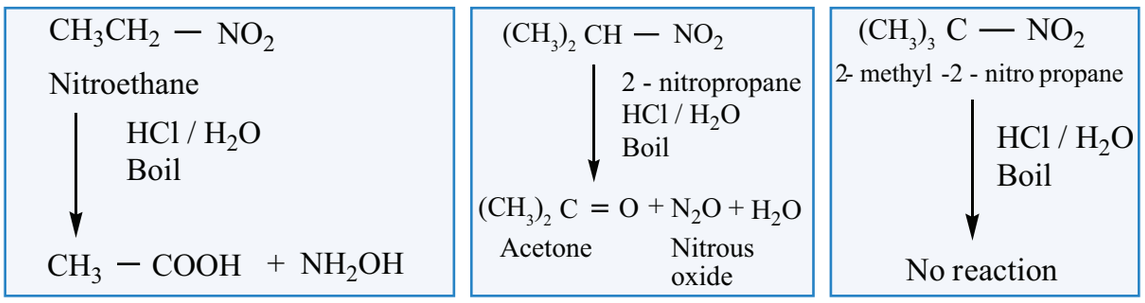
Ethylnitrite on reduction with Sn / HCl gives ethanol

$$CH_3CH_2 - O - N = O + 6[H] \xrightarrow{Sn / HCl} CH_3CH_2 - OH + NH_3 + H_2O$$

ii. Hydrolysis of nitroalkanes

Hydrolysis can be effected using conc. HCl or conc. H_2SO_4. Primary nitroalkanes on hydrolysis gives carboxylic acid, and the secondary nitroalkanes give ketones. The tertiary nitroalkanes have no reaction.

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On the other hand, the acid or base hydrolysis of ethyl nitrite gives ethanol.

$$\underset{\text{Ethylnitrite}}{CH_3CH_2-O-N=O} + HOH \xrightarrow[(or)\ H^+]{OH^-} \underset{\text{Ethanol}}{CH_3CH_2-OH} + HNO_2$$

iii. Halogenation of nitroalkanes

Primary and secondary nitroalkanes on treatement with Cl_2 or Br_2 in the presence of NaOH give halonitroalkanes. The α - H atom of nitroalkanes are successively replaced by halogen atoms.

$$CH_3 - NO_2 + 3Cl_2 \xrightarrow{NaOH} \underset{\text{Chloropicrin (trichloronitromethane)}}{CCl_3 - NO_2} + 3HCl$$

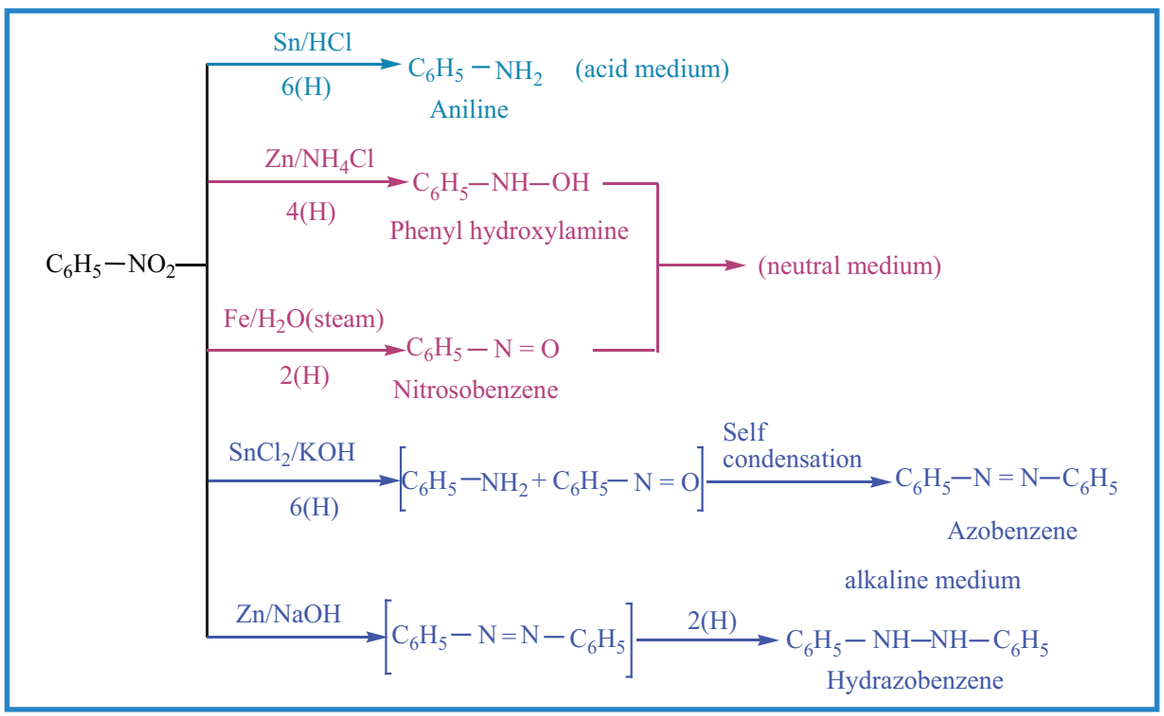
Toxicity

Nitroethane is suspected to cause genetic damage and be harmful to the nervous system.

iv. Nef carbonyl synthesis :

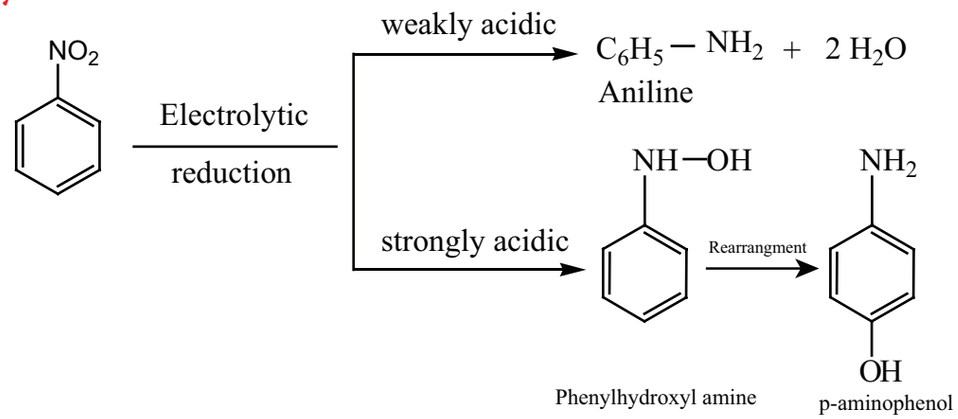
$$CH_3CH_2NO_2 \xrightarrow{KOH} CH_3-CH=N\begin{matrix}O^{\ominus}\\ \diagup\\ \diagdown\\ OH\end{matrix} \xrightarrow{H_2O/H^+} \underset{\text{Nitroxyl azanone}}{CH_3-CHO + HNO}$$

Chemical Properties of nitrobenzene



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Electrolytic reduction:

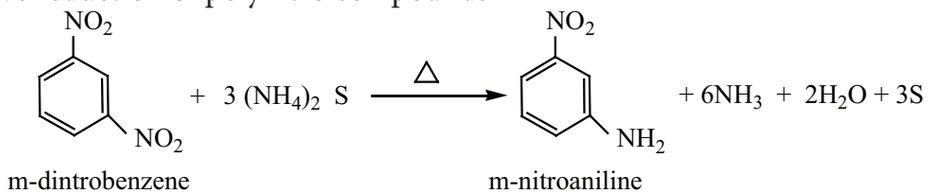


Reduction of catalytic and metal hydrides

Nitrobenzene reduction with Ni (or) Pt, (or) $LiAlH_4$ to give aniline

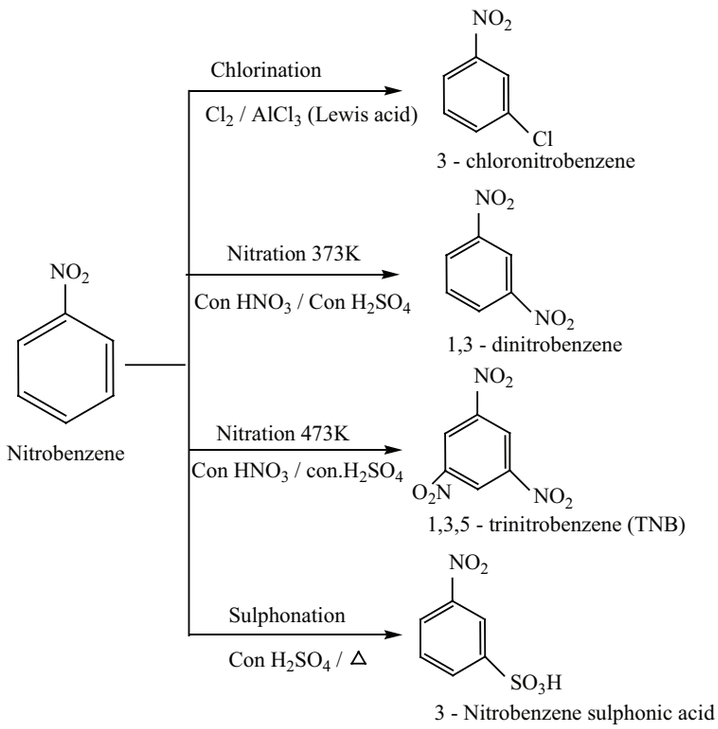
$$C_6H_5 - NO_2 + 6\,[H] \xrightarrow[(or)\ LiAlH_4]{Ni\ (or)\ Pt\ /\ H_2} C_6H_5 - NH_2 + 2\,H_2O$$

Selective reduction of polynitro compounds



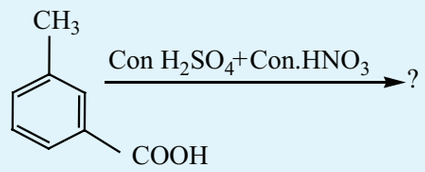
Electrophilic substitution reaction

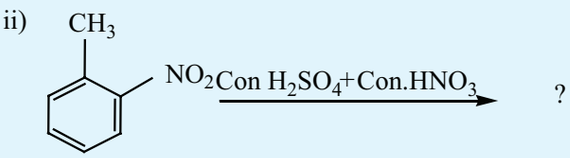
The electrophilic substitution reactions of nitrobenzene are usually very slow and vigorous reaction condition have to be employed (- NO_2 group is stongly deactivating and m – directing).

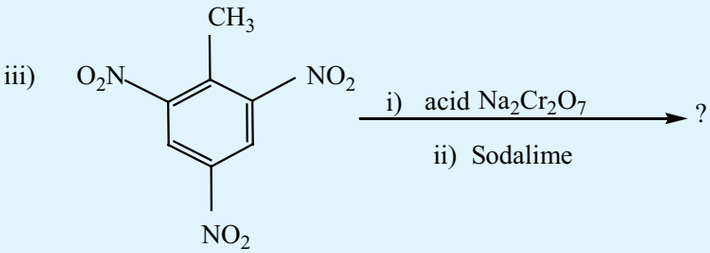


Nitrobenzene does not undergo Friedel – Crafts reactions due to the strong deactivating nature of $-NO_2$ group.

Evaluate yourself Predict the major product that would be obtained on nitration of the following compounds

i) 

ii) 

iii) 

13.2 Amines - clasification

Amines

- Aliphatic amines
- Aromatic amines

		Aliphatic amines	Aromatic amines
Primary		$CH_3-CH_2-NH_2$ ethanamine	$C_6H_5-NH_2$ benzenamine(aniline)
Secondary	simple	$CH_3-NH-CH_3$ N-methylmethanamine	$C_6H_5-NH-C_6H_5$ N-phenylbenzenamine
	mixed	$CH_3-NH-CH_2-CH_3$ N-methylethanamine	$C_6H_5-NH-CH_3$ N-phenylmethanamine
Tertiary	simple	$CH_3-N(CH_3)-CH_3$ N,N-dimethylmethanamine	$C_6H_5-N(C_6H_5)-C_6H_5$ N,N-diphenylbenzenamine
	mixed	$CH_3-N(CH_3-CH_2-CH_3)-CH(CH_3)-CH_3$ (N-ethyl-N-methyl) propan–2–amine	$C_6H_5-N(CH_3)-CH_2-CH_3$ N-methyl-N-phenylethanamine

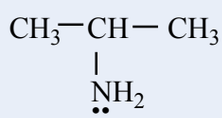
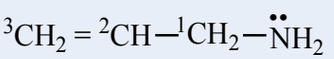
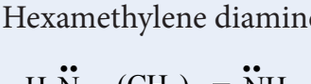
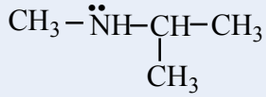
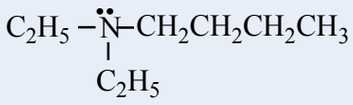
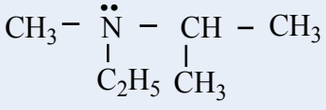
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13.2.1 Nomenclature

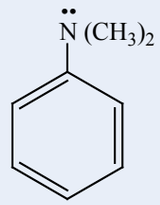
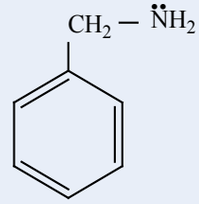
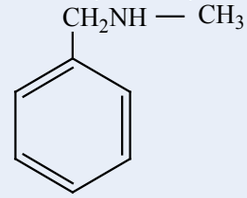
a) Common system:

In common system, an aliphatic amine is named by prefixing alkyl group to amine. The prefixes di-,tri-, and tetra-, are used to describe two, three(or) four same substituent's.

b) IUPAC System:

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Isopropylamine  Propan – 2- amine	–	prop	ane	2- amine
Allylamine  Prop-2-en-1-amine	–	prop	2-en	-1-amine
Hexamethylene diamine  Hexane – 1, 6 – diamine	–	Hex	ane	– 1, 6 – diamine
Methyl isopropyl amine  N – methyl propan – 2- amine	N – methyl	prop	ane	– 2- amine
Diethyl butylamine  N, N – Diethyl butan-1-amine	N, N – Diethyl	but	ane	-1-amine
Ethyl methyl isopropylamine  N – ethyl – N- methyl propan – 2 – amine	N – ethyl – N- methyl	prop	ane	-2-amine

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N,N – Dimethyl aniline  N,N – Dimethylbenzenamine	N,N – Dimethyl	benzene	–	amine
Benzylamine  Phenyl methanamine	Phenyl	meth	ane	amine
N – methyl benzylamine  N – methyl phenyl methanamine	N – methyl phenyl	meth	ane	amine

Evaluate yourself

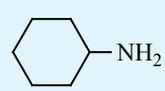
Draw the structure of the following compounds

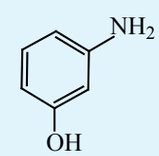
i. Neopentylamine
ii. Tert – butylamine
iii. α - amino propionaldehyde
iv. Tribenzylamine
v. N – ethyl – N – methylhexan – 3- amine

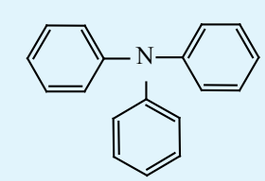
8) Give the correct IUPAC names for the following amines

i) $CH_3 - CH_2 - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CH_3$

ii) $CH_3 - CH_2 - \underset{\displaystyle NH\,CH_3}{\underset{|}{CH}} - CH_3$

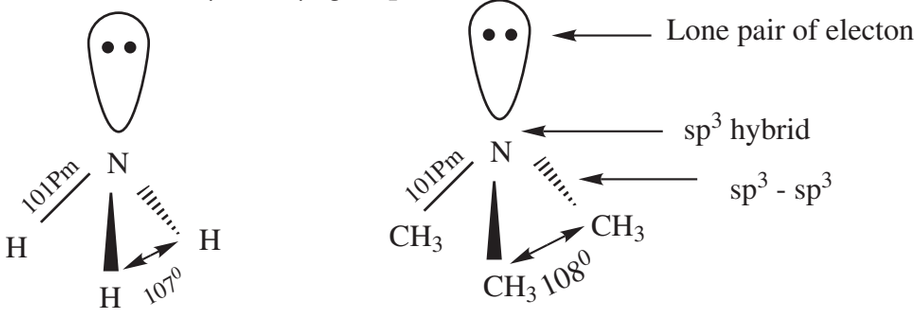
iii) 

iv) 

v) 

13.2.2 Structure of amines

Like, ammonia, nitrogen atom of amines is trivalent and carries a lone pair of electron and sp^3 hybridised, out of the four sp^3 hybridised orbitals of nitrogen, three sp^3 orbitals overlap with orbitals of hydrogen (or) alkyl groups of carbon, the fourth sp^3 orbital contains a lone pair of electron. Hence, amines posses pyramidal geometry. Due to presence of lone pair of electron C- N- H (or) C- N- C bond angle is less than the normal tetrahedral bond angle 109.5^0. For example, the C- N- C bond angle of trimethylamine is 108^0 which is lower than tetrahedral angle and higher than the H- N- H bond angle of 107°. This increase is due to the repulsion between the bulky methyl groups.



13.2.3 General methods of preparation Amines

Aliphatic and aromatic amines are prepared by the following methods.

1) From nitro compounds

Reduction of Nitro compounds using H_2 / Ni (or) Sn / HCl or Pd/H_2 gives primary amines.

$$CH_3CH_2 - NO_2 \xrightarrow[Fe\ /\ HCl,\ 6\ [H]]{3H_2\ /\ Ni\ (or)} CH_3CH_2 - NH_2 + 2\ H_2O$$

Nitroethane — ethanamine

$$C_6H_5 - NO_2 \xrightarrow[(or)\ Sn\ /\ HCl]{3H_2\ /\ Pt,\ 680\ K} C_6H_5 - NH_2 + 2\ H_2O$$

Nitrobenzene — Aniline

2) From nitriles

a) Reduction of alkyl or aryl cyanides with H_2/Ni (or) $LiAlH_4$ (or) Na / C_2H_5OH gives primary amines. The reduction reaction in which Na / C_2H_5OH is used as a reducing agent is called mendius reaction

$$CH_3 - CN \xrightarrow[4\ [H]]{Na(Hg)\ /\ C_2H_5OH} CH_3CH_2 - NH_2$$

ethanenitrile — ethanamine

b) Reduction of isocyanides with sodium amalgam / C_2H_5OH gives secondary amines

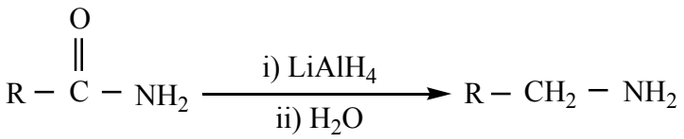
$$CH_3 - NC \xrightarrow[4\ [H]]{Na(Hg)\ /\ C_2H_5OH} CH_3 - NH - CH_3$$

Methyl isocyanide — N-methylmethanamine

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3) From amides

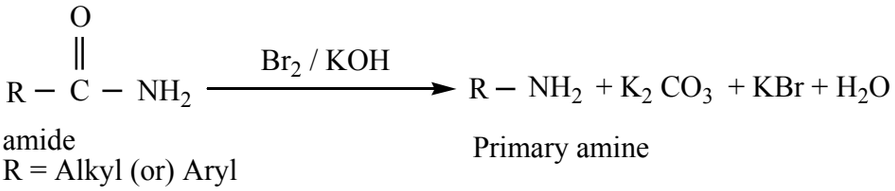
a) Reduction of amides with $LiAlH_4$ gives amines



b) Hoffmann's degradation reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

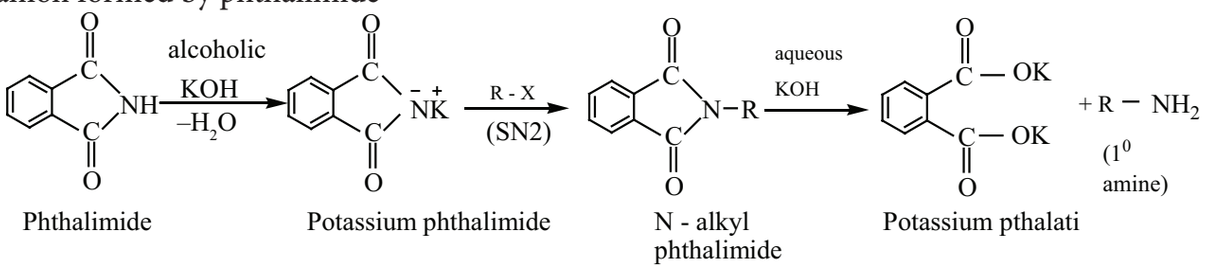
Example:



4) From alkyl halides

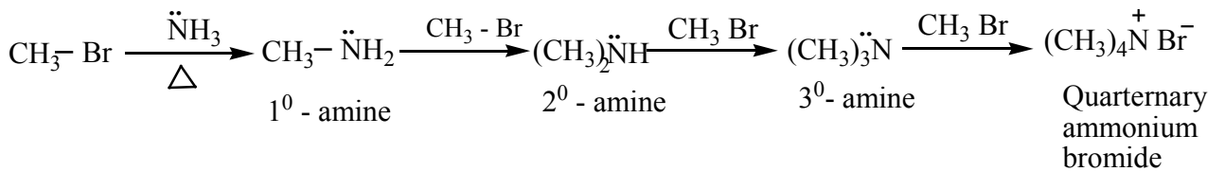
a) Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of Aliphatic primary amines. Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide



b) Hoffmann's ammonolysis

When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1^0, 2^0 and 3^0 amines and quaternary ammonium salts are obtained.



This is a nucleophilic substitution , the halide ion of alkyl halide is substituted by the $-NH_2$ group. The product primary amine so formed can also has a tendency to act as a nucleophile and hence if excess alkyl halide is taken, further nucleophilic substitution takes place leading

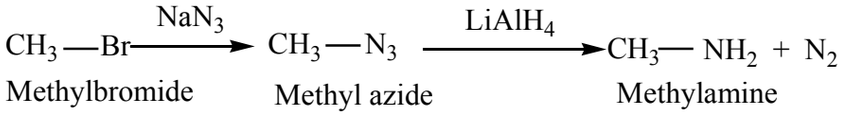
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to the formation of quarternary ammonium salt. However, if the process is carried out with excess ammonia, primary amine is obtained as the major product.

The order of reactivity of alkylhalides with amines.

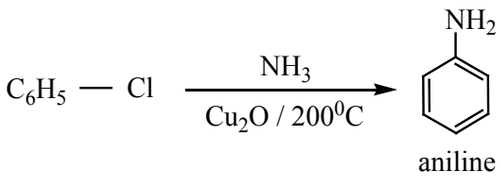
$$RI > RBr > RCl$$

c) Alkyl halide can also be converted to primary amine by treating it with sodium azide (NaN_3) followed by the reduction using lithium aluminium hydride.



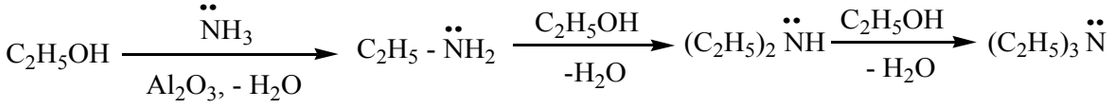
d) Preparation of aniline from chlorobenzene

When chlorobenzene is heated with alcoholic ammonia, aniline is obtained.

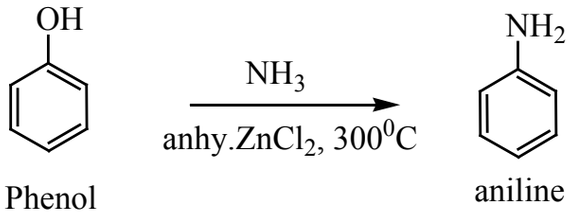


5) Ammonolysis of hydroxyl compounds

a) when vapour of an alcohol and ammonia are passed over alumina, W_2O_5 (or) silica at 400^0C, all types of amines are formed. This method is called **Sabatier – Mailhe** method.



b) Phenol reacts with ammonia at 300^0C in the presence of anhydrous $ZnCl_2$ to give aniline



13.2.4 Properties of amines

1. Physical state and smell

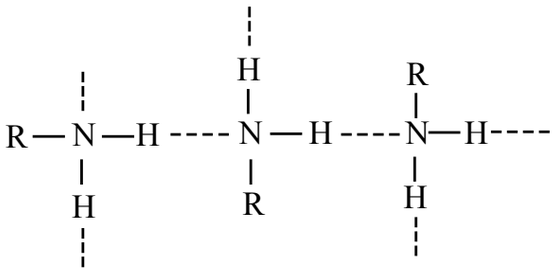
The lower aliphatic amines (C_1-C_2) are colourless gases and have ammonia like smell and those with four or more carbons are volatile liquids with fish like smell.

Aniline and other arylamines are usually colourless but when exposed to air they become coloured due to oxidation.

2. Boiling point

Due to the polar nature of primary and secondary amines, can form intermolecular hydrogen bonds using their lone pair of electorn on nitrogen atom. There is no such H-bonding in tertiary amines.

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The boiling point of various amines follows the order,

$$CH_3-\ddot{N}H_2 > (CH_3)_2\ddot{N}H > (CH_3)_3\ddot{N}$$

$$1^{\circ} > 2^{\circ} > 3^{\circ}$$

Amines have lower boiling point than alcohols because nitrogen has lower electronegative value than oxygen and hence the N-H bond is less polar than -OH bond.

Table Boiling points of amines, alcohols and alkanes of comparable molecular weight.

S.NO.	Compound	Molecular mass	Boiling point (K)
1.	$CH_3(CH_2)_2NH_2$	59	321
2.	C_2H_5-NH-CH_3	59	308
3.	$(CH_3)_3N$	59	277
4.	$CH_3CH(OH)CH_3$	60	355
5.	$CH_3CH_2CH_2CH_3$	58	272.5

3) Solubility

Lower aliphatic amines are soluble in water, because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molecular mass of amines due to increase in size of the hydrophobic alkyl group. Amines are insoluble in water but readily soluble in organic solvents like benzene, ether etc.

13.2.5 Chemical properties

The lone pair of electrons on nitrogen atom in amines makes them basic as well as nucleophilic. They react with acids to form salts and also react with electrophiles.

They form salts with mineral acids

Example:

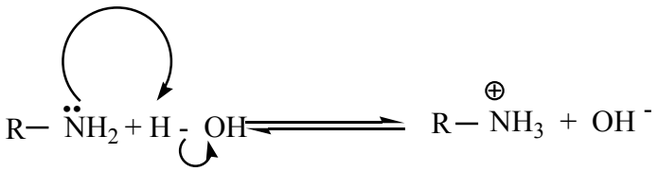
$$C_6H_5-\ddot{N}H_2 + HCl \rightleftharpoons C_6H_5-\overset{+}{N}H_3Cl^-$$

Aniline — Anilinium chloride

Expression for basic strength of amines

In the aqueous solutions, the following equilibrium exists and it lies far to the left, hence amines are weak bases compared to NaOH.

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basicity constant $K_b = \frac{\left[R\text{-}\overset{+}{N}H_3\right]\left[OH^-\right]}{\left[R\text{-}NH_2\right]}$

The basicity constant Kb gives a measure of the extent to which the amine accepts the hydrogen ion (H^+) from water,

we know that,

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

Table : pK_b values of Amines in Aqueous solution. (pK_b for NH_3 is 4.74)

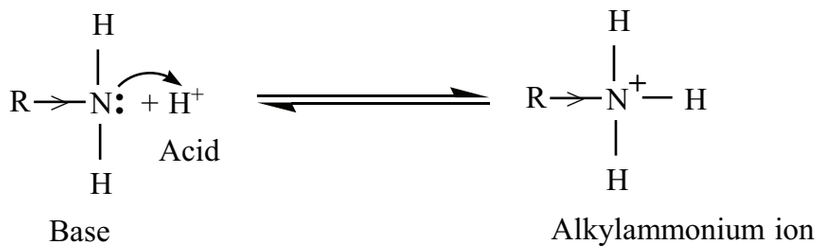
Amines	pK_b	Amines	pK_b	Amines	pK_b
$CH_3-\ddot{N}H_2$	3.38	$C_2H_5\ddot{N}H_2$	3.29	$C_6H_5CH_2-\ddot{N}H_2$	4.70
$(CH_3)_2\ddot{N}H$	3.28	$(C_2H_5)_2\ddot{N}H$	3.00	$C_6H_5-\ddot{N}HCH_3$	9.30
$(CH_3)_3\ddot{N}$	4.22	$(C_2H_5)_3\ddot{N}$	3.25	$C_6H_5\ddot{N}(CH_3)_2$	8.92

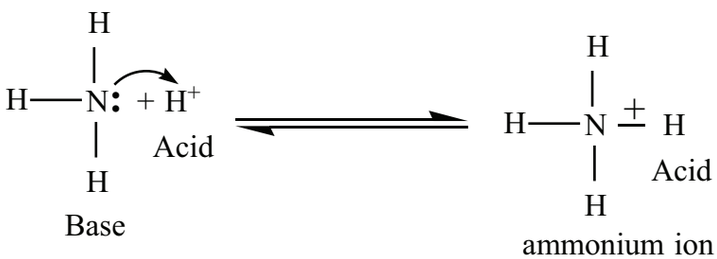
Influence of structure on basic character of amines

The factors which increase the availability of electron pair on nitrogen for sharing with an acid will increase the basic character of an amine. When a +I group like an alkyl group is attached to the nitrogen increase the electron density on nitrogen which makes the electron pair readily available for protonation.

a) Hence alkyl amines are stronger bases than ammonia.

Consider the reaction of an alkyl amine $(R\text{-}\ddot{N}H_2)$ with a proton





The electron – releasing alkyl group R pushes electron towards nitrogen in the amine ($R\text{-}\ddot{N}H_2$) and provide unshared electron pair more available for sharing with proton.

Therefore, the expected order of basicity of aliphatic amines (in gas phase) is

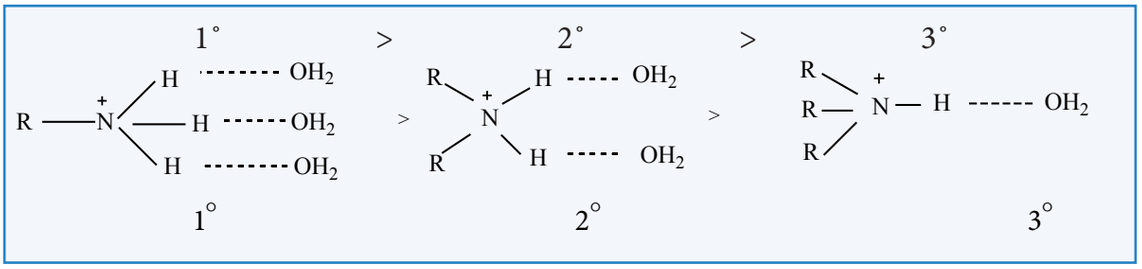
$$\underset{(3^0)}{R_3\ddot{N}} > \underset{(2^0)}{R_2\ddot{N}H} > \underset{(1^0)}{R\text{-}\ddot{N}H_2}$$

The above order is not regular in their aqueous solution as evident by their pKb values given in the table.

To compare the basicity of amines, the inductive effect, solvation effect, steric hindrance, etc., should be taken into consideration.

Solvation effect

In the aqueous solution, the substituted ammonium cations get stabilized not only by electron releasing (+I) effect of the alkyl group but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation. The order of stability of the protonated amines is greater the size of the ion, lesser is the solvation and lesser is the stability. In case of secondary and tertiary amines, due to steric hindrance, the alkyl groups decrease the number of water molecules that can approach the protonated amine. Therefore the order of basicity is,



Based on these effects we can conclude that the order of basic strength in case of alkyl substituted amines in aqueous solution is

$$(CH_3)_2\ddot{N}H > CH_3\text{-}\ddot{N}H_2 > (CH_3)_3\ddot{N} > \ddot{N}H_3$$

$$(C_2H_5)_2\ddot{N}H > (C_2H_5)_3\ddot{N} > C_2H_5\ddot{N}H_2 > \ddot{N}H_3$$

The resultant of +I effect, steric effect and hydration effect cause the 2^0 amine, more basic.

Basic strength of aniline

In aniline, the NH_2 group is directly attached to the benzene ring. The lone pair of electron on nitrogen atom in aniline gets delocalised over the benzene ring and hence it is less available for protonation makes the, aromatic amines (aniline) less basic than NH_3.

In case of substituted aniline, electron releasing groups like $-CH_3$,$-OCH_3$,$-NH_2$ increase the basic strength and electron withdrawing group like $-NO_2$,-X,-COOH decrease the basic strength.

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Table pK_b's of substituted anilines (pK_b value of aniline is 9.376)

Substituent	pK_b	Substituent	pK_b	Substituent	pK_b
o - CH_3	9.60	m - CH_3	9.31	p - CH_3	8.92
o - NH_2	9.52	m - NH_2	9.00	P - NH_2	7.83
o - OCH_3	9.52	m - OCH_3	9.70	p - OCH_3	8.70
o - NO_2	14.30	m - NO_2	11.52	p - NO_2	13.00
o - Cl	11.25	m - Cl	10.52	p - Cl	10.00

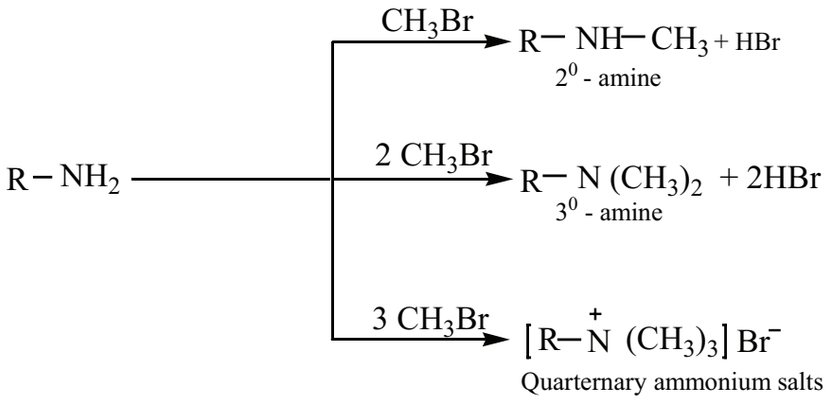
The relative basicity of amines follows the below mentioned order

Alkyl amines > Aralkyl amines > Ammonia > N – Aralkyl amines > Aryl amines

13.2.6 Chemical properties of amines

1) Alkylation

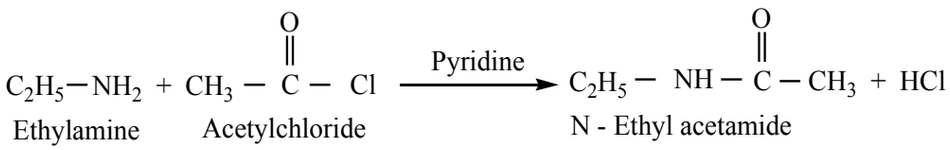
Amines reacts with alkyl halides to give successively 2^0 and 3^0 amines and quaternary ammonium salts.



2) Acylation

Aliphatic / aromatic primary and secondary amines react with acetyl chloride (or) acetic anhydride in presence of pyridine to form N – alkyl acetamide.

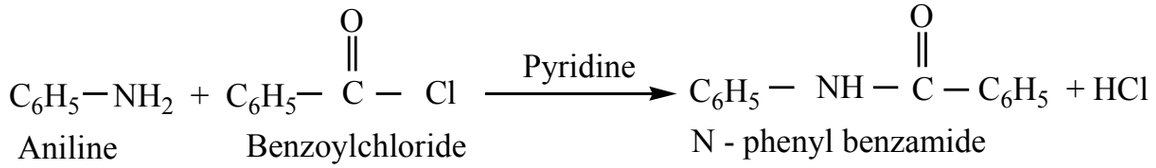
Example



3) Schotten – Baumann reaction

Aniline reacts with benzoylchloride (C_6H_5COCl) in the presence of NaOH to give N – phenyl benzamide. This reaction is known as Schotten – Baumann reaction. The acylation and benzoylation are nucleophilic substitutions.

XII U13-Organic Nitrogen Compounds.indd 214 16-12-2022 19:45:21



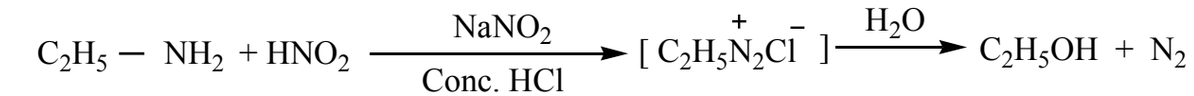
Aniline — Benzoylchloride — N - phenyl benzamide

4) Reaction with nitrous acid

Three classes of amines react differently with nitrous acid which is prepared in situ from a mixture of $NaNO_2$ and HCl .

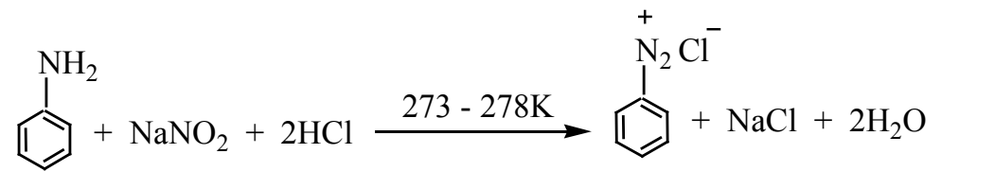
a) primary amines

i) Ethylamine reacts with nitrous acid to give ethyl diazonium chloride, which is unstable and it is converted to ethanol by liberating N_2.



Ethylamine — Unstable — Ethanol

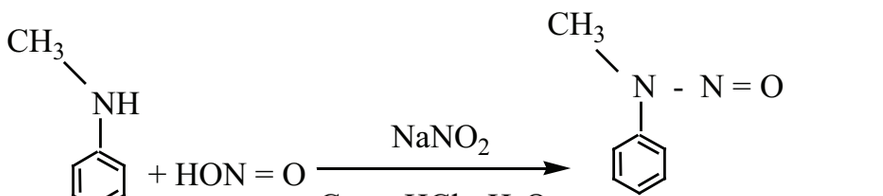
ii) Aniline reacts with nitrous acid at low temperature (273 – 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes even at low temperatures. This reaction is known as diazotization.



Aniline — Benzenediazonium chloride

b) secondary amines

Alkyl and aryl secondary amines react with nitrous acid to give N – nitroso amine as yellow oily liquid which is insoluble in water.



N - methylaniline — N - NitrosoN-methyl phenyl amine (yellow oil)

This reaction is known as Libermann's nitroso test,

c) Teritiary amine

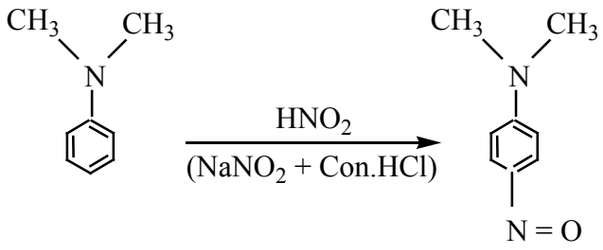
i) Aliphatic tertiary amine reacts with nitrous acid to form trialkyl ammonium nitrite salt, which is soluble in water.

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$$(CH_3)_3N + HNO_2 \longrightarrow [(CH_3)_3\overset{+}{N}H]\ NO_2^-$$

trimethylamine — trimethyl ammonium nitrite

ii) Aromatic tertiary amine reacts with nitrous acid at 273K to give p – nitroso compound.



N, N - dimethyl aniline — p - Nitroso N,N - dimethyl aniline

5) Carbylamine reaction

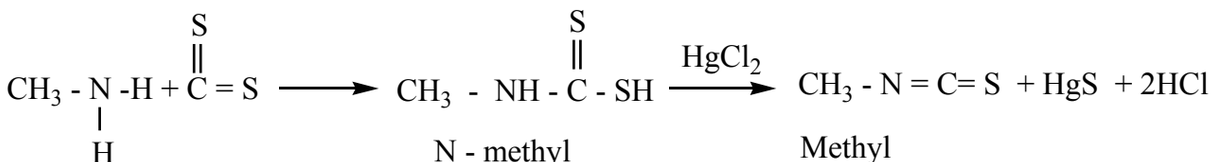
Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamine test. This test used to identify the primary amines.

$$C_2H_5 - NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5 - NC + 3KCl + 3H_2O$$

Ethylamine — Chloroform — Ethylisocyanide

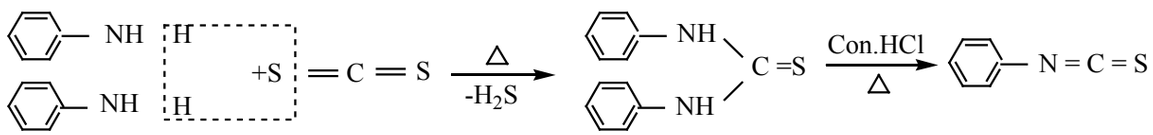
6) Mustard oil reaction

i) When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbamic acid is formed which on subsequent treatment with $HgCl_2$, give an alkyl isothiocyanate.



Methylamine — N - methyl dithiocarbamic acid — Methyl isothiocyanate (Mustard oil smell)

ii) When aniline is treated with carbon disulphide, or heated together, S- diphenylthio urea is formed, which on boiling with strong HCl, phenyl isothiocyanate (phenyl mustard oil), is formed.



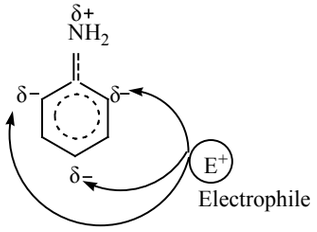
Aniline — S - diphenyl thiourea — Phenyl isothiocyanate

These reactions are known as Hofmann – Mustard oil reaction. This test is used to identify the primary amines.

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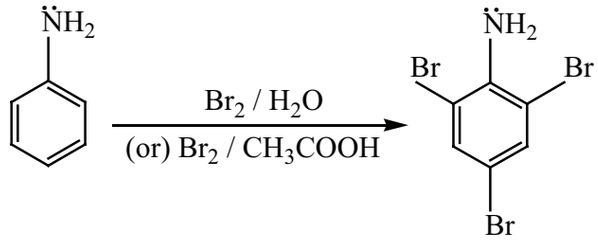
7. Electrophilic substitution reactions in Aniline

The $-\ddot{N}H_2$ group is a strong activating group. In aniline the NH_2 group is directly attached to the benzene ring, the lone pair of electrons on the nitrogen is in conjugation with benzene ring which increases the electron density at ortho and para position, thereby facilitating the electrophilic attack at ortho and para positions.



i) Bromination

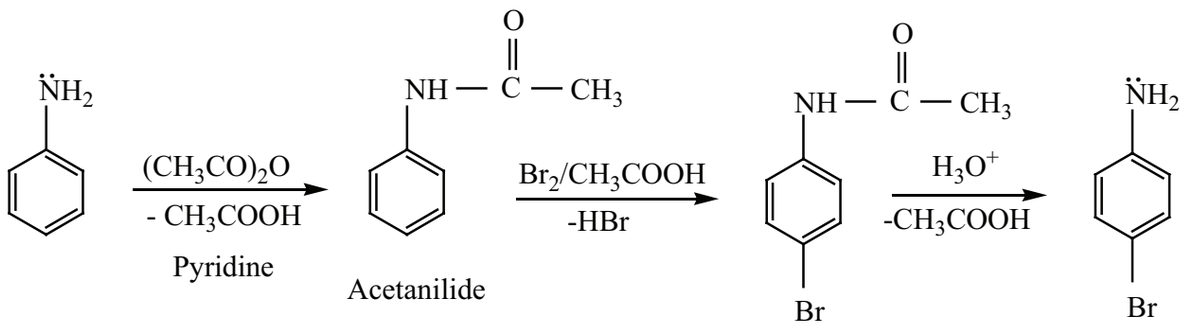
Aniline reacts with Br_2 / H_2O to give 2,4,6 – tribromo aniline a white precipitate.



Aniline

2,4,6, tribromo aniline
(white precipitate)

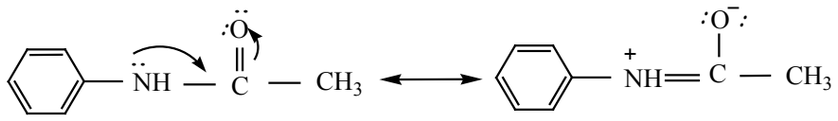
To get mono bromo compounds, - NH_2 is first acylated to reduce its activity.



p - bromo acetanilide

p-bromo aniline
(Major product)

When aniline is acylated, the lone pair of electron on nitrogen is delocalised by the neighbouring carbonyl group by resonance. Hence it is not easily available for conjugation with benzene ring.

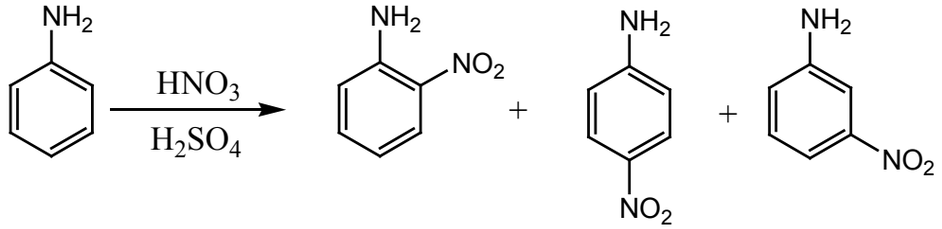


The acetylamino group is thus less activating than the amino group in electrophilic substitution reaction.

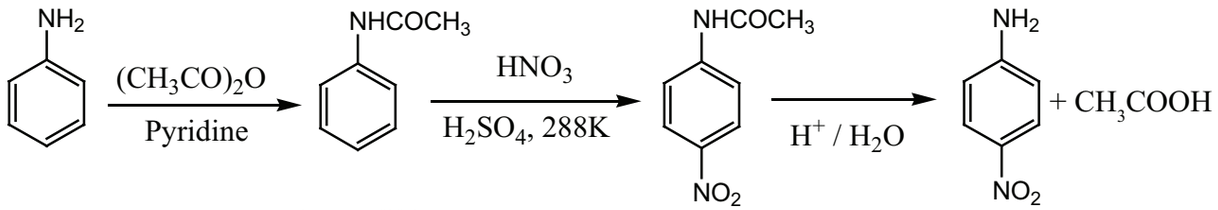
XII U13-Organic Nitrogen Compounds.indd 217 16-12-2022 19:45:22

ii) Nitration

Direct nitration of aniline gives o and p – nitro aniline along with dark coloured 'tars' due to oxidation. Moreover in a strong acid medium aniline is protonated to form anilinium ion which is m – directing and hence m – nitro aniline is also formed.



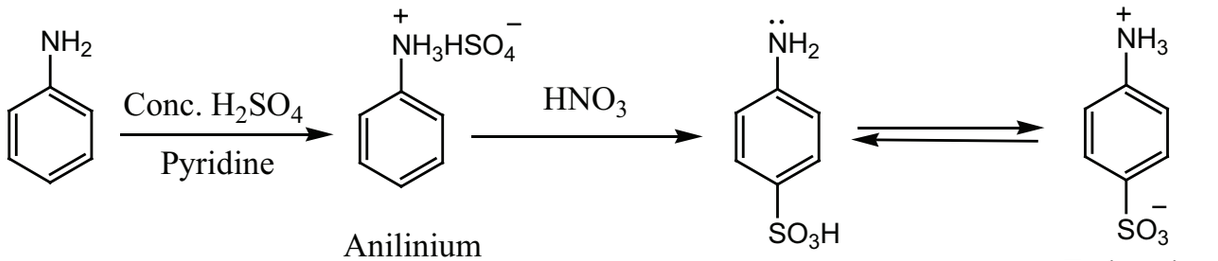
To get para product, the - NH_2 group is protected by acetylation with acetic anhydride. Then, the nitrated product is hydrolysed to form the product.



Acetanilide — P-nitroacetanilide — p-nitro aniline

iii) Sulphonation

Aniline reacts with Conc. H_2SO_4 to form anilinium hydrogen sulphate which on heating with H_2SO_4 at 453 – 473K gives p- aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.



Anilinium hydrogensulphate — Sulphanilic acid — Zwitter ion

iv) Aniline

It does not under go Friedel – Crafts reaction (alkylation and acetylation) we know aniline is basic in nature and it donates its lone pair to the lewis acid $AlCl_3$ to form an adduct which inhibits further the electrophilic substitution reaction.

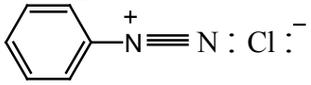
13.3 DIAZONIUM SALTS

13.3.1 Introduction

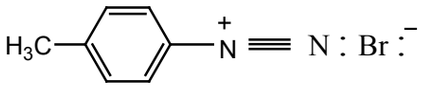
We have just learnt that aromatic amines on treatment with $(NaNO_2+HCl)$ gives diazonium salts. They are stable only for a short time and hence are used immediately after preparation.

XII U13-Organic Nitrogen Compounds.indd 218 16-12-2022 19:45:24

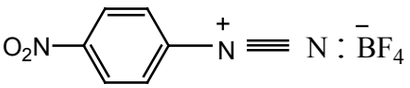
Example



Benzenediazonium Chloride



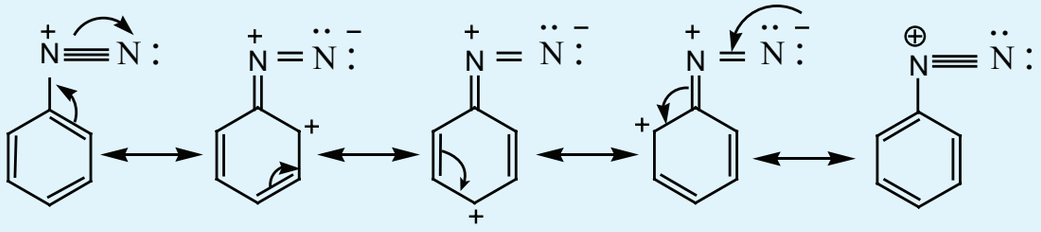
p - Toluenediazonium Bromide



p- Nitrobenzenediazonium tetra fluoroborate

13.3.2 Resonance structure

The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring.



Resonating structures of benzenediazonium salt

13.3.3 Method of preparation of Diazonium salts

We have already learnt that benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid (Which is produced by the reaction of $NaNO_2$ and HCl) at 273 – 278K

13.3.4 Physical properties

- Benzene diazonium chloride is a colourless, crystalline solid.
- These are readily soluble in water and stable in cold water. However it reacts with warm water.
- Their aqueous solutions are neutral to litmus and conduct electricity due to the presence to ions.
- Benzenediazonium tetrafluoro borate is soluble in water and stable at room temperature.

13.3.5 Chemical reactions

Benzene diazoniumchloride gives two types of chemical reactions

A. Replacement reactions involving loss of nitrogen

In these reactions diazonium group is replaced by nucleophiles such as X^-,CN^-,H^-,OH^- etc.,

B. Reactions involving retention of diazogroup.

Coupling reaction.

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A. Replacement reactions involving loss of nitrogen

1. Replacement by hydrogen

Benzene diazonium chloride on reduction with mild reducing agents like hypophosphrous acid (phosphinic acid) or ethanol in the presence of cuprous ion gives benzene. This reaction proceeds through a free-radical chain mechanism.

$$C_6H_5\text{-}\overset{+}{N}_2\,Cl^- + H_3PO_2 + H_2O \xrightarrow{CuCl} C_6H_6 + H_3PO_3 + HCl + N_2\uparrow$$

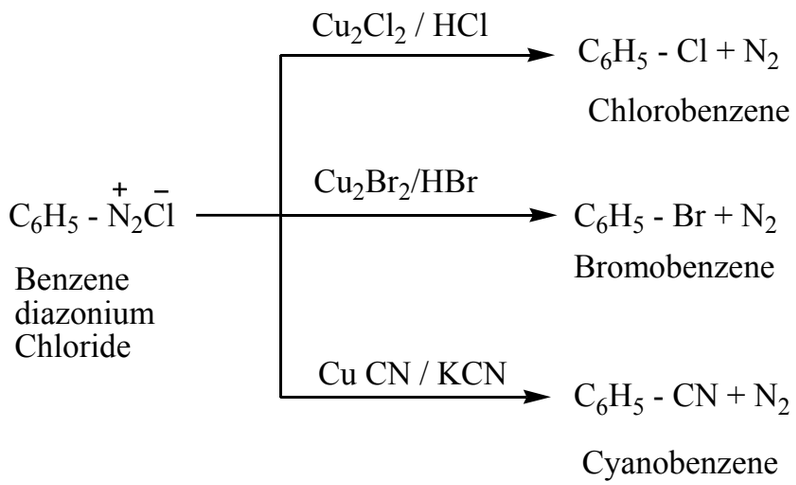
$$C_6H_5\text{-}\overset{+}{N}_2\,Cl^- + CH_3CH_2OH \rightarrow C_6H_6 + N_2 + CH_3CHO + HCl$$

2. Replacement by Chlorine, Bromine, Cyanide group

a) Sandmeyer reaction

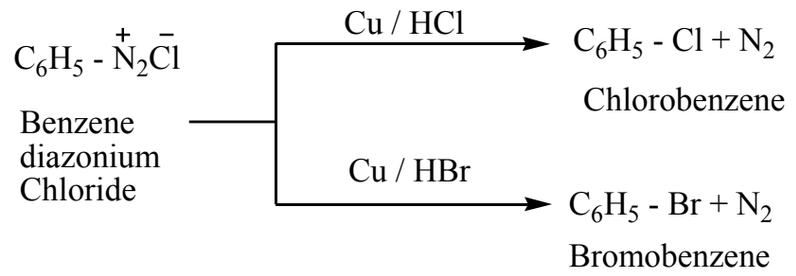
On mixing freshly prepared solution of benzene diazonium chloride with cuprous halides (chlorides and bromides), aryl halides are obtained. This reaction is called Sandmeyer reaction.

When diazonium salts are treated with cuprous cyanide, cyanobenzene is obtained.



b) Gattermann reaction

Conversion of benzene diazonium chloride into chloro / bromo arenes can also be effected using hydrochloric / hydrobromic acid and copper powder. This reaction is called Gattermann reaction.



The yield in Sandmeyer reaction is found to be better than the Gattermann reaction.

3. Replacement by iodine

Aqueous solution of benzene diazonium chloride is warmed with KI to form iodobenzene

XII U13-Organic Nitrogen Compounds.indd 220 16-12-2022 19:45:25

$$C_6H_5\text{-}\overset{+}{N}_2Cl^- + KI \rightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + KCl + N_2$$

4. Replacement of fluorine (Baltz – schiemann reaction)

When benzene diazonium chloride is treated with fluoroboric acid, benezene diazonium tetra fluoroborate is precipitated which on heating decomposes to give fluorobenzene.

$$\underset{\substack{\text{Fluoroboric}\\ \text{acid}}}{C_6H_5\text{-}\overset{+}{N}_2Cl^- + HBF_4} \longrightarrow \underset{\substack{\text{Benzenediazonium}\\ \text{fluoroborate}}}{C_6H_5\text{-}\overset{+}{N}_2BF_4^-} \xrightarrow{\Delta} \underset{\text{Fluorobenzene}}{C_6H_5\text{-}F} + BF_3 + N_2$$

5. Replacement by hydroxyl group

Benzene diazonium chloride solution is added slowly to a large volume of boiling water to get phenol.

$$C_6H_5\text{-}N_2Cl + H_2O \xrightarrow[283K]{\Delta} \underset{\text{Phenol}}{C_6H_5\text{-}OH} + N_2 + HCl$$

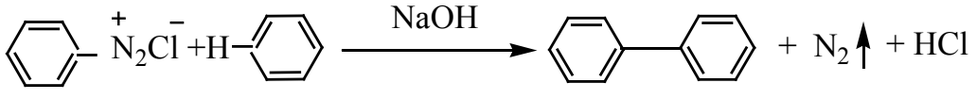
6. Replacement by nitrogroup

When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-NO_2$ group.

$$\underset{\substack{\text{Fluoroboric}\\ \text{acid}}}{C_6H_5\text{-}\overset{+}{N}_2Cl^- + HBF_4} \longrightarrow C_6H_5\text{-}\overset{+}{N}_2BF_4^- \xrightarrow[Cu,\ \Delta]{NaNO_2} \underset{\text{Nitrobenzene}}{C_6H_5\text{-}NO_2} + N_2 + NaBF_4$$

7. Replacement by aryl group (Gomberg reaction)

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



Benzene — Biphenyl

8. Replacement by carboxylic acid group

When diazonium fluoroborate is heated with acetic acid, benzoic acid is obtained. This reaction is used to convert the of aliphatic carboxylic acid into aromatic carboxylic acid.

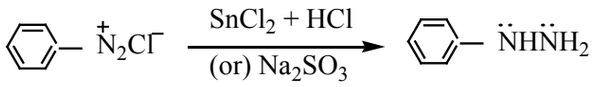
$$\underset{\substack{\text{Benzene diazonium}\\ \text{fluoroborate}}}{C_6H_5\text{-}N_2BF_4} + CH_3\text{-}COOH \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5\text{-}COOH} + BF_3 + CH_3F + N_2$$

XII U13-Organic Nitrogen Compounds.indd 221 16-12-2022 19:45:25

B. Reactions involving retention of diazo group

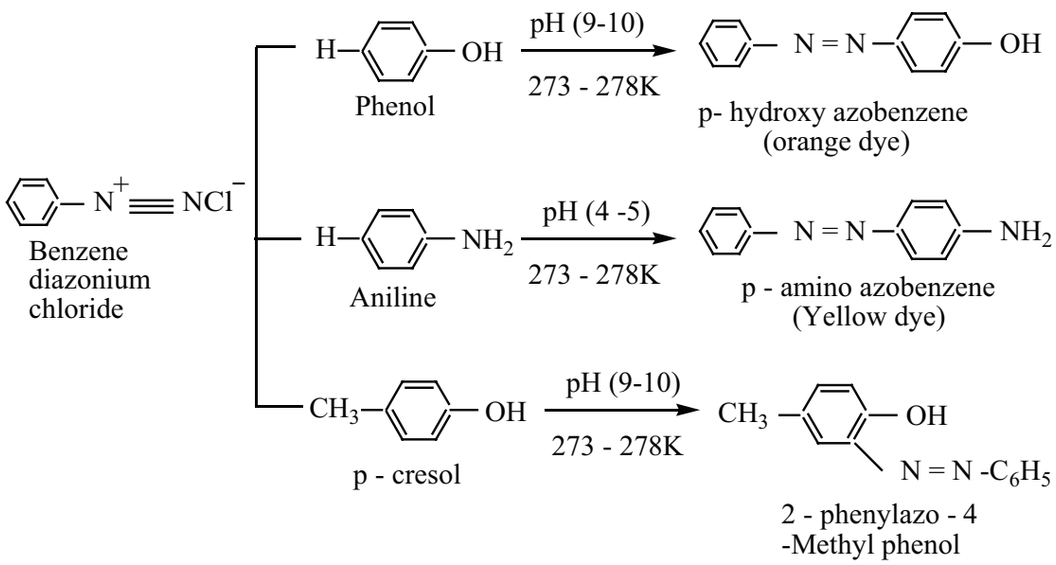
9. Reduction to hydrazines

Certain reducing agents like $SnCl_2$ / HCl; Zn dust / CH_3COOH, sodium hydrosulphite, sodium sulphite etc. reduce benzene diazonium chloride to phenyl hydrazine.



10. Coupling reactions

Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds. Coupling generally occurs at the para position. If para position is occupied then coupling occurs at the ortho position. Coupling tendency is enhanced if an electron donating group is present at the para – position to $-N_2^+Cl^-$ group. This is an electrophilic substitution.



Aryl fluorides and iodides cannot be prepared by direct halogenation and the cyano group cannot be introduced by nucleophilic substitution of chlorine in chlorbenzene. For introducing such a halide group, cyano group -OH, NO_2 etc.. benzenediazonium chloride is a very good intermediate Diazo compounds obtained from the coupling reactions of diazonium salts are coloured and are used as dyes.

13.4 CYANIDES AND ISOCYANIDES

13.4.1 Introduction

These are the derivatives of hydrocyanic acid (HCN), and is known to exist in two tautomeric forms

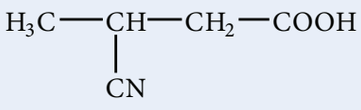
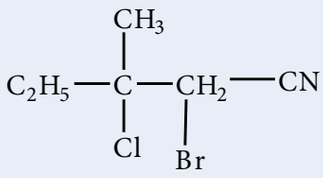


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Two types of alkyl derivatives can be obtained. Those derived by replacement of H – atom of hydrogen cyanide by the alkyl groups are known as alkyl cyanides (R-C ≡ N). and those obtained by the replacement of H – atom of hydrogen isocyanide are known as alkyl isocyanides (R-N ⟹ C)

In IUPAC system, alkyl cyanides are named as "alkanenitriles" whereas aryl cyanides as " arenecarbonitrile".

Table : Nomenclature of cyanides

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
acetonitrile CH_3-CN Ethane nitrile	–	Eth	ane	nitrile
Propiononitrile CH_3CH_2-CN Propanenitrile	–	Prop	ane	nitrile
Butyronitrile $CH_3CH_2CH_2$-CN butanenitrile	–	But	ane	nitrile
Isobutronitrile  2-methylpropanenitrile	2-methyl–	prop	ane	nitrile
Benzonitrile C_6H_5-CN Benzene Carbonitrile	–	Benzene	Carbo	nitrile
 3-Cyanobutanoicacid	3-Cyano	but	ane	oicacid
 2-Bromo-3-chloro-3- methyl pentanenitrile.	2-Bromo-3-chloro-3- methyl	pent	ane	nitrile

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13.4.2 Methods of preparation of cyanides

1) From alkyl halides

When alkyl halides are treated in the solution NaCN (or) KCN , alkyl cyanides are obtained. In this reaction a new carbon – carbon bond is formed.

Example

$$KCN + CH_3CH_2 - Br \longrightarrow CH_3CH_2 - CN + KBr$$

Ethyl bromide — Propanenitrile

Aryl cyanide cannot be prepared in this method because of their less reactivity towards nucleophilic substitution. Aryl cyanides are prepared using Sandmeyers reactions.

2. By dehydration of primary amides and aldoximes with P_2O_5

$$CH_3 - CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3 - CN$$

Acetamide — Ethanenitrile

$$CH_3 - CH{=}NOH \xrightarrow[-H_2O]{P_2O_5} CH_3 - CN$$

Acetaldoximes

3. By dehydration of ammonium carboxylates with P_2O_5

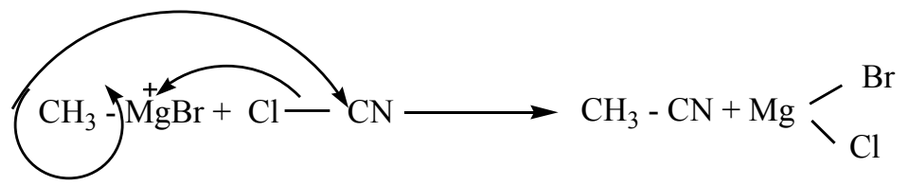
$$CH_3 - COONH_4 \xrightarrow[\Delta]{P_2O_5} CH_3 - CN + 2H_2O$$

Ammonium acetate — Ethanenitrile

This method suitable for large scale preparation of alkyl cyanides.

4. From Grignard reagent

Methyl magnesium bromide on treatment with cyanogen chloride (Cl - CN) forms ethanenitrile.



methyl magnesium bromide — ethanenitrile

13.4.3 Properties Of Cyanides

Physical Properties

The lower members (up to C_{14}) are colourless liquids with a strong characteristic sweet smell. The higher members are crystalline solids, They are moderately soluble in water but freely souble in organic solvents. They are poisonous.

They have higher boiling points than analogous acetylenes due to their high dipole moments.

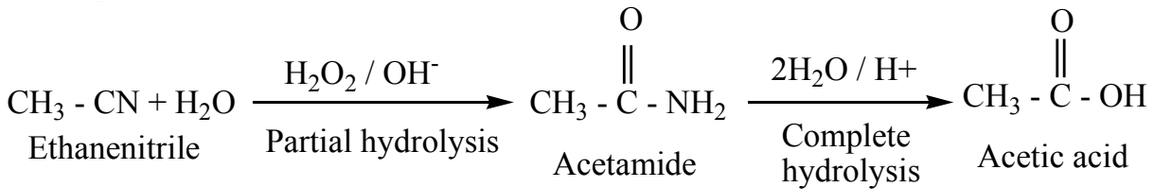
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13.4.4 Chemical properties

1. Hydrolysis

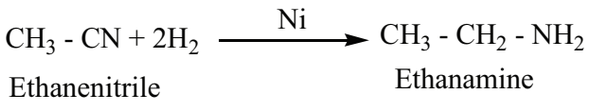
On boiling with alkali (or) a dilute mineral acid, the cyanides are hydrolysed to give carboxylic acids.

For example



2. Reduction

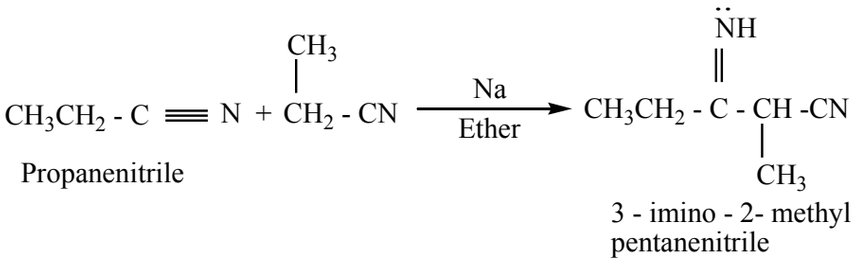
On reduction with $LiAlH_4$ (or) Ni / H_2, alkyl cyanides yields primary amines.



3. Condensation reaction

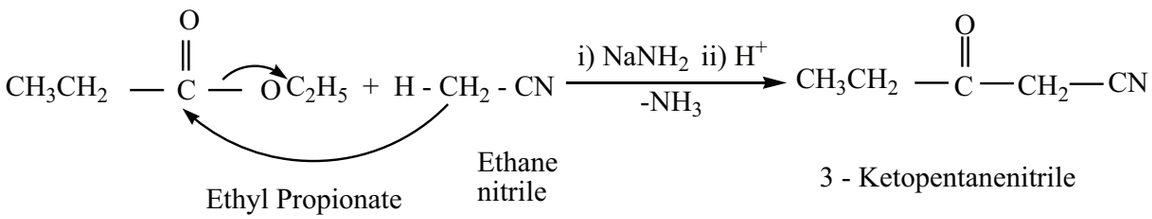
a) Thorpe nitrile condensation

Self condensation of two molecules of alkyl nitrile (containing α–H atom) in the presence of sodium to form iminonitrile.



b) The nitriles containing α-**hydrogen** also undergo condensation with esters in the presence of sodamide in ether to form ketonitriles. This reaction is known as " Levine and Hauser" acetylation

This reaction involves replacement of ethoxy (OC_2H_5) group by methylnitrile $(-CH_2CN)$ group and is called as cyanomethylation reaction.



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13.4.5 Alkyl Isocyanides (Carbylamines)

Nomenclature of isocyanides

They are commonly named as Alkyl isocyanides. The IUPAC system names them as alkylcarbylamines

Table : Nomenclature of alkylisocyanides

Structural formula	Common name	IUPAC name
$CH_3 — NC$	Methyl isocyanide	Methylcarbylamine
$CH_3CH_2 — NC$	Ethylisocyanide	Ethylcarbylamine
$CH_3CH_2CH_2 — NC$	Propyl isocyanide	Propylcarbylamine
$C_6H_5 — NC$	Phenyl isocynaide	Phenylcarbylamine

13.4.6 Methods of preparation of isocyanides

1. From primary amines (carbylamines reaction)

Both aromatic as well as aliphatic amines on treatment with $CHCl_3$ in the presence of KOH give carbylamines

$$\underset{\text{Methylamine}}{CH_3—NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{Methyl isocyanide}}{CH_3 — N \equiv C} + 3KCl + 3H_2O$$

$$\underset{\text{Aniline}}{C_6H_5—NH_2} + CH.Cl_3 + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5 — N \equiv C} + 3KCl + 3H_2O$$

2. From alkyl halides

Ethyl bromide on heating with ethanolic solution of AgCN give ethyl isocyanide as major product and ethyl cyanide as minor product.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2 — Br} + AgCN \xrightarrow[\text{heat}]{C_2H_5OH} \underset{\text{Ethyl isocyanide}}{CH_3CH_2 - NC} + AgBr$$

3. From N – alkyl formamide. By reaction with $POCl_3$ in pyridine.

$$CH_3 — NH — \overset{\overset{O}{\|}}{C} — H \xrightarrow[\text{(Pyridine)}]{POCl_3} CH_3 — N \equiv C + H_2O$$

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13.4.7 Properties of isocyanides

Physical properties

- They are colourless, highly unpleasant smelling volatile liquids and are much more poisonous than the cyanides.
- They are only slightly soluble in water but are soluble in organic solvents.
- They are relatively less polar than alkyl cyanides. Thus, their melting point and boiling point are lower than cyanides.

13.4.8 Chemical properties

1) **Hydrolysis**: Alkyl isocyanides are not hydrolysed by alkalies. However they are hydrolysed with dilute mineral acids to give primary amines and formic acids.

$$CH_3 - NC + 2H_2O \xrightarrow{\text{acid}} CH_3 - NH_2 + HCOOH$$

Methyl isocyanide — Methylamine — Formicacid

2. **Reduction:** When reduced catalytically (or) by nascent hydrogen, they give secondary amines.

$$CH_3 - NC + 4[H] \xrightarrow[\text{(or) } Ni / H_2]{Na / C_2H_5OH} CH_3 - NH - CH_3$$

Methyl isocyanide — Dimethylamine

3. **Isomerisation:** When Alkyl isocyanides and heated at 250^0C, they change into the more stable, isomeric cyanides

$$CH_3 - N \equiv C \xrightarrow[250^0C]{\text{Heat}} CH_3 - C \equiv N:$$

Methyl isocyanide — Methylcyanide

4. **Addition reaction**. Alkyl isocyanides add on halogen, sulphur, and oxygen to form the corresponding addition compounds.

a) $R - N \equiv C + X_2 \longrightarrow R - \ddot{N} = C\begin{matrix} X \\ X \end{matrix}$

b) $R - N \equiv C + S \longrightarrow R - \ddot{N} = C = S$

Alkyl isothiocyanate

c) $R - N \equiv C + O \xrightarrow[\text{(or) } O_3]{2HgO} R - \ddot{N} = C = O + Hg_2O$

Alkyl isocyanate

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13.4.9 Uses of organic nitrogen compounds

nitroalkanes

1. Nitromethane is used as a fuel for cars
2. Chloropicrin (CCl_3NO_2) is used as an insecticide
3. Nitroethane is used as a fuel additive and precursor to explosive and they are good solvents for polymers, cellulose ester, synthetic rubber and dyes etc.,
4. 4% solution of ethylnitrite in alcohol is known as sweet spirit of nitre and is used as diuretic.

nitrobenzene

1 Nitrobenzene is used to produce lubricating oils in motors and machinery.

2 It is used in the manufacture of dyes, drugs, pesticides, synthetic rubber, aniline and explosives like TNT, TNB.

cyanides and isocyanides

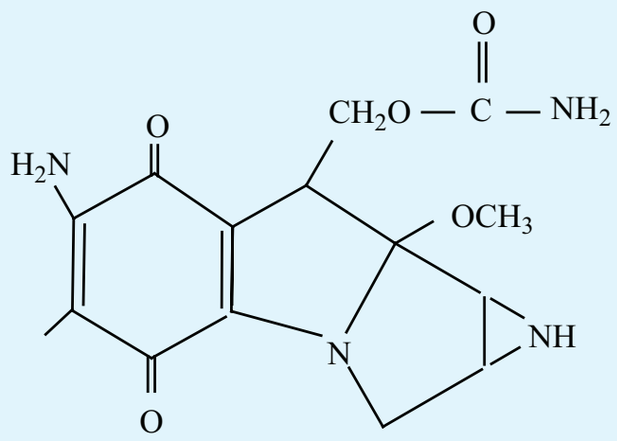
1. Alkyl cyanides are important intermediates in the organic synthesis of larger number of compounds like acids, amides, esters, amines etc.

2 Nitriles are used in textile industry in the manufacture of nitrile rubber and also as a solvent particularly in perfume industry.



Cancer Drug

Mitomycin C, and anticancer agent used to treat stomach and colon cancer, contains an aziridine ring. The aziridine functional group participates in the drug's degradation by DNA, resulting in the death of cancerous cells.



Mitomycin

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EVALUATION

Choose the correct answer:

1. Which of the following reagent can be used to convert nitrobenzene to aniline

   a) Sn / HCl b) ZnHg / NaOH c) Zn/NH_4Cl d) All of these

2. The method by which aniline cannot be prepared is

   a) degradation of benzamide with Br_2 / NaOH

   b) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

   c) reduction of Nitrobenzene with $LiAlH_4$

   d) reduction of nitrobenzene by Sn / HCl.

3. Which one of the following will not undergo Hofmann bromamide reaction

   a) $CH_3CONHCH_3$ b) $CH_3CH_2CONH_2$

   c) CH_3CONH_2 d) $C_6H_5CONH_2$

4. Assertion : Acetamide on reaction with KOH and bromine gives acetic acid

   Reason : Bromine catalyses hydrolysis of acetamide.

   a) if both assertion and reason are true and reason is the correct explanation of assertion.

   b) if both assertion and reason are true but reason is not the correct explanation of assertion.

   c) assertion is true but reason is false

   d) both assertion and reason are false.

5. $CH_3CH_2Br \xrightarrow[\Delta]{\text{aq NaOH}} A \xrightarrow[\Delta]{KMnO_4/H^+} B \xrightarrow[\Delta]{NH_3} C \xrightarrow{Br_2/NaOH} D$ 'D' is

   a) bromomethane b) α - bromo sodium acetate

   c) methanamine d) acetamide



6. Which one of the following nitro compounds does not react with nitrous acid

   a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}NO_2$ b) $(CH_3)_2CH\text{-}CH_2NO_2$

   c) $(CH_3)_3C\,NO_2$ d) $CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-NO_2$

7. Aniline + benzoylchloride $\xrightarrow{NaOH}$ $C_6H_5\text{-}NH\text{-}COC_6H_5$ this reaction is known as

   a) Friedel – crafts reaction b) HVZ reaction

   c) Schotten – Baumann reaction d) none of these

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8. The product formed by the reaction an aldehyde with a primary amine (NEET)

a) carboxylic acid b) aromatic acid

c) schiff's base d) ketone

9. Which of the following reaction is not correct.

a) $CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH + N_2$

b) $(CH_3)_2N$–C$_6$H$_4$ $\xrightarrow{NaNO_2 / HCl}$ $(CH_3)_2N$–C$_6$H$_4$–N = NCl

c) $CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$ d) none of these

10. When aniline reacts with acetic anhydride the product formed is

a) o – aminoacetophenone b) m-aminoacetophenone

c) p – aminoacetophenone d) acetanilide

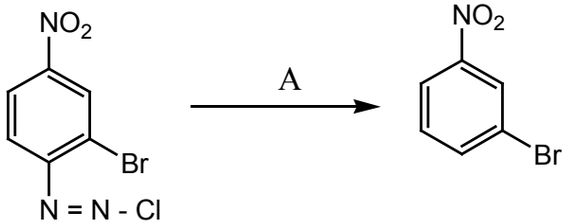
11. The order of basic strength for methyl substituted amines in aqueous solution is

a) $N(CH_3)_3 > N(CH_3)_2H > N(CH_3)H_2 > NH_3$

b) $N(CH_3)H_2 > N(CH_3)_2H > N(CH_3)_3 > NH_3$

c) $NH_3 > N(CH_3)H_2 > N(CH_3)_2H > N(CH_3)_3$

d) $N(CH_3)_2H > N(CH_3)H_2 > N(CH_3)_3 > NH_3$

12. 

'A' is (NEET)

a) H_3PO_2 and H_2O b) H^+ / H_2O

c) $HgSO_4 / H_2SO_4$ d) Cu_2Cl_2

13. $C_6H_5NO_2 \xrightarrow{Fe / Hcl} A \xrightarrow[273K]{NaNO_2 / HCl} B \xrightarrow[283K]{H_2O} C$ 'C' is

a) C_6H_5- OH b) C_6H_5 - CH_2OH

c) C_6H_5 - CHO d) $C_6H_5NH_2$

14. Nitrobenzene on reaction with Con HNO_3 / H_2SO_4 at 80-100°C forms which one of the following products?

a) 1,4 – dinitrobenzene b) 2,4,6 – tirnitrobenzene

c) 1,2 – dinitrobenzene d) 1,3 – dinitrobenzene

15. $C_5H_{13}N$ reacts with HNO_2 to give an optically active compound – The compound is

a) pentan – 1- amine b) pentan – 2- amine

c) N,N – dimethylpropan -2-amine d) diethyl methyl amine

16. Secondary nitro alkanes react with nitrous acid to form

a) red solution b) blue solution c) green solution d) yellow solution

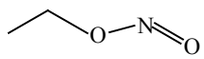
17. Which of the following amines does not undergo acetylation?

a) t – butylamine b) ethylamine c) diethylamine d) triethylamine

18. Which one of the following is most basic?

a) 2,4 – dichloroaniline b) 2,4 – dimethyl aniline

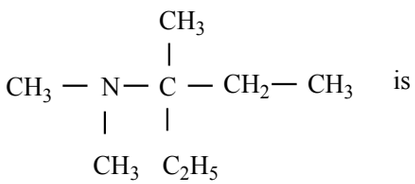
c) 2,4 – dinitroaniline d) 2,4 – dibromoaniline

19. When  is reduced with Sn / HCl the pair of compounds formed are

a) Ethanol, hydroxylamine hydrochloride b) Ethanol, ammonium hydroxide

c) Ethanol, . NH_2OH . d) $C_3H_5NH_2$, H_2O

20. IUPAC name for the amine

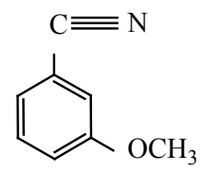
 is

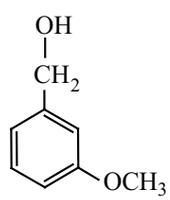
a) 3 – Bimethylamino – 3 – methyl pentane

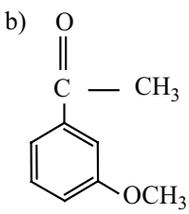
b) 3 (N,N – Triethyl) – 3- amino pentane

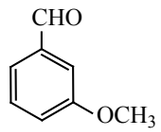
c) 3 – N,N – trimethyl pentanamine

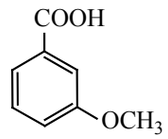
d) N,N – dimethyl – 3- methyl - pentan - 3 amine

21.  $+ CH_3MgBr \xrightarrow{H_3O^+}$ P Product 'P' in the above reaction is

a) 

b) 

c) 

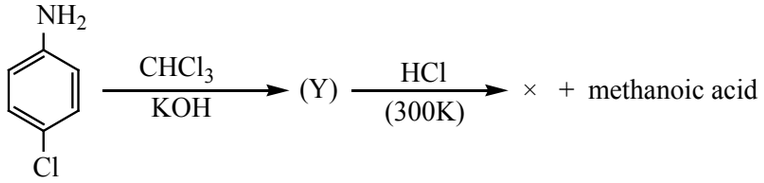
d) 

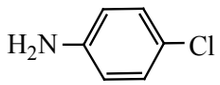
22. Ammonium salt of benzoic acid is heated strongly with P_2O_5 and the product so formed is reduced and then treated with $NaNO_2$ / HCl at low temperature. The final compound formed is

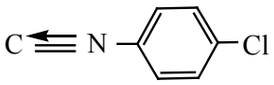
a) Benzene diazonium chloride b) Benzyl alcohol

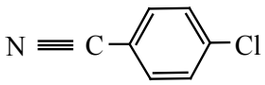
c) Phenol d) Nitrosobenzene

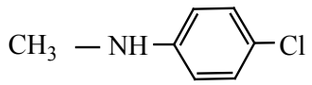
23. Identify X in the sequence given below.



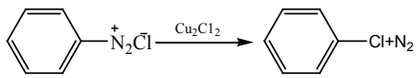
a) 

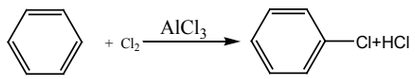
b) 

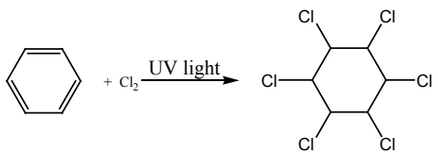
c) 

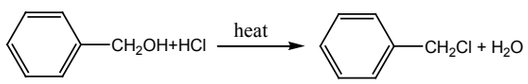
d) 

24. Among the following, the reaction that proceeds through an electrophilic substitution, is :

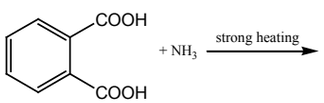
a) 

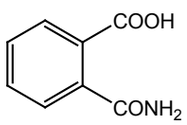
b) 

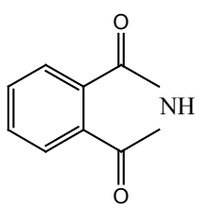
c) 

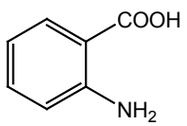
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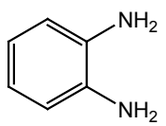
25. The major product of the following reaction



a) 

b) 

c) 

d) 

Short answer Questions

1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names
2. There are two isomers with the formula CH_3NO_2. How will you distinguish between them?
3. What happens when
   i. 2 – Nitropropane boiled with HCl
   ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.
   iii. Oxidation of tert – butylamine with $KMnO_4$
   iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.
4. How will you convert nitrobenzene into
   i. 1,3,5 - trinitrobenzene
   ii. o and p- nitrophenol
   iii. m – nitro aniline
   iv. azoxybenzene
   v. hydrozobenzene
   vi. N – phenylhydroxylamine
   vii. aniline
5. Identify compounds A,B and C in the following sequence of reactions.

i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

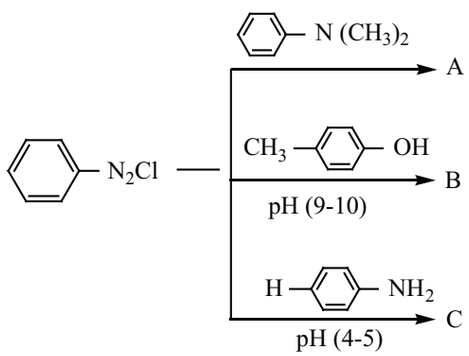
ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O\,/\,H^+} B \xrightarrow{NH_3} C$

iii) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

iv) $CH_3NH_2 \xrightarrow{CH_3\ Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

v) $C_6H_5NH_2 \xrightarrow[\text{pyridine}]{(CH_3CO)_2O} A \xrightarrow[H_2SO_4,288K]{HNO_3} B \xrightarrow{H_2O\,/\,H^+} C$

vi)



vii) $CH_3CH_2NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[ii)H_2O]{i)NaNO_2\ /\ HCl} C$

6. Write short notes on the following
   i. Hofmann's bromide reaction
   ii. Ammonolysis
   iii. Gabriel phthalimide synthesis
   iv. Schotten – Baumann reaction
   v. Carbylamine reaction
   vi. Mustard oil reaction
   vii. Coupling reaction
   viii. Diazotisation
   ix. Gomberg reaction
7. How will you distinguish between primary secondary and tertiary alphatic amines.
8. Account for the following
   i. Aniline does not undergo Friedel – Crafts reaction
   ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines
   iii. pK_b of aniline is more than that of methylamine
   iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.
   v. Ethylamine is soluble in water whereas aniline is not
   vi. Amines are more basic than amides
   vii. Although amino group is o – and p – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m – nitroaniline.
9. Arrange the following
   i. In increasing order of solubility in water, $C_6H_5NH_2$,$(C_2H_5)_2NH$,$C_2H_5NH_2$
   ii. In increasing order of basic strength
   a) aniline, p- toludine and p – nitroaniline
   b) $C_6H_5NH_2$,$C_6H_5NHCH_3$,p-Cl-C_6H_4-NH_2
   iii. In decreasing order of basic strength in gas phase
   $(C_2H_5)NH_2$,$(C_2H_5)_2NH$,$(C_2H_5)_3$ N and NH_3
   iv. In increasing order of boiling point
   C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$
   v. In decreasing order of the pK_b values
   $C_2H_5NH_2$, $C_6H_5NHCH_3$,$(C_2H_5)_2NH$ and CH_3NH_2
   vi. Increasing order of basic strength
   $C_6H_5NH_2$,$C_6H_5N(CH_3)_2$,$(C_2H_5)_2$ NH and CH_3 NH_2

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vii. In decreasing order of basic strength

$CH_3CH_2NH_2$, O_2N–C$_6$H$_4$–NH_2, C$_6$H$_5$–NH_2 , CH_3 - NH_2

10. How will you prepare propan – 1- amine from

i) butane nitrile ii) propanamide ii) 1- nitropropane

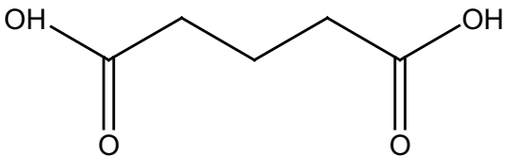
11. Identify A,B,and C

CH_3-NO_2 $\xrightarrow{Li\,AlH_4}$ A $\xrightarrow{2CH_3CH_2Br}$ B $\xrightarrow{H_2SO_4}$ C

12. How will you convert diethylamine into

i) N, N – diethylacetamide ii) N – nitrosodiethylamine

13. Identify A,B and C

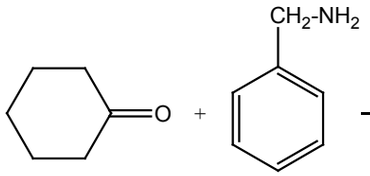


$\xrightarrow{SOCl_2}$ A $\xrightarrow{NH_3}$ B $\xrightarrow{LiAlH_4}$ (C)

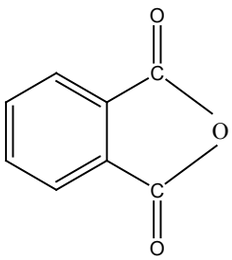
14. Identify A

aniline+benzaldehyde $\rightarrow$ A

15. Complete the following reaction



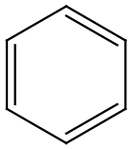
16. Predict A,B,C and D for the following reaction



$\xrightarrow{NH_3\,/\,\Delta}$ A $\xrightarrow[ii)\ (B)]{i)\ KOH}$ (C) $\xrightarrow{H_2O\,/\,H^+}$ D + H_2N — CH(—CH_3) — CH_3

17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2. (B) on heating with liquid ammonia followed by treating with Br_2/KOH gives (c) which on treating with $NaNO_2$ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.

18. Identify A to E in the following sequence of reactions.



$\xrightarrow[AlCl_3]{CH_3Cl}$ A $\xrightarrow{HNO_3\,/\,H_2SO_4}$ B (Major product) $\xrightarrow{Sn\,/\,HCl}$ (C) $\xrightarrow[0^\circ C]{NaNO_2\,/\,HCl}$ D $\xrightarrow{CuCN}$ E

NITRO COMPOUNDS

Chemical properties of Nitro alkane (RNO_2)

Reduction

$R - NO_2$ → (Sn / HCl, acid) RNH_2

$R - NO_2$ → (Zn / NH_4Cl, Neutral) $RNHOH$

$R - NO_2$ → (Catalyst) $R - NH_2$

Hydrolysis

$RCH_2NO_2 \xrightarrow[\Delta]{HCl / H_2O} RCOOH$

$R_2CHNO_2 \xrightarrow{HCl / H_2O} R_2CO + N_2O + H_2O$ (Ketone)

Halogenation

$CH_3NO_2 \xrightarrow[NaOH]{Cl_2} CCl_3NO_2 + 3\,HCl$ (Chloropicrin)

Methods of preparation of $R - NO_2$ and RONO

From alkyl halides

$R - X \xrightarrow{2\,AgNO_2} RNO_2 + RONO + 2AgI$ (Nitroalkane (Major), Alkylnitrite (Minor))

$R - X \xrightarrow{KNO_2} RNO_2 + R - O - N = O$ (Minor) (Major)

Nitration of alkane

$CH_3 - CH_3 \xrightarrow{HNO_3} CH_3CH_2NO_2 + CH_3NO_2$

Nitration of arenes

$C_6H_6 + HNO_3 \xrightarrow{Con\ H_2SO_4} C_6H_5NO_2$

$HNO_3 + H_2SO_4$ nitratingmixture

NO_2^+ electrophile

Electrophilic Substituion Reaction

Nitrogroup is meta - directing

Nitration: $C_6H_5NO_2 \xrightarrow{Conc.HNO_3 + H_2SO_4} C_6H_4(NO_2)_2$ — m - dinitobenzene

Sulphonation: $C_6H_5NO_2 \xrightarrow{Conc.H_2SO_4} C_6H_4(NO_2)SO_3H$ — m - nitrobenzene sulphonic acid

Halogenation: $C_6H_5NO_2 \xrightarrow{Cl_2 / Fe} C_6H_4(NO_2)Cl$ — m - chloronitrobenzene

Nitrobenzene (oil of mirabane) – reduction

$C_6H_5NO_2$

Acidmedium, Sn / HCl → $C_6H_5NH_2 + H_2O$ (Aniline)

Neutral, $Zn + NH_4Cl$ → C_6H_5NHOH (N - Phenylhydroxylamine)

Alkaline medium, $Na_3AsO_3/NaOH$ → $C_6H_5 - N = N - C_6H_5$ (Azoxybenzene)

Alkaline medium, $Zn / NaOH / CH_3OH$ (or) $LiAlH_4$ → $C_6H_5 - N = N - C_6H_5$ (Azobenzene)

Alkaline medium, $Zn / NaOH$ → $C_6H_5 - NH - NH\,C_6H_5$ (Hydrazobenzene)

Electrolytic reduction, Weaklyacidic, Medium → $C_6H_5NH_2$ (Aniline)

Electrolytic reduction, Stronglyacidic, $Conc\ H_2SO_4$ → $H_2N - C_6H_4 - OH$ (P - nitrophenol)

UNIT
14

BIOMOLECULES



G.N. Ramachandran

Dr. G.N. Ramachandran received Master's Degree in Physics from Madras University. In 1954, he identified and published the Triple helical structure of Collagen using X-ray diffraction. He pioneered the field of protein structure validation through the study of available crystal structures of peptides. From his studies, in 1962, he developed the Ramachandran Plot which is used even today for stereochemical validation of protein structures.

AFUC5

Learning Objectives

After studying this unit, students will be able to

- Describe the importance of carbohydrates and their classification based on structures/functions.
- Explain the structure of glucose and fructose and their elucidation.
- List the twenty amino acids and explain the peptide bond formation
- Explain the four levels of structure of proteins
- Outline the mechanism of enzyme catalysis
- Summarise the sources and deficiency diseases of vitamins
- Outline the composition and the structure of nucleic acids.
- Differentiate RNA from DNA and explain DNA finger printing
- Appreciate the importance of biomolecules in our life

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INTRODUCTION

All living things are made up of many biomolecules such as carbohydrates, proteins, lipids and nucleic acids etc... The major elements present in the human body are carbon, hydrogen, oxygen, nitrogen and phosphorous, and they combine to form a variety of biomolecules. These biomolecules are used as fuel to provide the necessary energy for the various functions of living systems in addition to many other biological functions. The field of studying about the chemistry behind the biological processes is called 'Biochemistry'. In this unit, we will learn about some essential informations of the biomolecules, their structure and their importance.

14.1 Carbohydrates:

Carbohydrates are the most abundant organic compounds in every living organism. They are also known as saccharides (derived from Greek word '*sakcharon*' which means sugar) as many of them are sweet. They are considered as hydrates of carbon, containing hydrogen and oxygen in the same ratio as in water. Chemically, they are defined as polyhydroxy aldehydes or ketones with a general formula $C_n(H_2O)_n$. Some common examples are glucose (monosaccharide), sucrose (disaccharide) and starch (polysaccharide)

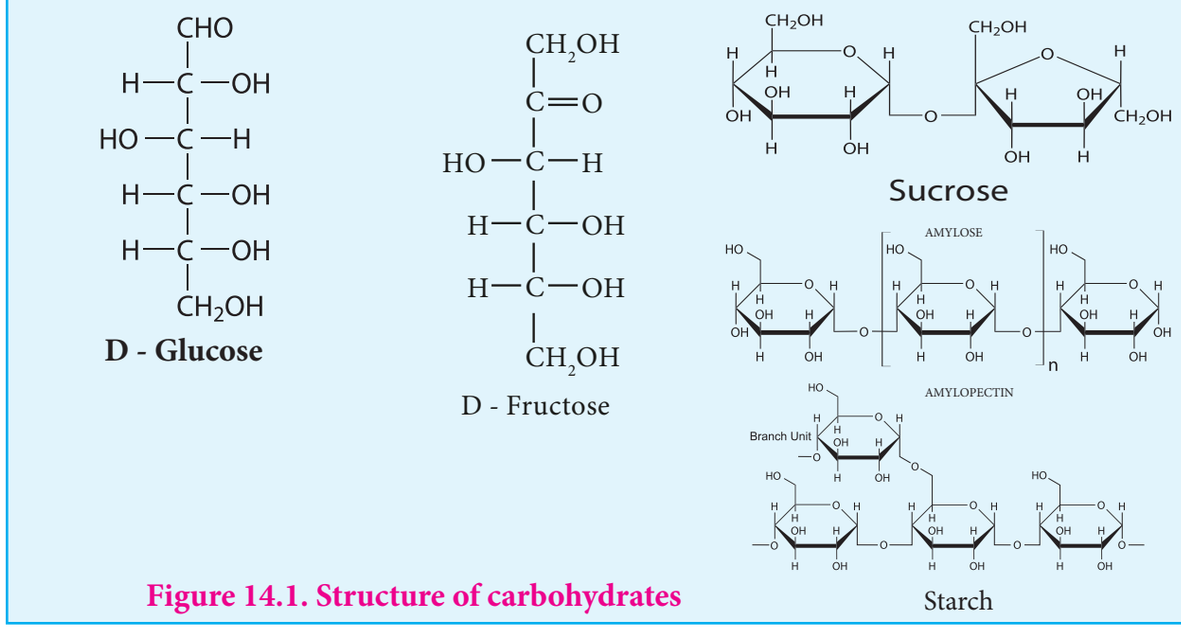


Figure 14.1. Structure of carbohydrates

Carbohydrates are synthesised by green leaves during photo synthesis, a complex process in which sun light provides the energy to convert carbon dioxide and water into glucose and oxygen. Glucose is then converted into other carbohydrates and is consumed by animals.

$$6CO_2 + 6\,H_2O \xrightarrow{\text{Sun light}} C_6H_{12}O_6 + 6O_2$$

14.1.1 Configuration of carbohydrates:

Almost all carbohydrates are optically active as they have one or more chiral carbons. The number of optical isomers depends on the number of chiral carbons (2^n isomers, where n is the total number of chiral carbons). We have already learnt in XI standard to represent an

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organic compound using Fischer projection formula. Fischer has devised a projection formula to relate the structure of a carbohydrate to one of the two enantiomeric forms of glyceraldehyde (Figure 14.2). Based on these structures, carbohydrates are named as D or L.The carbohydrates are usually named with two prefixes namely D or L and followed by sign either (+) or (-). Carbohydrates are assigned the notation (D/L) by comparing the configuration of the carbon that is attached to -CH_2OH group with that of glyceraldehyde.For example D-glucose is so named because the H and OH on C5 carbon are in the same configuration as the H and OH on C2 carbon in D-Glyceraldehyde.

There + and – sign indicates the dextro rotatory and levo rotatory respectively. Dextro rotatory compounds rotate the plane of plane polarised light in clockwise direction while the levo rotatory compounds rotate in anticlockwise direction. The D or L isomers can either be dextro or levo rotatory compounds. Dextro rotatory compounds are represented as D-(+) or L-(+) and the levo rotatory compounds as D-(–) or L-(–)

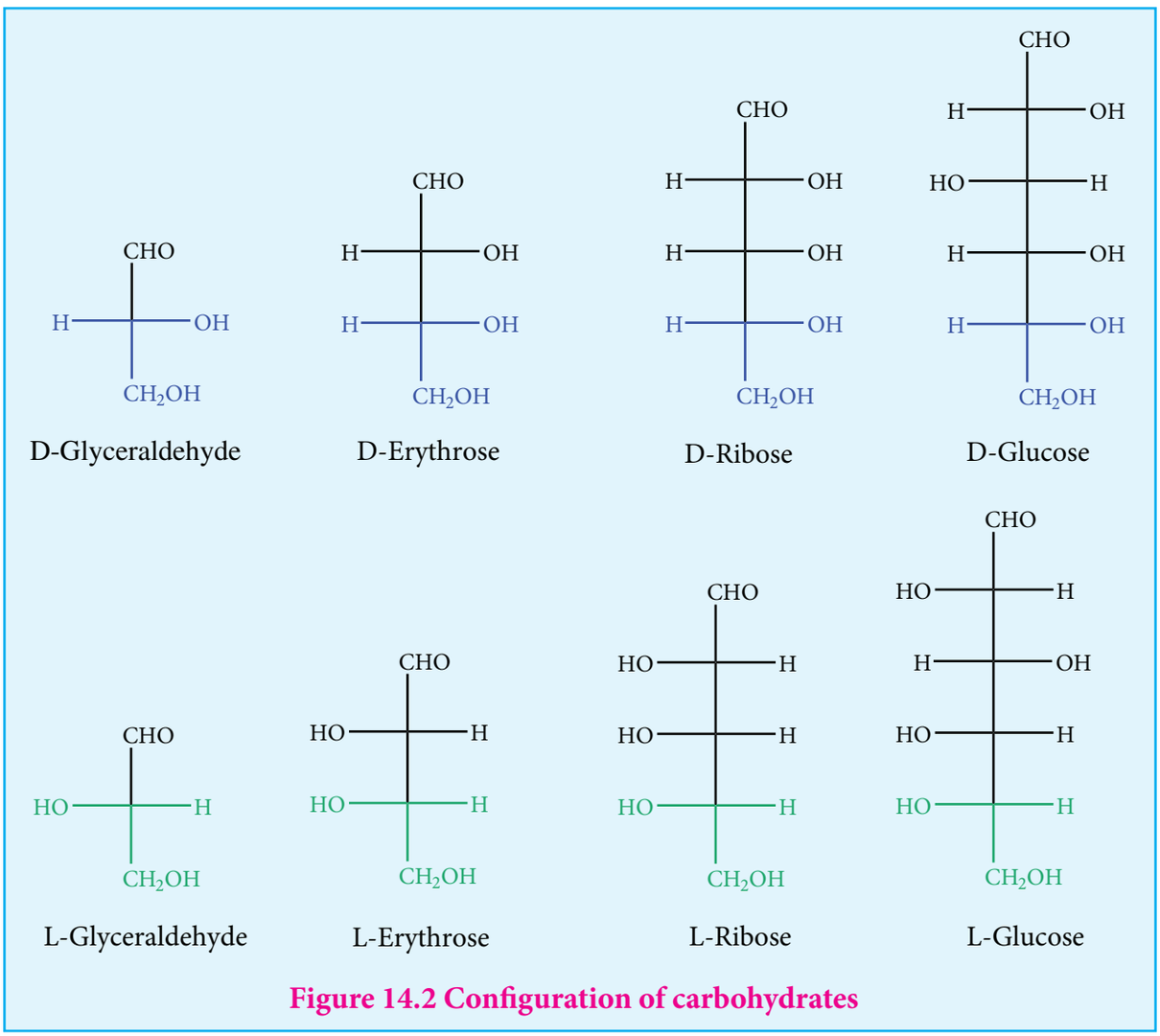


Figure 14.2 Configuration of carbohydrates

14.1.2 Classification of carbohydrates:

Carbohydrates can be classified into three major groups based on their product of hydrolysis, namely monosaccharides, oligosaccharides and polysaccharides.

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Monosaccharides: Monosaccharides are carbohydrates that cannot be hydrolysed further and are also called simple sugars. Monosaccharides have general formula $C_n(H_2O)_n$. While there are many monosaccharides known only about 20 of them occur in nature. Some common examples are glucose, fructose, ribose, erythrose

Monosaccharides are further classified based on the functional group present (aldoses or ketoses) and the number of carbon present in the chain (trioses, tetroses, pentoses, hexoses etc...). If the carbonyl group is an aldehyde, the sugar is an aldose. If the carbonyl group is a ketone, the sugar is a ketose. The most common monosaccharides have three to eight carbon atoms.

Table 14.1 Different types of monosaccharides:

No. of carbon atoms in the chain	Functional group present	Type of sugar	Example
3	Aldehyde	Aldotriose	Glyceraldehyde
3	Ketone	Ketotriose	Dihydroxy acetone
4	Aldehyde	Aldotetrose	Erythrose
4	Ketone	Ketotetrose	Erythrulose
5	Aldehyde	Aldopentose	Ribose
5	Ketone	Ketopentose	Ribulose
6	Aldehyde	Aldohexose	Glucose
6	Ketone	Ketohexose	Fructose

14.1.3 Glucose

Glucose is a simple sugar which serves as a major energy source for us. It is the most important and most abundant sugar. It is present in honey, sweet fruits such as grapes and mangoes etc... Human blood contains about 100 mg/dL of glucose, hence it is also known as blood sugar. In the combined form it is present in sucrose, starch, cellulose etc.,

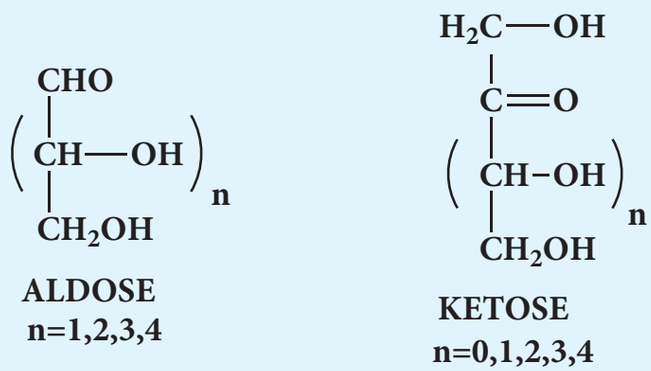


Figure 14.3 Structure of aldoses and ketoses

Preparation of glucose

1. When sucrose (*cane sugar*) is boiled with dilute H_2SO_4 in alcoholic solution, it undergoes hydrolysis and give glucose and fructose.

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

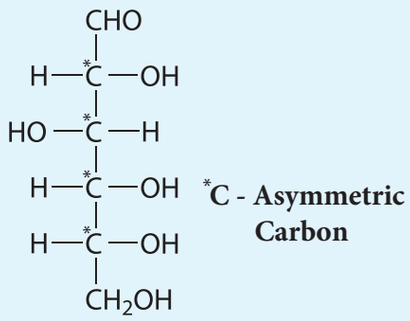
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2. Glucose is produced commercially by the hydrolysis of starch with dilute HCl at high temperature under pressure.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + n\,H_2O \xrightarrow[\text{2-3 atm}]{H^+,\ 393K} \underset{\text{Glucose}}{n\,C_6H_{12}O_6}$$

Structure of Glucose

Glucose is an aldohexose. It is optically active with four asymmetric carbons. Its solution is dextrorotatory and hence it is also called as dextrose. The proposed structure of glucose is shown in the figure 14.4 which was derived based on the following evidences.



D - (+)Glucose

Figure 14.4 Structure of D(+) glucose

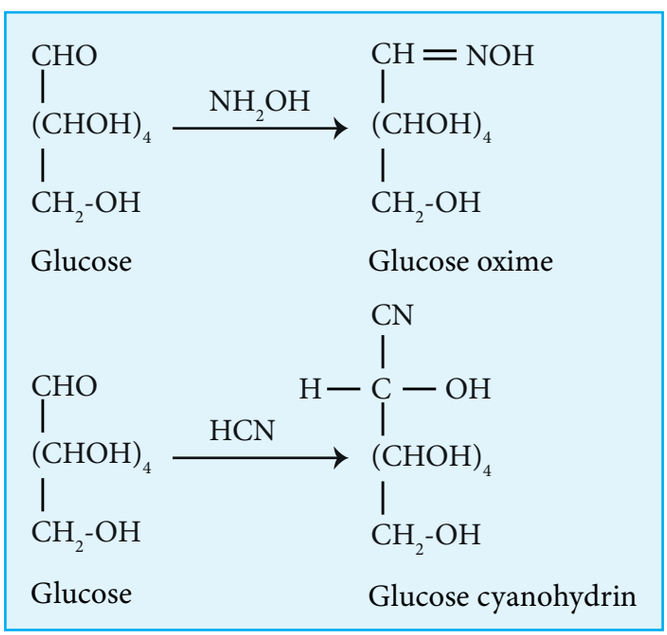
1. Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$.

2. On reduction with concentrated HI and red phosphorus at 373K, glucose gives a mixture of n hexane and 2–iodohexane indicating that the six carbon atoms are bonded linearly.

$$\text{Glucose} \xrightarrow[373\ K]{HI\ /\ P} CH_3\text{-}(CH_2)_4\text{-}CH_3 + CH_3\text{-}(CH_2)_3\text{-}\underset{\displaystyle I}{CH}\text{-}CH_3$$

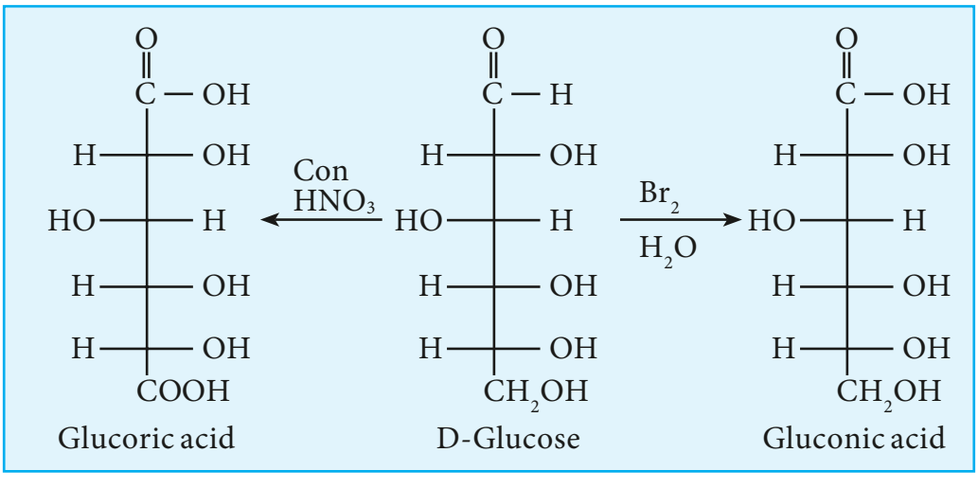
n-hexane	2-iodohexane
Major product	**Minor product**

3. Glucose reacts with hydroxylamine to form oxime and with HCN to form cyanohydrin. These reactions indicate the presence of carbonyl group in glucose.

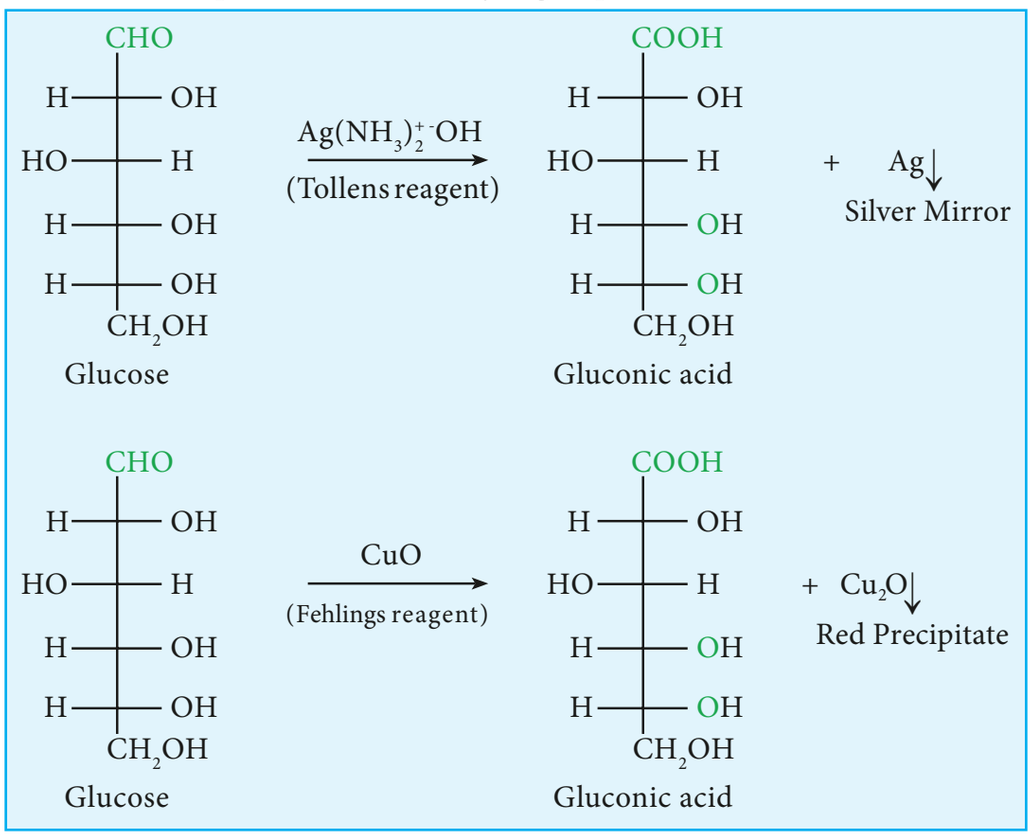


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4. Glucose gets oxidized to gluconic acid with mild oxidizing agents like bromine water suggesting that the carbonyl group is an aldehyde group and it occupies one end of the carbon chain. When oxidised using strong oxidising agent such as conc. nitric acid gives glucaric acid (saccharic acid) suggesting the other end is occupied by a primary alcohol group.

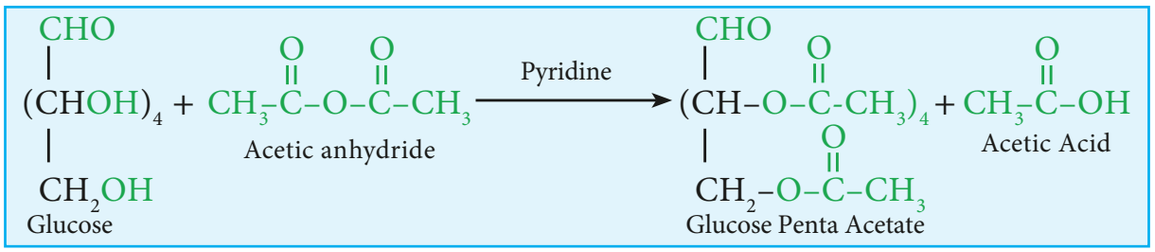


5. Glucose is oxidised to gluconic acid with ammonical silver nitrate (Tollen's reagent) and alkaline copper sulphate (Fehling's solution). Tollen's reagent is reduced to metallic silver and Fehling's solution to cuprous oxide which appears as red precipitate. These reactions further confirm the presence of an aldehyde group



6. Glucose forms penta acetate with acetic anhydride suggesting the presence of five alcohol groups.

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7. Glucose is a stable compound and does not undergo dehydration easily. It indicates that not more than one hydroxyl group is bonded to a single carbon atom. Thus the five the hydroxyl groups are attached to five different carbon atoms and the sixth carbon is an aldehyde group.
8. The exact spacial arrangement of -OH groups was given by Emil Fischer as shown in Figure 14.4. The glucose is referred to as D(+) glucose as it has D configuration and is dextrorotatory.

Cyclic structure of glucose

Fischer identified that the open chain penta hydroxyl aldehyde structure of glucose, that he proposed, did not completely explain its chemical behaviour. Unlike simple aldehydes, glucose did not form crystalline bisulphite compound with sodium bisulphite. Glucose does not give Schiff's test and the penta acetate derivative of glucose was not oxidized by Tollen's reagent or Fehling's solution. This behaviour could not be explained by the open chain structure.

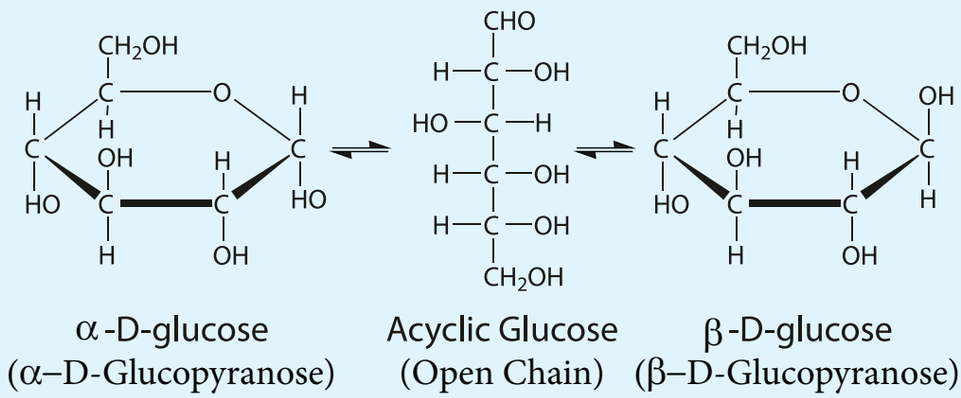


Figure 14.5 Cyclic structures of glucose

In addition, glucose is found to crystallise in two different forms depending upon the crystallisation conditions with different melting points (419 and 423 K). In order to explain these it was proposed that one of the hydroxyl group reacts with the aldehyde group to form a cyclic structure (hemiacetal form) as shown in figure 14.5. This also results in the conversion of the achiral aldehyde carbon into a chiral one leading to the possibility of two isomers. These two isomers differ only in the configuration of C1 carbon. These isomers are called **anomers.** The two anomeric forms of glucose are called α and β-forms. This cyclic structure of glucose is similar to pyran, a cyclic compound with 5 carbon and one oxygen atom, and hence is called pyranose form. The specific rotation of pure α- and β-(D) glucose are 112° & 18.7° respectively. However, when a pure form of any one of these sugars is dissolved in

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water, slow interconversion of α-D glucose and β-D glucose via open chain form occurs until equilibrium is established giving a constant specific rotation + 53°. This phenomenon is called **mutarotation**.

Epimers and epimerisation:

Sugar differing in configuration at an asymmetric centre is known as epimers. The process by which one epimer is converted into other is called epimerisation and it requires the enzymes epimerase. Galactose is converted to glucose by this manner in our body.

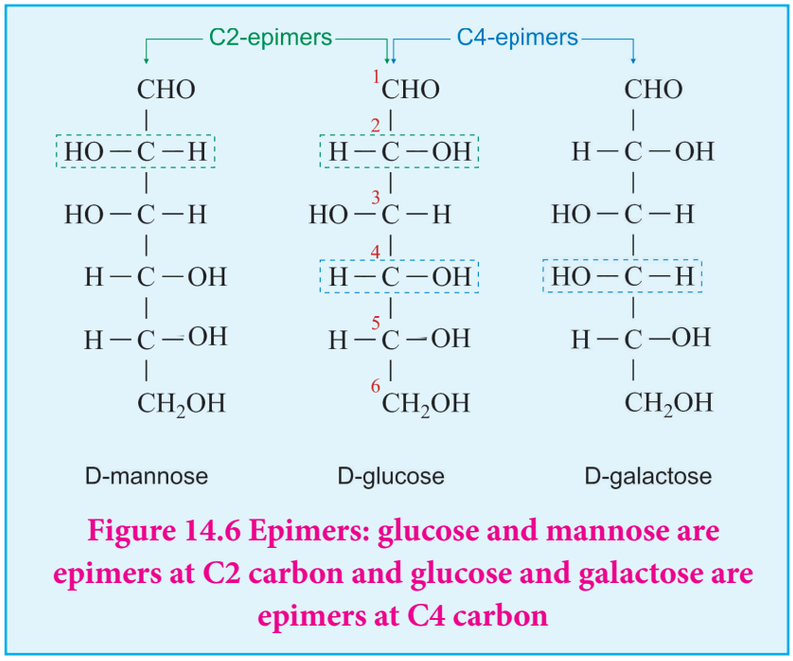


Figure 14.6 Epimers: glucose and mannose are epimers at C2 carbon and glucose and galactose are epimers at C4 carbon

14.1.4 Fructose

Fructose is another commonly known monosaccharide having the same molecular formula as glucose. It is levorotatory and a ketohexose. It is present abundantly in fruits and hence it is also called as fruit sugar.

Preparation

1. From sucrose

Fructose is obtained from sucrose by heating with dilute H_2SO_4 or with the enzyme invertase

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Invertase}]{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Fructose is separated by crystallisation. The mixture having equal amount of glucose and fructose is termed as invert sugar.

2. From Inulin

Fructose is prepared commercially by hydrolysis of Inulin (a polysaccharide) in an acidic medium.

$$\underset{\text{Inulin}}{(C_6H_{12}O_5)_n} + n\ H_2O \xrightarrow{H^+} n\ \underset{\text{Fructose}}{C_6H_{12}O_6}$$

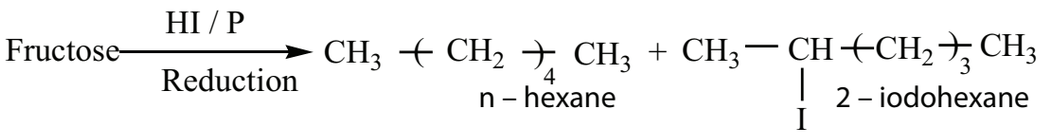
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Structure of fructose:

Fructose is the sweetest of all known sugars. It is readily soluble in water. Fresh solution of fructose has a specific rotation -133^0 which changes to – 92^0 at equilibrium due to mutarotation. Similar to glucose the structure of fructose is deduced from the following facts.

1. Elemental analysis and molecular weight determination of fructose show that it has the molecular formula $C_6H_{12}O_6$

2. Fructose on reduction with HI and red phosphorus gives a mixture of n – hexane (major product) and 2 – iodohexane (minor product). This reaction indicates that the six carbon atoms in fructose are in a straight chain.

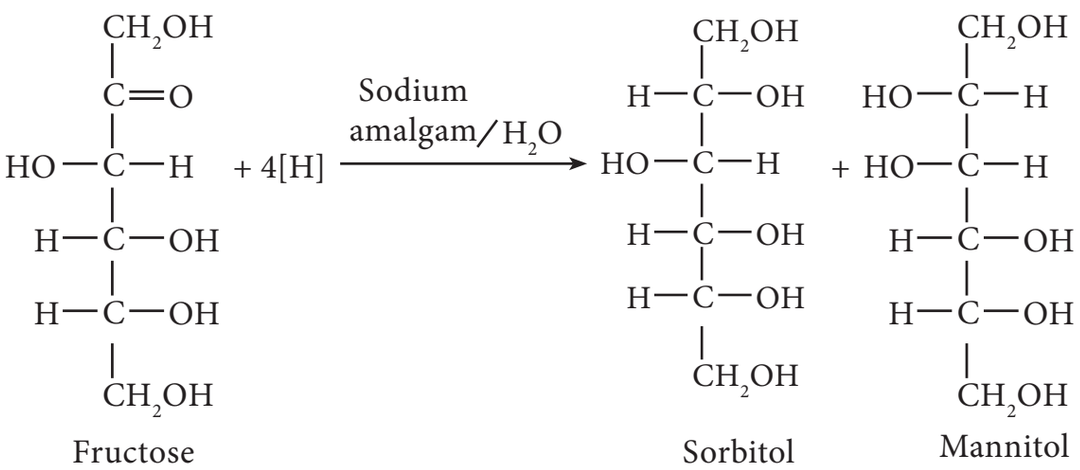


3. Fructose reacts with NH_2OH and HCN. It shows the presence of a carbonyl groups in the fructose.

4. Fructose reacts with acetic anhydride in the presence of pyridine to form penta acetate. This reaction indicates the presence of five hydroxyl groups in a fructose molecule.

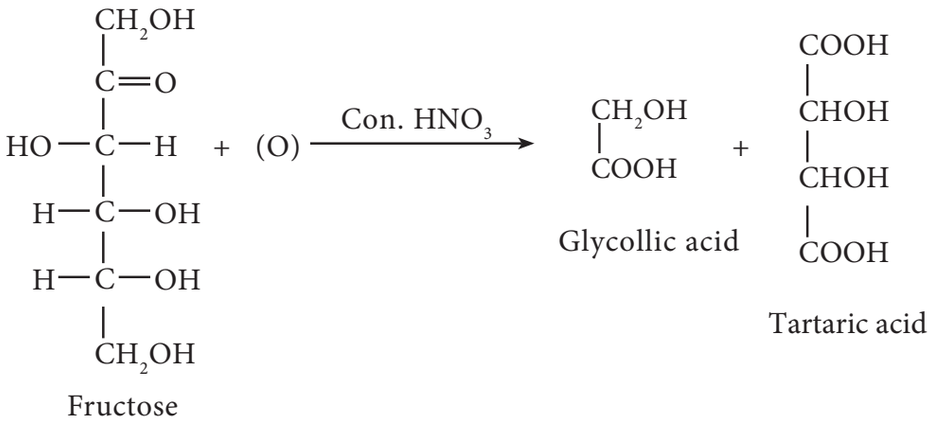
5. Fructose is not oxidized by bromine water. This rules out the possibility of absence of an aldehyde (-CHO) group.

6. Partial reduction of fructose with sodium amalgam and water produces mixtures of sorbitol and mannitol which are epimers at the second carbon. New asymmetric carbon is formed at C-2. This confirms the presence of a keto group.



7. On oxidation with nitric acid, it gives glycollic acid and tartaric acids which contain smaller number of carbon atoms than in fructose.

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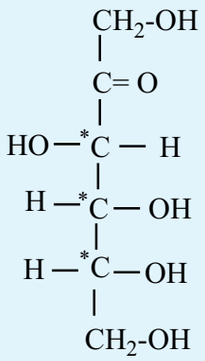


Fructose

Glycollic acid

Tartaric acid

This shows that a keto group is present in C-2. It also shows that 1^{O} alcoholic groups are present at C- 1 and C- 6. Based on these evidences, the following structure is proposed for fructose (Figure 14-7)



*C- asymmetric carbon

Figure 14.7 Structure of D(+) Fructose

Cyclic structure of fructose

Like glucose, fructose also forms cyclic structure. Unlike glucose it forms a five membered ring similar to furan. Hence it is called furanose form. When fructose is a component of a saccharide as in sucrose, it usually occurs in furanose form.

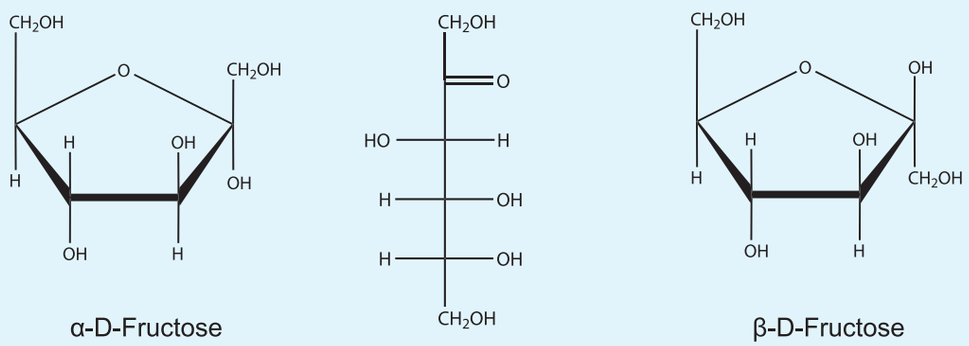


Figure 14.8 Cyclic Structures of fructose

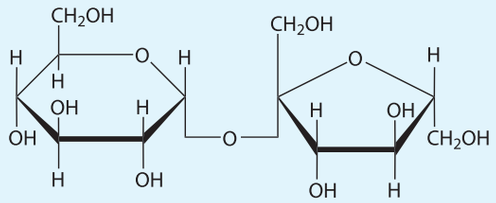
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14.1.5 Disaccharides

Disaccharides are sugars that yield two molecules of monosaccharides on hydrolysis. This reaction is usually catalysed by dilute acid or enzyme. Disaccharides have general formula $C_n(H_2O)_{n-1}$.In disaccharides two monosaccharides are linked by *oxide linkage* called '*glycosidic linkage*', which is formed by the reaction of the anomeric carbon of one monosaccharide reacts with a hydroxyl group of another monosaccharide.

Example: Sucrose, Lactose, Maltose

Sucrose: Sucrose, commonly known as table sugar is the most abundant disaccharide. It is obtained mainly from the juice of sugar cane and sugar beets. Insects such as honey bees have the enzyme called invertases that catalyzes the hydrolysis of sucrose to a glucose and fructose mixture. Honey in fact, is primarily a mixture of glucose, fructose and sucrose.



Sucrose

(α-D-glucopyranosyl-β-D-fructofuranoside)

Figure 14.9 Structure of sucrose

On hydrolysis sucrose yields equal amount of glucose and fructose units.

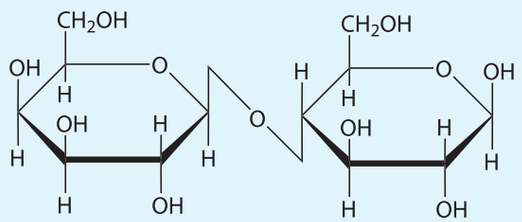
$$\text{Sucrose} \xrightarrow{\text{Invertase}} \text{Glucose+Fructose}$$

Sucrose (+66.6°) and glucose (+52.5°) are dextrorotatory compounds while fructose is levo rotatory (-92.4°). During hydrolysis of sucrose the optical rotation of the reaction mixture changes from dextro to levo. Hence, sucrose is also called as invert sugar.

Structure:

In sucrose, C1 of α-D-glucose is joined to C2 of β-D-fructose. The glycosidic bond thus formed is called α-1,2 glycosidic bond. Since, both the carbonyl carbons (reducing groups) are involved in the glycosidic bonding, sucrose is a non-reducing sugar.

Lactose: Lactose is a disaccharide found in milk of mammals and hence it is referred to as milk sugar. On hydrolysis, it yields galactose and glucose. Here, the β-D–galactose and β-D–glucose are linked by β-1,4 glycosidic bond as shown in the figure 14.10 . The aldehyde carbon is not involved in the glycosidic bond hence, it retains its reducing property and is called a reducing sugar.



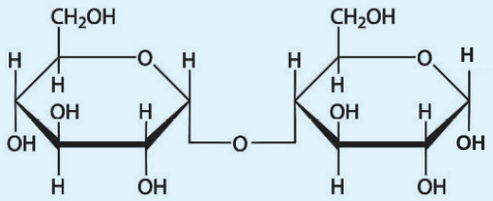
Lactose

(β-D-galactopyranosyl-(1→4)β-D-glucopyranose)

Figure 14.10 Structure of Lactose

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Maltose: Maltose derives its name from malt from which it is extracted. It is commonly called as malt sugar. Malt from sprouting barley is the major source of maltose. Maltose is produced during digestion of starch by the enzyme α-amylase.



Maltose

(α-D-glucopyranosyl-(1→4) α-D-glucopyranose)

Figure 14.11 Structure of Maltose

Maltose consists two molecules of α-D-glucose units linked by an α-1,4 glycosidic bond between anomeric carbon of one unit and C-4 of the other unit. Since one of the glucose has the carbonyl group intact, it also acts as a reducing sugar.

14.1.6 Polysaccharides:

Polysaccharides consist of large number of monosaccharide units bonded together by glycosidic bonds and are the most common form of carbohydrates. Since, they do not have sweet taste polysaccharides are called as non-sugars. They form linear and branched chain molecules.

Polysaccharides are classified into two types, namely, homopolysaccharides and heteropolysaccharides depending upon the constituent monosaccharides. Homopolysaccharides are composed of only one type of monosaccharides while the heteropolysaccharides are composed of more than one. Example: starch, cellulose and glycogen (homopolysaccharides); hyaluronic acid and heparin (heteropolysaccharides).

STARCH

Starch is used for energy storage in plants. Potatoes, corn, wheat and rice are the rich sources of starch. It is a polymer of glucose in which glucose molecules are lined by α(1,4) glycosidic bonds. Starch can be separated into two fractions namely, water soluble amylose and water insoluble amylopectin. Starch contains about 20 % of amylose and about 80% of amylocpectin.

Amylose is composed of unbranched chains upto 4000 α-D-glucose molecules joined by α(1,4)glycosidic bonds. Amylopetin contains chains upto 10000 α-D-glucose molecules linked by α(1,4)glycosidic bonds. In addition, there is a branching from linear chain. At branch points, new chains of 24 to 30 glucose molecules are linked by α(1,6)glycosidic bonds. With iodine solution amylose gives blue colour while amylopectin gives a purple colour.

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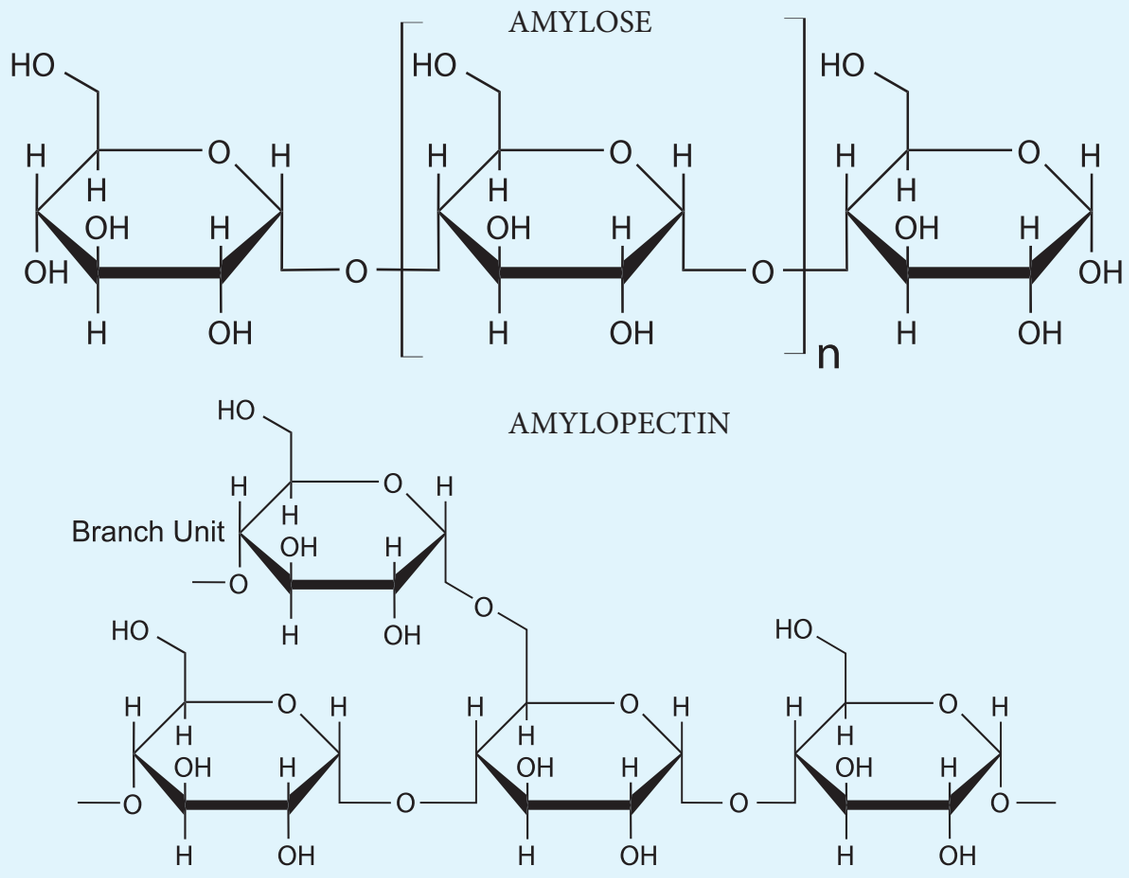


Figure 14.12 Structure of Starch (Amylose & Amylopectin)

Cellulose

Cellulose is the major constituent of plant cell walls. Cotton is almost pure cellulose. On hydrolysis cellulose yields D-glucose molecules. Cellulose is a straight chain polysaccharide. The glucose molecules are linked by β(1,4)glycosidic bond.

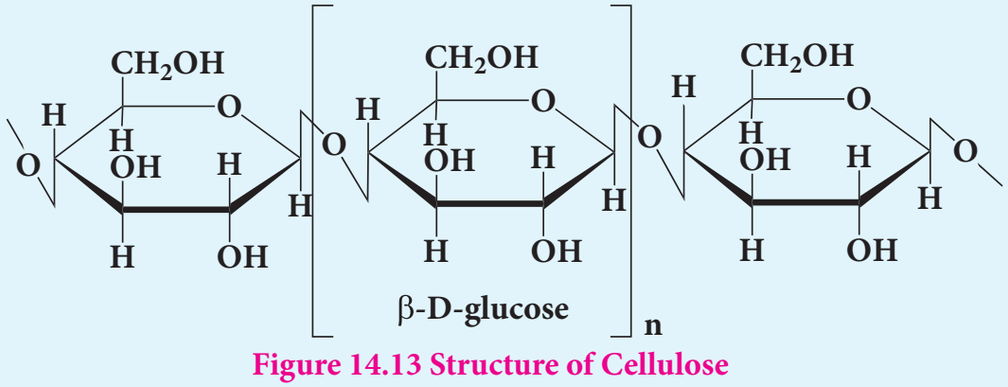


Figure 14.13 Structure of Cellulose

Cellulose is used extensively in the manufacturing paper, cellulose fibres, rayon explosive, (Gun cotton – Nitrated ester of cellulose) and so on. Human cannot use cellulose as food because our digestive systems do not contain the necessary enzymes (glycosidases or cellulases) that can hydrolyse the cellulose.

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Glycogen: Glycogen is the storage polysaccharide of animals. It is present in the liver and muscles of animals. Glycogen is also called as animal starch. On hydrolysis it gives glucose molecules. Structurally, glycogen resembles amylopectin with more branching. In glycogen the branching occurs every 8-14 glucose units opposed to 24-30 units in amylopectin. The excessive glucose in the body is stored in the form of glycogen.

14.1.7 Importance of carbohydrates

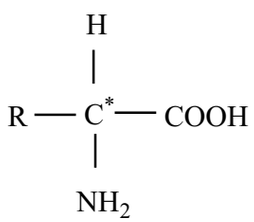
1. Carbohydrates, widely distributed in plants and animals, act mainly as energy sources and structural polymers.
2. Carbohydrate is stored in the body as glycogen and in plant as starch.
3. Carbohydrates such as cellulose which is the primary components of plant cell wall, is used to make paper, furniture (wood) and cloths (cotton)
4. Simple sugar glucose serves as an instant source of energy.
5. Ribose sugars are one of the components of nucleic acids.
6. Modified carbohydrates such as hyaluronate (glycosaminoglycans) act as shock absorber and lubricant.

14.2 Proteins

Proteins are most abundant biomolecules in all living organisms. The term protein is derived from Greek word '*Proteious*' meaning primary or holding first place. They are main functional units for the living things. They are involved in every function of the cell including respiration. Proteins are polymers of α-amino acids.

14.2.1 Amino acids

Amino acids are compounds which contain an amino group and a carboxylic acid group. The protein molecules are made up α-amino acids which can be represented by the following general formula.



There are 20 α-amino acids commonly found in the protein molecules. Each amino acid is given a trivial name, a three letter code and a one letter code. In writing the amino acid sequence of a protein, generally either one letter or three letter codes are used.

14.2.2 Classification of α-amino acids

The amino acids are classified based on the nature of their R groups commonly known as side chain. They can be classified as acidic, basic and neutral amino acids. They can also be classified as polar and non-polar (hydrophobic) amino acids.

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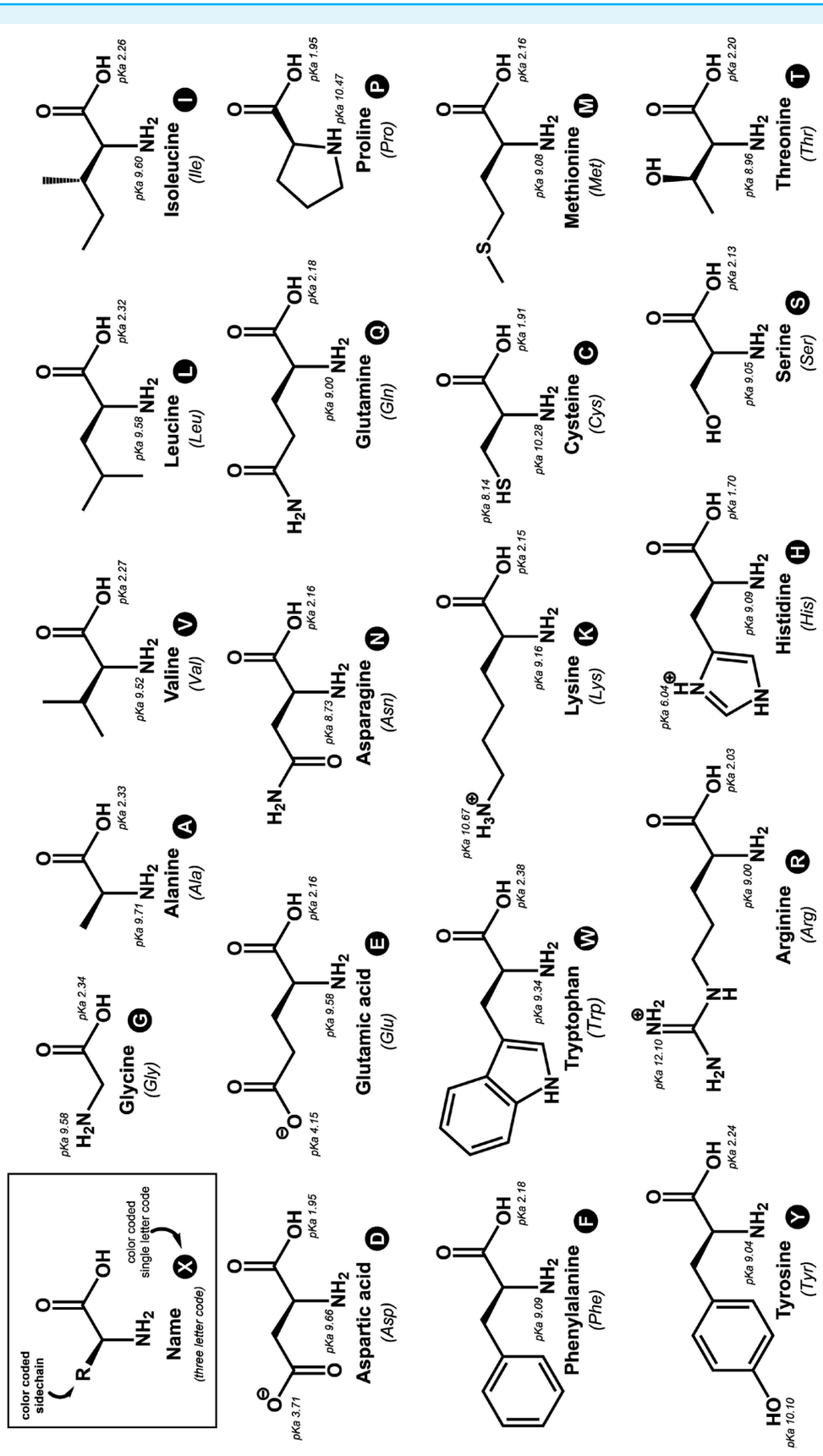


Figure 14.14 Structure of amino acids

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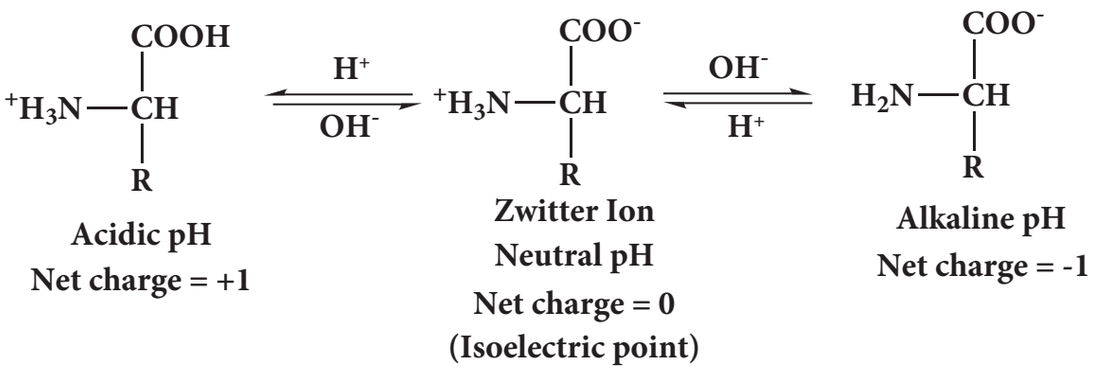
Amino acids can also be classified as essential and non-essential amino acids based on the ability to be synthesise by the human. The amino acids that can be synthesised by us are called non-essential amino acids (Gly, Ala, Glu, Asp, Gln, Asn, Ser, Cys, Tyr & Pro) and those needs to be obtained through diet are called essential amino acids (Phe, Val, Thr, Trp, Ile, Met, His, Arg, Leu and Lys). These ten essential amino acids can be memorised by mnemonic called PVT TIM HALL.

Although the vast majority of plant and animal proteins are formed by these 20 α- amino acids, many other amino acids are also found in the cells. These amino acids are called as non–protein amino acids. Example: ornithine and citrulline (components of urea cycle where ammonia is converted into urea)

14.2.3 Properties of amino acid

Amino acids are colourless, water soluble crystalline solids. Since they have both carboxyl group and amino group their properties differ from regular amines and carboxylic acids. The carboxyl group can lose a proton and become negatively charged or the amino group can accept a proton to become positively charged depending upon the pH of the solution. At a specific pH the net charge of an amino acid is neutral and this pH is called **isoelectric point**. At a pH above the isoelectric point the amino acid will be negatively charged and positively charged at pH values below the isoelectric point.

In aqueous solution the proton from carboxyl group can be transferred to the amino group of an amino acid leaving these groups with opposite charges. Despite having both positive and negative charges this molecule is neutral and has amphoteric behaviour. These ions are called zwitter ions.



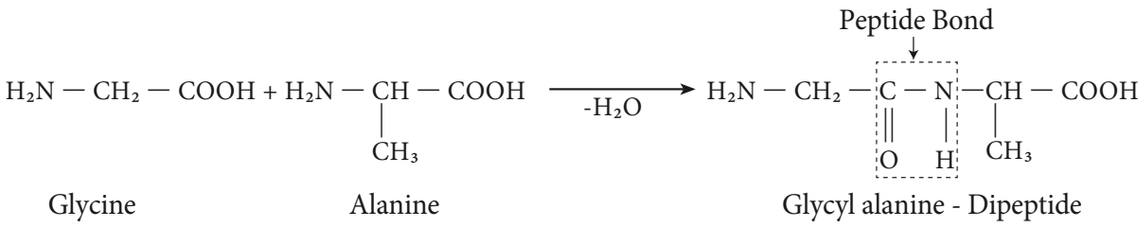
Except glycine all other amino acids have at least one chiral carbon atom and hence are optically active. They exist in two forms namely D and L amino acids. However, L-amino acids are used predominantly by the living organism for synthesising proteins. Presence of D-amino acids has been observed rarely in certain organisms.

14.2.4 Peptide bond formation

The amino acids are linked covalently by peptide bonds. The carboxyl group of the first amino acid react with the amino group of the second amino acid to give an amide linkage between these amino acids. This amide linkage is called **peptide bond**. The resulting compound is called a dipeptide. Addition an another amino acid to this dipeptide a second peptide bond results in tripeptide. Thus we can generate tetra peptide, penta peptide etc… When you have

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more number of amino acids linked this way you get a polypeptide. If the number of amino acids are less it is called as a polypeptide, if it has large number of amino acids (and preferably has a function) then it is called a protein.



The amino end of the peptide is known as N-terminal or amino terminal while the carboxy end is called C-terminal or carboxy terminal. In general protein sequences are written from N-Terminal to C-Terminal. The atoms other than the side chains (R-groups) are called main chain or the back bone of the polypeptide.

14.2.5 Classification of proteins

Proteins are classified based on their structure (overall shape) into two major types. They are fibrous proteins and globular proteins.

Fibrous proteins

Fibrous proteins are linear molecules similar to fibres. These are generally insoluble in water and are held together by disulphide bridges and weak intermolecular hydrogen bonds. The proteins are often used as structural proteins. Example: Keratin, Collagen etc…

Globular proteins

Globular proteins have an overall spherical shape. The polypeptide chain is folded into a spherical shape. These proteins are usually soluble in water and have many functions including catalysis (enzyme). Example: myoglobin, insuline

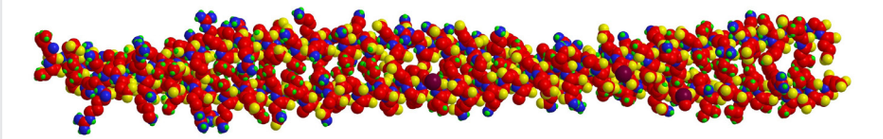


Figure 14.15 (a) Structure of fibrous proteins

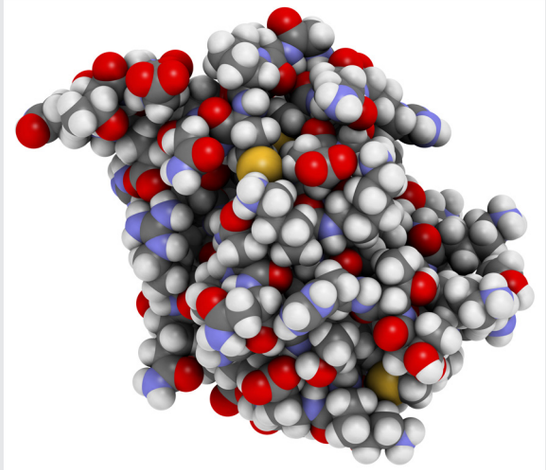


Figure 14.15 (b) Structure of globular proteins

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14.2.6 Structure of proteins

Proteins are polymers of amino acids. Their three dimensional structure depends mainly on the sequence of amino acids (residues). The protein structure can be described at four hierarchal levels called primary, secondary, tertiary and quaternary structures as shown in the figure 14.16

1. Primary structure of proteins:

Proteins are polypeptide chains, made up of amino acids are connected through peptide bonds. The relative arrangement of the amino acids in the polypeptide chain is called the primary structure of the protein. Knowledge of this is essential as even small changes have potential to alter the overall structure and function of a protein.

$$H_2N\text{—}Gly\text{—}Met\text{—}Phe\text{—}Cys\text{—}Arg\text{—}Asp\text{—}COOH$$

2. Secondary structure of proteins:

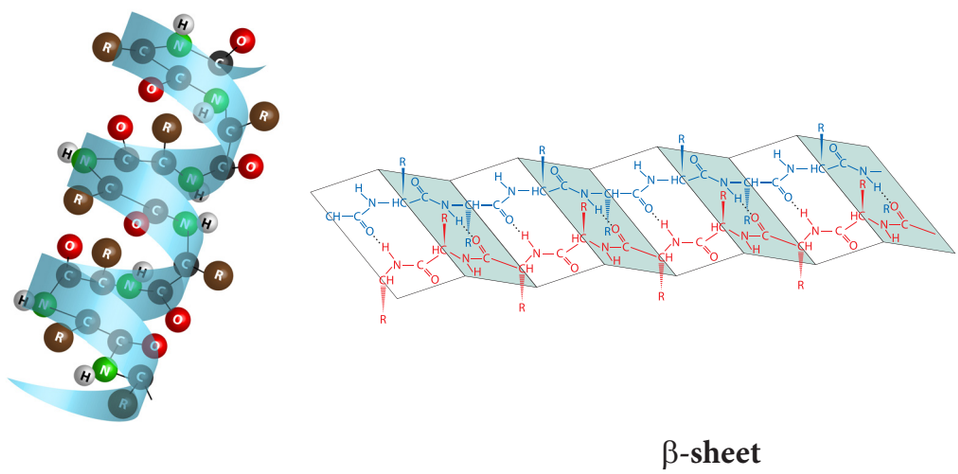
The amino acids in the polypeptide chain forms highly regular shapes (sub-structures) through the hydrogen bond between the carbonyl oxygen (>C=O) and the neighbouring amine hydrogen (-NH)of the main chain.α-Helix and β-strands or sheets are two most common sub-structures formed by proteins.

α-Helix

In the α-helix sub-structure, the amino acids are arranged in a right handed helical (spiral) structure and are stabilised by the hydrogen bond between the carbonyl oxygen of one amino acid (n^{th} residue) with amino hydrogen of the fifth residue ($n+4^{th}$ residue). The side chains of the residues protrude outside of the helix. Each turn of an α-helix contains about 3.6 residues and is about 5.4 Å long. The amino acid proline produces a kink in the helical structure and often called as a helix breaker due to its rigid cyclic structure.

β-Strand

β-Strands are extended peptide chain rather than coiled. The hydrogen bonds occur between main chain carbonyl group one such strand and the amino group of the adjacent strand resulting in the formation of a sheet like structure. This arrangement is called β-sheets.



α-Helix β-sheet

Figure 14.16 Secondary structure of proteins

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3. Tertiary structure:

The secondary structure elements (α-helix & β-sheets) further folds to form the three dimensional arrangement. This structure is called tertiary structure of the polypeptide (protein). Tertiary structure of proteins are stabilised by the interactions between the side chains of the amino acids. These interactions include the disulphide bridges between cysteine residues, electrostatic, hydrophobic, hydrogen bonds and van der Waals interactions.

4. Quaternary Structure

Some proteins are made up of more than one polypeptide chains. For example, the oxygen transporting protein, haemoglobin contains four polypeptide chains while DNA polymerase enzyme that make copies of DNA, has ten polypeptide chains. In these proteins the individual polypeptide chains (subunits) interacts with each other to form the multimeric structure which are known as quaternary structure. The interactions that stabilises the tertiary structures also stabilises the quaternary structures.

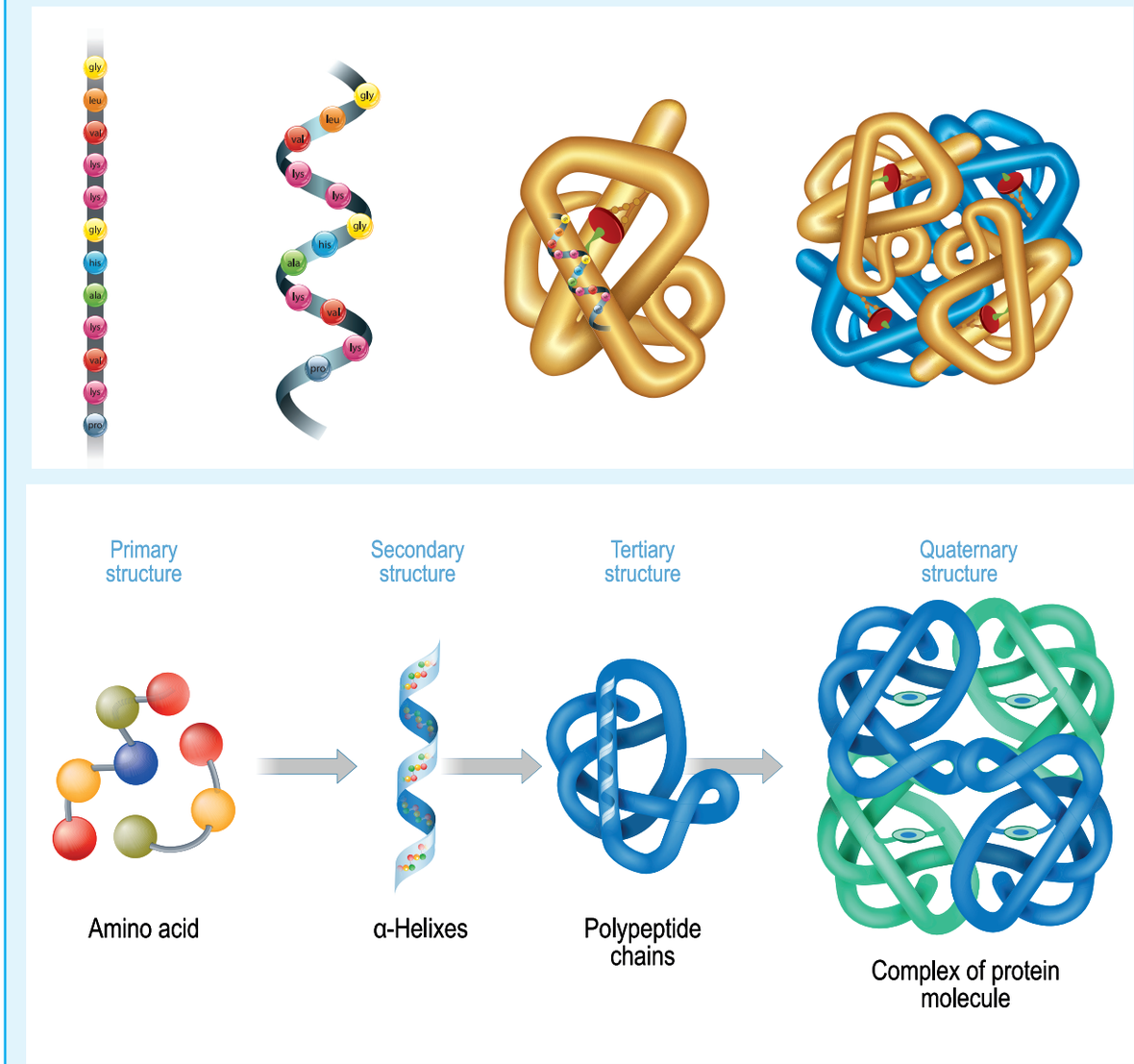


Figure 14.17 Four levels of protein structure

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14.2.7 Denaturation of proteins

Each protein has a unique three-dimensional structure formed by interactions such as disulphide bond, hydrogen bond, hydrophobic and electrostatic interactions. These interactions can be disturbed when the protein is exposed to a higher temperature, by adding certain chemicals such as urea, alteration of pH and ionic strength etc., It leads to the loss of the three-dimensional structure partially or completely. The process of a losing its higher order structure without losing the primary structure, is called denaturation. When a protein denatures, its biological function is also lost.

Since the primary structure is intact, this process can be reversed in certain proteins. This can happen spontaneously upon restoring the original conditions or with the help of special enzymes called cheperons (proteins that help proteins to fold correctly).

Example: coagulation of egg white by action of heat.

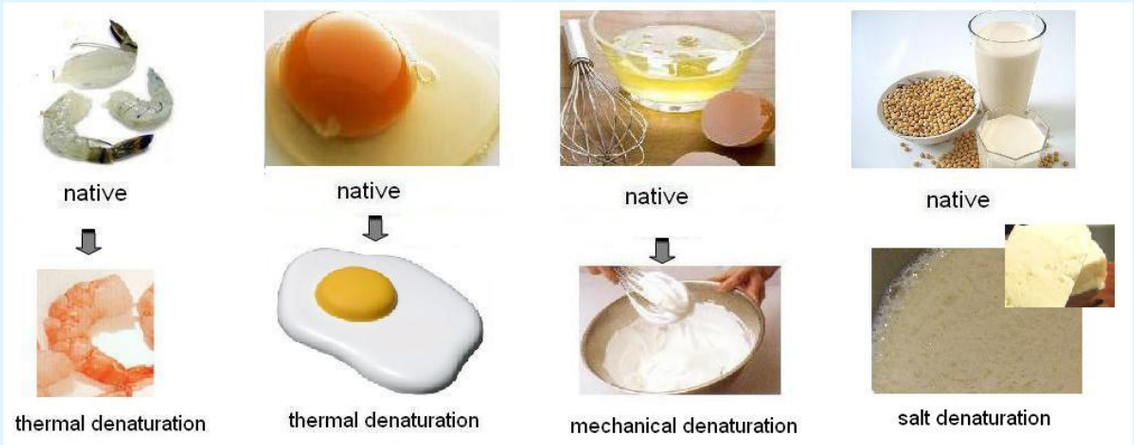


Figure 14.18 Denaturation of proteins

14.2.8 Importance of proteins

Proteins are the functional units of living things and play vital role in all biological processes

1. All biochemical reactions occur in the living systems are catalysed by the catalytic proteins called enzymes.
2. Proteins such as keratin, collagen act as structural back bones.
3. Proteins are used for transporting molecules (Haemoglobin), organelles (Kinesins) in the cell and control the movement of molecules in and out of the cells (Transporters).
4. Antibodies help the body to fight various diseases.
5. Proteins are used as messengers to coordinate many functions. Insulin and glucagon control the glucose level in the blood.
6. Proteins act as receptors that detect presence of certain signal molecules and activate the proper response.
7. Proteins are also used to store metals such as iron (Ferritin) etc.

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14.2.9 Enzymes:

There are many biochemical reactions that occur in our living cells. Digestion of food and harvesting the energy from them, and synthesis of necessary molecules required for various cellular functions are examples for such reactions. All these reactions are catalysed by special proteins called enzymes. These biocatalysts accelerate the reaction rate in the orders of 10^5 and also make them highly specific. The high specificity is followed allowing many reactions to occur within the cell. For example, the *Carbonic anhydrase* enzyme catalyses the interconversion of carbonic acid to water and carbon dioxide. Sucrase enzyme catalyses the hydrolysis of sucrose to fructose and glucose. Lactase enzyme hydrolyses the lactose into its constituent monosaccharides, glucose and galactose.

14.2.10 Mechanism of enzyme action:

Enzymes are biocatalysts that catalyse a specific biochemical reaction. They generally activate the reaction by reducing the activation energy by stabilising the transition state. In a typical reaction enzyme (E) binds with the substrate (S) molecule reversibly to produce an enzyme-substrate complex (ES). During this stage the substrate is converted into product and the enzyme becomes free, and ready to bind to another substrate molecule. More detailed mechanism is discussed in the unit XI surface chemistry.

$$\underset{Enzyme}{E} + \underset{Substate}{S} \rightleftharpoons \underset{Enzyme\text{ - substrate complex}}{[ES]}$$

$$[ES] \rightarrow E+P$$

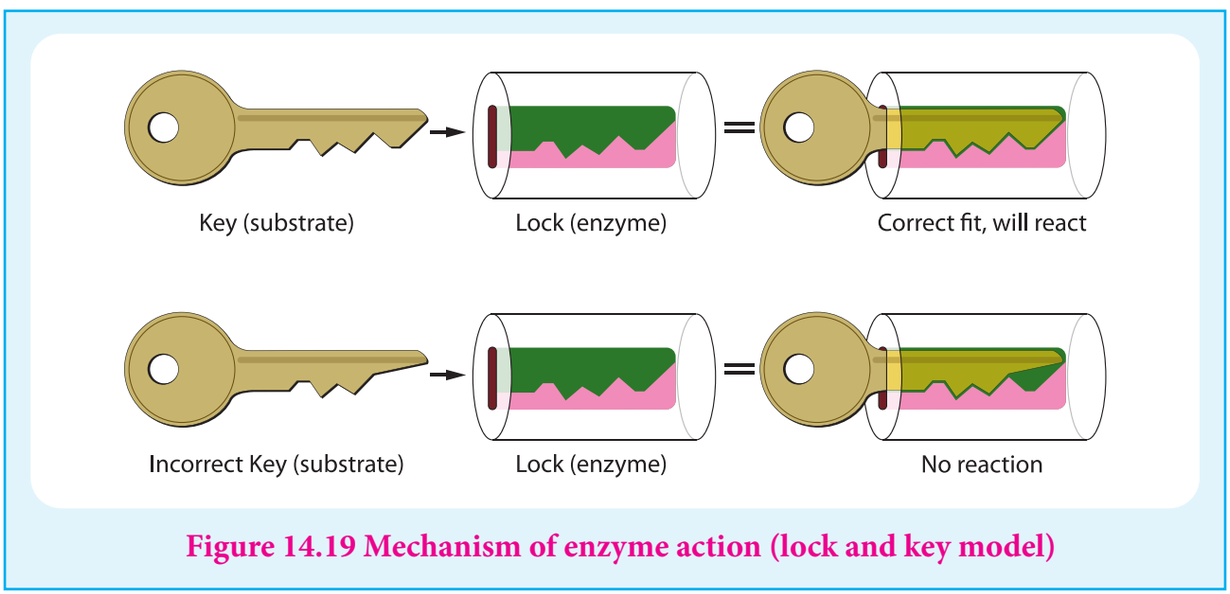


Figure 14.19 Mechanism of enzyme action (lock and key model)

14.3 Lipids:

Lipids are organic molecules that are soluble in organic solvents such as chloroform and methanol and insoluble in water. The word lipid is derived from the Greek word *'lipos'* meaning fat. They are the principal components of cell membranes. In addition, they also act as energy source for living systems. Fat provides 2-3 fold higher energy compared to carbohydrates / proteins.

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14.3.1 Classification of lipids:

Based on their structures lipids can be classified as simple lipids, compound lipids and derived lipids. Simple lipids can be further classified into fats, which are esters of long chain fatty acids with glycerol (triglycerides) and waxes which are the esters of fatty acids with long chain monohydric alcohols (Bees wax).

Compound lipids are the esters of simple fatty acid with glycerol which contain additional groups. Based on the groups attached, they are further classified into phospholipids, glycolipids and lipoproteins. Phospholipids contain a phospho-ester linkage while the glycolipids contain a sugar molecule attached. The lipoproteins are complexes of lipid with proteins.

14.3.2 Biological importance of lipids

1. Lipids are the integral component of cell membrane. They are necessary of structural integrity of the cell.
2. The main function of triglycerides in animals is as an energy reserve. They yield more energy than carbohydrates and proteins.
3. They act as protective coating in aquatic organisms.
4. Lipids of connective tissue give protection to internal organs.
5. Lipids help in the absorption and transport of fat soluble vitamins.
6. They are essential for activation of enzymes such as lipases.
7. Lipids act as emulsifier in fat metabolism.

14.4 Vitamins:

Vitamins are small organic compounds that cannot be synthesised by our body but are essential for certain functions. Hence, they must be obtained through diet. The requirements of these compounds are not high, but their deficiency or excess can cause diseases. Each vitamin has a specific function in the living system, mostly as co enzymes. They are not served as energy sources like carbohydrates, lipids, etc.,

The name 'Vitamin' is derived from 'vital amines', referring to the vitamins earlier identified amino compounds. Vitamins are essential for the normal growth and maintenance of our health.

14.4.1 Classification of vitamins

Vitamins are classified into two groups based on their solubility either in water or in fat.

Fat soluble vitamins: These vitamins absorbed best when taken with fatty food and are stored in fatty tissues and livers. These vitamins do not dissolve in water. Hence they are called fat soluble vitamins. Vitamin A, D, E & K are fat-soluble vitamins.

Water soluble vitamins: Vitamins B (B_1, B_2, B_3, B_5, B_6, B_7, B_9 and B_{12}) and C are readily soluble in water. On the contrary to fat soluble vitamins, these can't be stored. The excess vitamins present will be excreted through urine and are not stored in our body. Hence, these two

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vitamins should be supplied regularly to our body. The missing numbers in B vitamins are once considered as vitamins but no longer considered as such, and the numbers that were assigned to them now form the gaps.

Table 14.2: Vitamins, their Sources, Functions and their Deficiency disease

Vitamin	Sources	Functions	Deficiency Disease
Vitamin A (Retinol)	Liver oil, Fish, Carrot, Milk, spinach and fruits such as Papaya and mango	Vision and growth	Night blindness, Xerophthalmia Keratinisation of skin
Vitamin B_1 (Thiamine)	Yeast, Milk, Cereals, Green vegetables, Liver, Pork	Co – enzyme in the form of Thiamine pyro phosphate (TPP) in glycolysis	Beri – Beri (peripheral nerve damage)
Vitamin B_2 (Riboflavin)	Soybean, Green vegetable Yeast, Egg white, Milk, Liver kidney	Co enzyme in the form of FMN (Flavin mono nucleotide)and FAD (Flavin adenine dinucleotide) in redox reactions	Cheilosis (lesions of corner of mouth, lips and tongue)
Vitamin B_3 (Niacin)	Cereals, Green leafy vegetables, Liver, Kidney	Co enzyme in the form of NAD and $NADP^+$ in redox reactions.	Pellagra (photo sensitive dermatitis)
Vitamin B_5 (Pantothenic acid)	Mushroom, Avocado, Egg yolk, Sunflower oil	Part of coenzyme A in carbohydrate protein and Fat metabolism	Inadequate growth
Vitamin B_6 (Pyridoxine)	Meat, Cereals, Milk, Whole grains, Egg.	Co enzyme in amino acid metabolism, formation of Heme in Hemoglobin	Convulsions
Vitamin B_7 (Biotin)	Liver, kidney, Milk, Egg yolk, Vegetables, Grains	Co enzyme in fatty acid Biosynthesis	Depression, Hair loss, muscle pain.
Vitamin B_9 (Folic acid)	Egg, Meat, Beet root, Leafy vegetables, Cereals, Yeast	Nucleic acid synthesis, maturation of red blood cells	Megaloblastic anaemia

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Vitamin	Sources	Functions	Deficiency Disease
Vitamin B_{12} (Cobalamin)	Egg, Meat, Fish	Co-enzyme in amino acid metabolism, Red blood cells maturation	Pernicious Anaemia
Vitamin C (Ascorbic acid)	Citrus fruits (Orange, Lemon etc…),Tomato, Amla, Leafy Vegetables	Coenzyme in Antioxidant, building of collagen	Scurvy (bleeding gums)
Vitamin D Cholecalciferol(D3), Ergocalciferol (D2)	Fish liver oil, Milk, Egg yolk, (exposure to sunlight)	Absorption and maintenance of calcium	Rickets (children), Osteomalacia (adults)
Vitamin E (Tocopherols)	Cotton seed oil, Sun flower oil, wheat germ oil, Vegetable oils	Antioxidant	muscular dystrophy (muscular weakness) and neurological dysfunction
Vitamin K (Phylloquinone& Menaquinones)	Green leafy vegetable, soybean oil, tomato	Blood clotting	Increased blood clotting time, Haemorrhagic diseases

14.5 Nucleic acids

The inherent characteristics of each and every species are transmitted from one generation to the next. It has been observed that the particles in nucleus of the cell are responsible for the transmission of these characteristics. They are called chromosomes and are made up of proteins and another type of biomolecules called nucleic acids. There are mainly two types nucleic acids, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). They are the molecular repositories that carry genetic information in every organism.

14.5.1 Composition and structure of nucleic acids

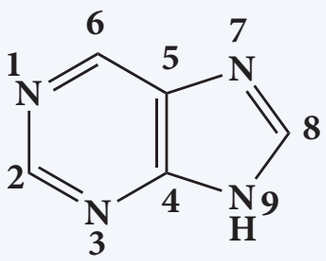
Nucleic acids are biopolymers of nucleotides. Controlled hydrolysis of DNA and RNA yields three components namely a nitrogenous base, a pentose sugar and phosphate group.

Nitrogen base

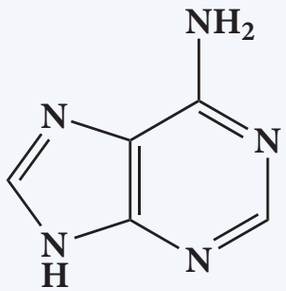
These are nitrogen containing organic compounds which are derivatives of two parent

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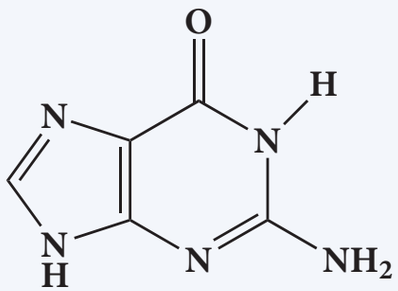
compounds, **pyrimidine** and **purine**. Both DNA and RNA have two major purine bases, **adenine** (A) and **guanine** (G). In both DNA and RNA, one of the pyrimidines is **cytosine** (C), but the second pyrimidine is **thymine** (T) in DNA and **uracil** (U) in RNA.



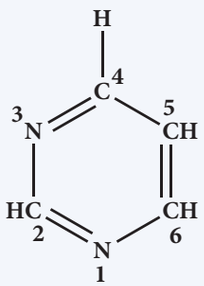
Purine



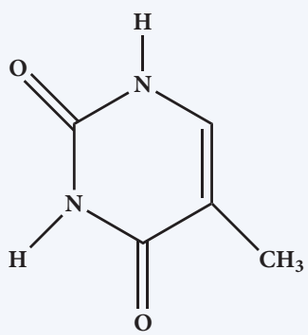
Adenine



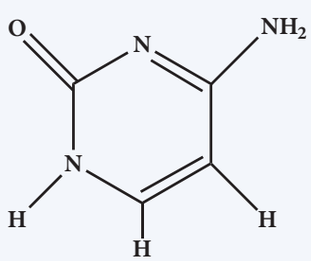
Guanine



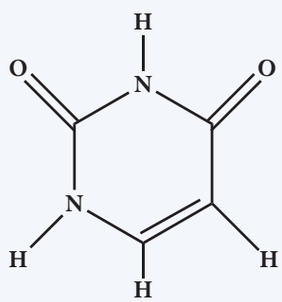
Pyrimidine



Thymine (T)



Cytosine (C)

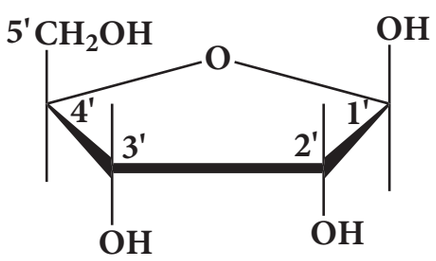


Uracil (U)

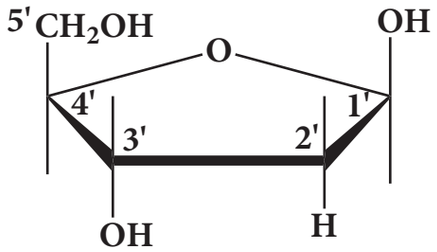
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Pentose sugar:

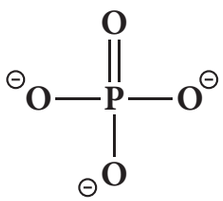
Nucleic acids have two types of pentoses. The recurring deoxyribonucleotide units of DNA contain **2'-deoxy-D-ribose** and the ribonucleotide units of RNA contain **D-ribose**. In nucleotides, both types of pentoses are in their β-furanose (closed five membered rings) form.



Ribose



Deoxyribose



Phosphate group

Phosphoric acid forms phospho diester bond between nucleotides. Based on the number of phosphate group present in the nucleotides, they are classified into mono nucleotide, dinucleotide and trinucleotide.

Nucleosides and nucleotides:

The molecule without the phosphate group is called a **nucleoside**. A **nucleotide** is derived from a nucleoside by the addition of a molecule of phosphoric acid. Phosphorylation occurs generally in the 5' OH group of the sugar. Nucleotides are linked in DNA and RNA by phospho diester bond between 5' OH group of one nucleotide and 3' OH group on another nucleotide.

Sugar + Base ⟶ Nucleoside

Nucleoside + Phosphoric acid ⟶ Nucleotide

nNucleotide ⟶ Polynucleotide (Nucleic Acid)

14.5.2 Double strand helix structure of DNA

In early 1950s, Rosalind Franklin and Maurice Wilkins used X-ray diffraction to unravel the structure of DNA. The DNA fibers produced a characteristic diffraction pattern.

The central X shaped pattern indicates a helix, whereas the heavy black arcs at the top and bottom of the diffraction pattern reveal the spacing of the stacked bases.

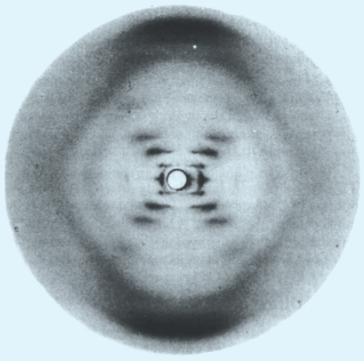
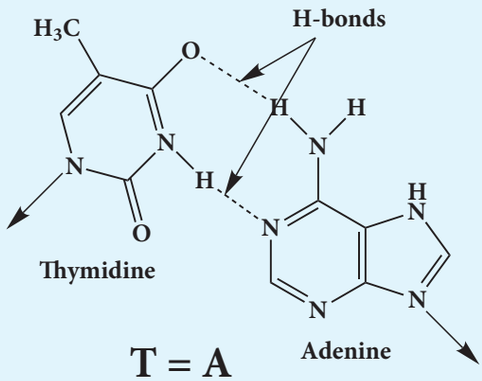


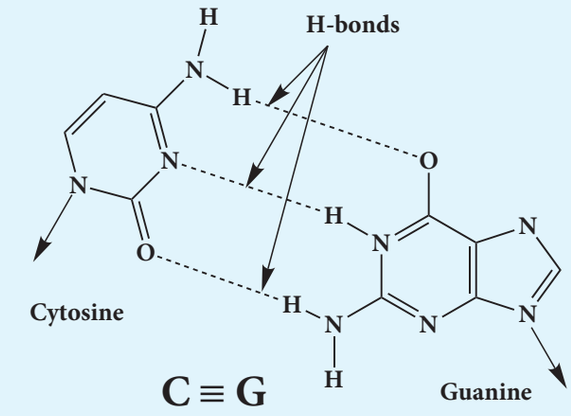
Figure 14.20 DNA X-ray diffraction

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The structure elucidation of DNA by Watson and Crick in 1953 was a momentous event in science. They postulated a 3-dimensional model of DNA structure which consisted of two antiparallel helical DNA chains wound around the same axis to form a right-handed double helix.

The hydrophilic backbones of alternating deoxyribose and phosphate groups are on the outside of the double helix, facing the surrounding water. The purine and pyrimidine bases of both strands are stacked inside the double helix, with their hydrophobic and ring structures very close together and perpendicular to the long axis, thereby reducing the repulsions between the charged phosphate groups. The offset pairing of the two strands creates a major groove and minor groove on the surface of the duplex.





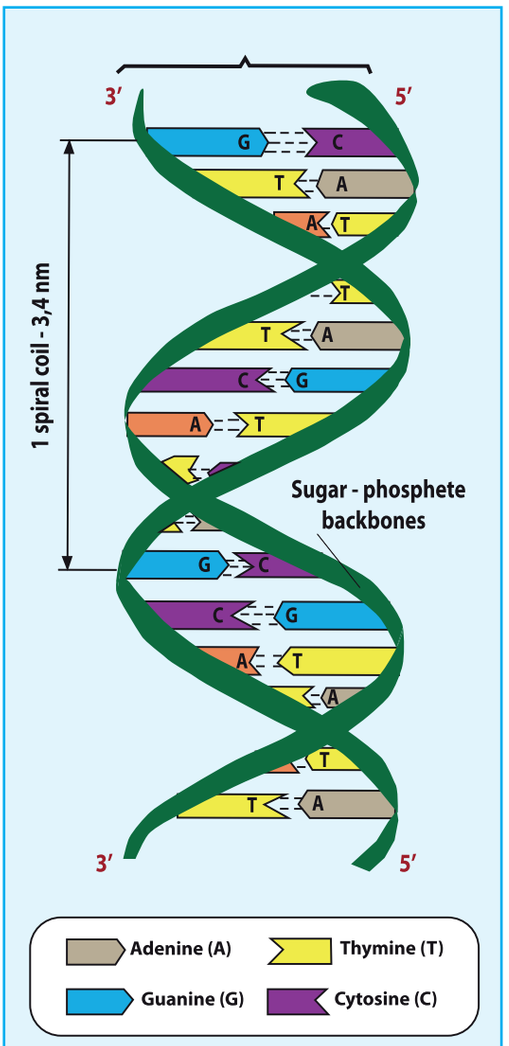


Figure 14.21 DNA Double Helix

The model revealed that, there are 10.5 base pairs (36 Å) per turn of the helix and 3.4 Å between the stacked bases. They also found that each base is hydrogen bonded to a base in opposite strand to form a planar base pair.

Two hydrogen bonds are formed between adenine and thymine and three hydrogen bonds are formed between guanine and cytosine. Other pairing tends to destabilize the double helical structure. This specific association of the two chains of the double helix is known

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as complementary base pairing. The DNA double helix or duplex is held together by two forces,

a) Hydrogen bonding between complementary base pairs

b) Base-stacking interactions

The complementary between the DNA strands is attributable to the hydrogen bonding between base pairs but the base stacking interactions are largely non-specific, make the major contribution to the stability of the double helix.

14.5.3 Types of RNA molecules

Ribonucleic acids are similar to DNA. Cells contain up to eight times high quantity of RNA than DNA. RNA is found in large amount in the cytoplasm and a lesser amount in the nucleus. In the cytoplasm it is mainly found in ribosomes and in the nucleus, it is found in nucleolus.

RNA molecules are classified according to their structure and function into three major types

i. Ribosomal RNA (rRNA) ii. Messenger RNA (mRNA)

iii. Transfer RNA (tRNA)

rRNA

rRNA is mainly found in cytoplasm and in ribosomes, which contain 60% RNA and 40% protein. Ribosomes are the sites at which protein synthesis takes place.

tRNA

tRNA molecules have lowest molecular weight of all nucleic acids. They consist of 73 – 94 nucleotides in a single chain. The function of tRNA is to carry amino acids to the sites of protein synthesis on ribosomes.

mRNA

mRNA is present in small quantity and very short lived. They are single stranded, and their synthesis takes place on DNA. The synthesis of mRNA from DNA strand is called transcription. mRNA carries genetic information from DNA to the ribosomes for protein synthesis. This process is known as translation

Table 14.3 Difference between DNA and RNA

DNA	RNA
It is mainly present in nucleus, mitochondria and chloroplast	It is mainly present in cytoplasm, nucleolus and ribosomes
It contains deoxyribose sugar	It contains ribose sugar
Base pair A = T. G ≡ C	Base pair A = U. C ≡ G
Double stranded molecules	Single stranded molecules
It's life time is high	It is Short lived
It is stable and not hydrolysed easily by alkalis	It is unstable and hydrolyzed easily by alkalis
It can replicate itself	It cannot replicate itself. It is formed from DNA.

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More to know

DNA finger printing

Traditionally, one of the most accurate methods for placing an individual at the scene of a crime has been a fingerprint. With the advent of recombinant DNA technology, a more powerful tool is now available: DNA fingerprinting is (also called DNA typing or DNA profiling). It was first invented by Professor Sir Alec Jeffreysin 1984. The DNA finger print is unique for every person and can be extracted from traces of samples from blood, saliva, hair etc…By using this method we can detect the individual specific variation in human DNA.

In this method, the extracted DNA is cut at specific points along the strand with restriction of enzymes resulting in the formation of DNA fragments of varying lengths which were analysed by technique called gel electrophoresis. This method separates the fragments based on their size. The gel containing the DNA fragments is then transferred to a nylon sheet using a technique called blotting. Then, the fragments will undergo autoradiography in which they were exposed to DNA probes (pieces of synthetic DNA that were made radioactive and that bound to the fragments). A piece of X-ray film was then exposed to the fragments, and a dark mark was produced at any point where a radioactive probe had become attached. The resultant pattern of marks could then be compared with other samples. DNA fingerprinting is based on slight sequence differences (usually single base-pair changes) between individuals. These methods are proving decisive in court cases worldwide.

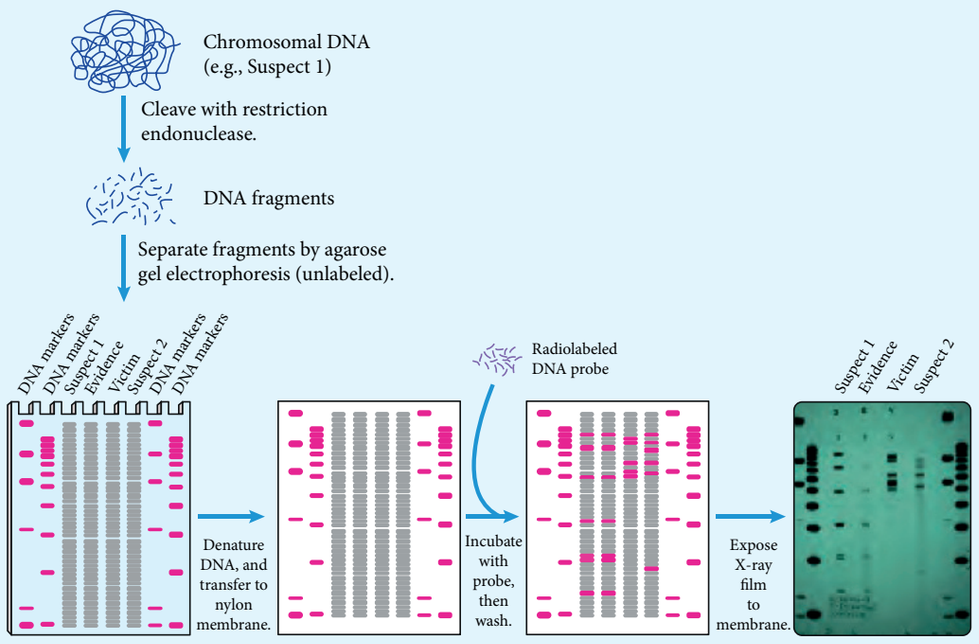


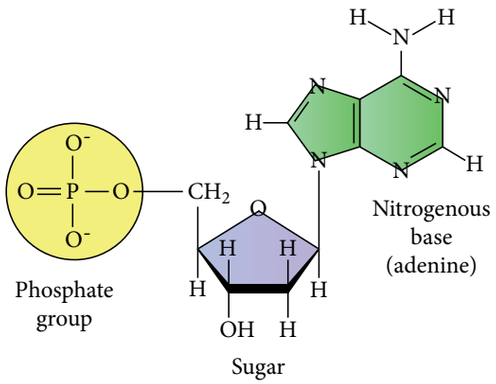
Figure 14.22 DNA finger printing

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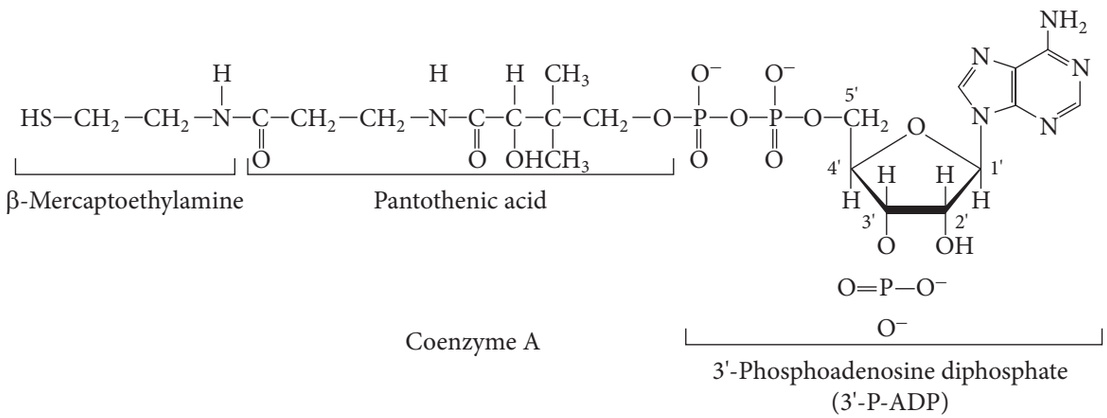
14.5.4 Biological functions of nucleic acids

In addition to their roles as the subunits of nucleic acids, nucleotides have a variety of other functions in every cell such as,

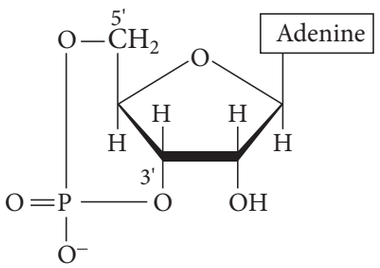
i. Energy carriers (ATP)



ii. Components of enzyme cofactors (Example: Coenzyme A, NAD^+, FAD)



iii. Chemical messengers (Example: Cyclic AMP, cAMP)



Adenosine 3', 5'-cyclic monophosphate
(cyclic AMP; cAMP)

14.6 HORMONES

Hormone is an organic substance (e.g. a peptide or a steroid) that is secreted by one tissue. it limits the blood stream and induces a physiological response (e.g. growth and metabolism) in other tissues. It is an intercellular signalling molecule. Virtually every

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process in a complex organism is regulated by one or more hormones: maintenance of blood pressure, blood volume and electrolyte balance, embryogenesis, hunger, eating behaviour, digestion - to name but a few. Endocrine glands, which are special groups of cells, make hormones. The major endocrine glands are the pituitary, pineal, thymus, thyroid, adrenal glands, and pancreas. In addition, men produce hormones in their testes and women produce them in their ovary. Chemically, hormones may be classified as either protein (e.g. insulin, epinephrine) or steroids (e.g. estrogen, androgen).Hormones are classified according to the distance over which they act as, endocrine, paracrine and autocrine hormones

Endocrine hormones act on cells distant from the site of their release. Example: insulin and epinephrine are synthesized and released in the bloodstream by specialized ductless endocrine glands.

Paracrine hormones (alternatively, local mediators) act only on cells close to the cell that released them. For example, interleukin-1 (IL-1)

Autocrine hormones act on the same cell that released them. For example, protein growth factor interleukin-2 (IL-2).

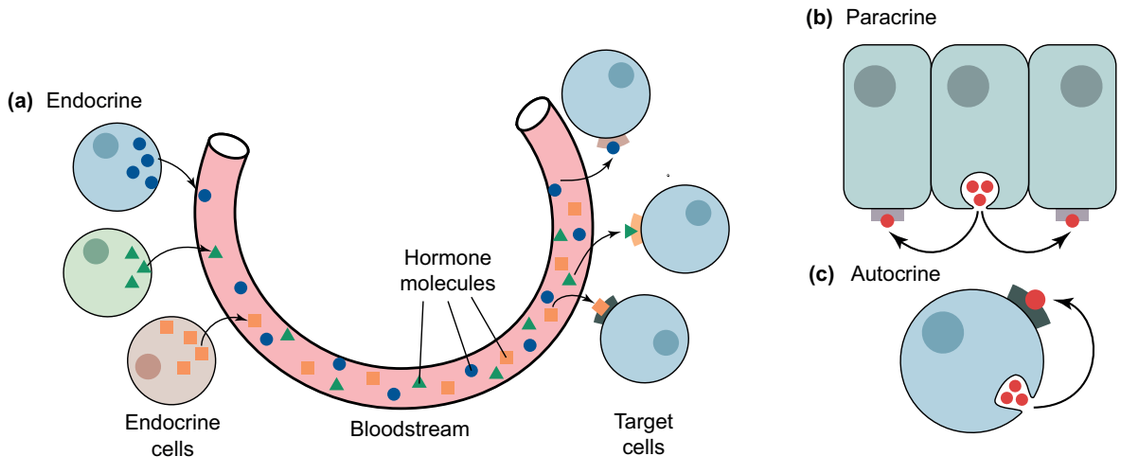


Figure 14.22 Endocrine Paracrine and Autocrine hormones

Only those cells with a specific receptor for a given hormone will respond to its presence even though nearly all cells in the body may be exposed to the hormone. Hormonal messages are therefore quite specifically addressed.

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EVALUATION

Choose the correct answer:

1. Which one of the following rotates the plane polarized light towards left? (NEET Phase – II)

   a) D(+) Glucose (b) L(+) Glucose (c)D(-) Fructose d) D(+) Galactose

2. The correct corresponding order of names of four aldoses with configuration given below Respectively is, (NEET Phase – I)1551

   a) *L*-Erythrose, *L*-Threose, *L*-Erythrose, *D*-Threose

   b)*D*-Threose,*D*-Erythrose, *L*-Threose, *L*-Erythrose,

   c)*L*-Erythrose, *L*-Threose, *D*-Erythrose, *D*-Threose

   d) *D*-Erythrose, *D*-Threose, *L*-Erythrose, *L*-Threose

   BQEYA

3. Which one given below is a non-reducing sugar? (NEET Phase – I)

   a) Glucose b) Sucrose c) maltose d) Lactose.

4. Glucose $\xrightarrow{(HCN)}$ Product $\xrightarrow{(hydrolysis)}$ Product $\xrightarrow{(HI + Heat)}$ A, the compound A is

   a) Heptanoic acid b) 2-Iodohexane c) Heptane d) Heptanol

5. Assertion: A solution of sucrose in water is dextrorotatory. But on hydrolysis in the presence of little hydrochloric acid, it becomes levorotatory. (AIIMS)

   Reason: Sucrose hydrolysis gives equal amounts of glucose and fructose. As a result of this change in sign of rotation is observed.

   a)If both accretion and reason are true and reason is the correct explanation of assertion

   b) If both assertion and reason are true but reason is not the correct explanation of assertion

   c) If assertion is true but reason is false.

   d) if both assertion and reason are false.

6. The central dogma of molecular genetics states that the genetic information flows from (NEET Phase – II)

   a) Amino acids $\longrightarrow$ Protein $\longrightarrow$ DNA

   b) DNA $\longrightarrow$ Carbohydrates $\longrightarrow$ Proteins

   c) DNA $\longrightarrow$ RNA $\longrightarrow$ Proteins

   d) DNA $\longrightarrow$ RNA $\longrightarrow$ Carbohydrates

7. In a protein, various amino acids linked together by (NEET Phase – I)

   a) Peptide bond b) Dative bond

   c) α - Glycosidic bond d) β - Glycosidic bond

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8. Among the following the achiral amino acid is (AIIMS)

a) 2-ethylalanine b) 2-methylglycine

c) 2-hydroxymethylserine d) Tryptophan

9. The correct statement regarding RNA and DNA respectively is (NEET Phase – I)

a) the sugar component in RNA is an arabinos and the sugar component in DNA is ribose

b) the sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose

c) the sugar component in RNA is an arabinose and the sugar component in DNA is 2'-deoxyribose

d) the sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose

10. In aqueous solution of amino acids mostly exists in,

a) NH_2-CH(R)-COOH b) NH_2-CH(R)-COO^-

c) H_3N^+-CH(R)-COOH d) H_3N^+-CH(R)-COO^-

11. Which one of the following is not produced by body?

a) DNA b) Enzymes c) Harmones d) Vitamins

12. The number of sp2 and sp3 hybridised carbon in fructose are respectively

a) 1 and 4 b) 4 and 2 c) 5 and 1 d) 1 and 5

13. Vitamin B2 is also known as

a) Riboflavin b) Thiamine c) Nicotinamide d) Pyridoxine

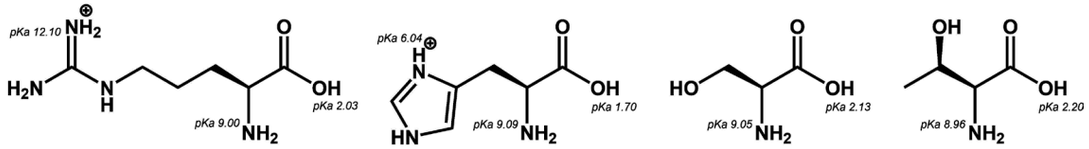
14. The pyrimidine bases present in DNA are

a) Cytosine and Adenine b) Cytosine and Guanine

c) Cytosine and Thiamine d) Cytosine and Uracil

15. Among the following L-serine is

a) b) c) d)



16. The secondary structure of a protein refers to

a) fixed configuration of the polypeptide backbone

b) hydrophobic interaction

c) sequence of α-amino acids

d) α-helical backbone.

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17. Which of the following vitamins is water soluble?

a) Vitamin E b) Vitamin K c) Vitamin A d) Vitamin B

18. Complete hydrolysis of cellulose gives

a) L-Glucose b) D-Fructose c) D-Ribose d) D-Glucose

19. Which of the following statement is not correct?

a) Ovalbumin is a simple food reserve in egg-white

b) Blood proteins thrombin and fibrinogen are involved in blood clotting

c) Denaturation makes protein more active

d) Insulin maintains the sugar level of in the human body.

20. Glucose is an aldose. Which one of the following reactions is not expected with glucose?

a) It does not form oxime

b) It does not react with Grignard reagent

c) It does not form osazones

d) It does not reduce tollens reagent

21. If one strand of the DNA has the sequence 'ATGCTTGA', then the sequence of complementary strand would be

a) TACGAACT b) TCCGAACT c) TACGTACT d) TACGRAGT

22. Insulin, a hormone chemically is

a) Fat b) Steroid c) Protein d) Carbohydrates

23. α-D (+) Glucose and β-D (+) glucose are

a) Epimers b) Anomers

c) Enantiomers d) Conformational isomers

24. Which of the following are epimers

a) D(+)-Glucose and D(+)-Galactose (b) D(+)-Glucose and D(+)-Mannose

c) Neither (a) nor (b) (d) Both (a) and (b)

25. Which of the following amino acids are achiral?

a) Alanine b) Leucine c) Proline d) Glycine

Short Answer Questions

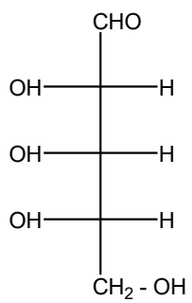
1. What type of linkages hold together monomers of DNA?
2. Give the differences between primary and secondary structure of proteins.
3. Name the Vitamins whose deficiency cause i) rickets ii) scurvy
4. Write the Zwitter ion structure of alanine

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5. Give any three difference between DNA and RNA
6. Write a short note on peptide bond
7. Give two difference between Hormones and vitamins
8. Write a note on denaturation of proteins
9. What are reducing and non – reducing sugars?
10. Why carbohydrates are generally optically active.
11. Classify the following into monosaccharides, oligosaccharides and polysaccharides.

    i) Starch ii) fructose iii) sucrose

    iv) lactose iv) maltose
12. How are vitamins classified
13. What are harmones? Give examples
14. Write the structure of all possible dipeptides which can be obtained form glycine and alanine
15. Define enzymes
16. Write the structure of α-D (+) glucophyranose
17. What are different types of RNA which are found in cell
18. Write a note on formation of α-helix .
19. What are the functions of lipids in living organism.
20. Is the following sugar, D – sugar or L – sugar?



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UNIT 15

CHEMISTRY IN EVERYDAY LIFE



Vladimir Prelog

Prof. Vladimir Prelog was a Swiss Chemist who shared 1975 Nobel Prize for Chemistry with John W Cornforth for his work on Stereo Chemistry. He has done wide ranging research on alkaloids, antibiotics, enzymes and other natural compounds. He was distinguished for his contribution to the development of modern stereo chemistry. Prelog synthesized many natural products and worked on problems of stereo chemistry like adamenline, boromycin analoids and rifamycins

YVAO5

Learning Objectives

After studying this unit, the students will be able to

- recognize the term drug and chemotherapy
- classify the drugs based on their properties
- describe the drug-target interaction.
- discuss some important classes of drugs.
- explain the chemistry of cleansing agents
- describe the chemicals in food
- explain the important terms in polymer chemistry.
- describe the preparation of some important synthetic polymers
- appreciate the importance of polymers in today life

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INTRODUCTION

Chemistry touches every aspect of our lives. The three-basic requirement of our life: food, clothes, shelter are all basically chemical compounds. Infact, life itself is a complicated system of interrelated chemical process. In this unit, we will learn the chemistry involved in the field of medicines, food materials, cleansing agents and polymers.

15.1 Drug

The word drug is derived from the French word "*drogue*" meaning "*dry herb*". A drug is a substance that is used to modify or explore physiological systems or pathological states for the benefit of the recipient. It is used for the purpose of diagnosis, prevention, cure/relief of a disease.The drug which interacts with macromolecular targets such as proteins to produce a therapeutic and useful biological response is called medicine. The specific treatment of a disease using medicine is known as chemotherapy. An ideal drug is the one which is non-toxic, bio-compatible and bio-degradable, and it should not have any side effects. Generally, most of the drug molecules that are used now a days have the above properties at lower concentrations. However, at higher concentrations, they have side effects and become toxic. The medicinal value of a drug is measured in terms of its therapeutic index, which is defined as the ratio between the maximum tolerated dose of a drug (above which it become toxic) and the minimum curative dose (below which the drug is ineffective). Higher the value of therapeutic index, safer is the drug.

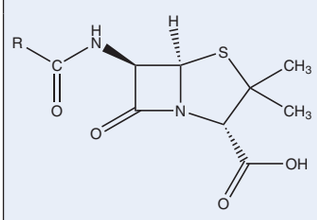
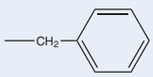
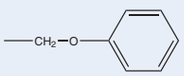
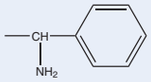
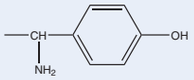
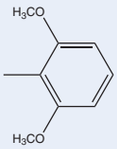
15.1.1 Classification of drugs:

Drugs are classified based on their properties such as chemical structure, pharmacological effect, target system, site of action etc. We will discuss some general classifications here.

Classification based on the chemical structure:

In this classification, drugs with a common chemical skeleton are classified into a single group. For example, ampicillin, amoxicillin, methicillin etc.. all have similar structure and are classified into a single group called penicillin. Similarly, we have other group of drugs such as opiates, steroids, catecholamines etc. Compounds having similar chemical structure are expected to have similar chemical properties. However, their biological actions are not always similar. For example, all drugs belonging to penicillin group have same biological action, while groups such as barbiturates, steroids etc.. have different biological action.

Penicillins

	R group-Drug Name				
	 Penicillin G	 Penicillin V	 Ampicillin	 Amoxicillin	 methicillin

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Classification based on Pharmacological effect:

In this classification, the drugs are grouped based on their biological effect that they produce on the recipient. For example, the medicines that have the ability to kill the pathogenic bacteria are grouped as antibiotics. This kind of grouping will provide the full range of drugs that can be used for a particular condition (disease). The physician has to carefully choose a suitable medicine from the available drugs based on the clinical condition of the recipient.

Examples:

Antibiotic drugs: amoxicillin, ampicillin,cefixime, cefpodoxime, erythromycin, tetracycline etc..

Antihypertensive drugs: propranolol, atenolol, metoprolol succinate, amlodipine etc…

Classification based on the target system (drug action):

In this classification, the drugs are grouped based on the biological system/process, that they target in the recipient. This classification is more specific than the pharmacological classification.For example, the antibiotics streptomycin and erythromycin inhibit the protein synthesis (target process) in bacteria and are classified in a same group. However, their mode of action is different. Streptomycin inhibits the initiation of protein synthesis, while erythromycin prevents the incorporation of new amino acids to the protein.

Classification based on the site of action (molecular target):

The drug molecule interacts with biomolecules such as enzymes, receptors etc,, which are referred as drug targets. We can classify the drug based on the drug target with which it binds. This classification is highly specific compared to the others. These compounds often have a common mechanism of action, as the target is the same.

15.1.2 Drug–target Interaction:

The biochemical processes such as metabolism (which is responsible for breaking down the food molecules and harvest energy in the form of ATP and biosynthesis of necessary biomolecules from the available precursor molecules using many enzymes),cell-signaling (senses any change in the environment using the receptor molecules and send signals to various processes to elicit an appropriate response) etc… are essential for the normal functioning of our body. These routine processes may be disturbed by any external factors such as microorganism, chemicals etc.. or by a disorder in the system itself. Under such conditions we may have to take medicines to restore the normal functioning of the body.

These drug molecules interact with biomolecules such as proteins, lipids, etc..that are responsible for different functions of the body. For example, proteins which act as biological catalysts are called enzymes and those which are important for communication systems are called receptors. The drug interacts with these molecules and modify the normal biochemical reactions either by modifying the enzyme activity or by stimulating/suppressing certain receptors.

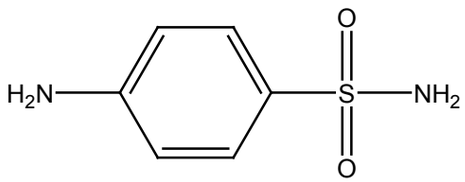
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Enzymes as drug targets:

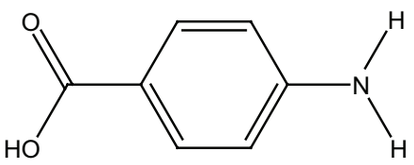
In all living systems, the biochemical reactions are catalysed by enzymes. Hence, these enzyme actions are highly essential for the normal functioning of the system. If their normal enzyme activity is inhibited, then the system will be affected. This principle is usually applied to kill many pathogens.

We have already learnt that in enzyme catalysed reactions, the substrate molecule binds to the active site of the enzyme by means of the weak interaction such as hydrogen bonding, van der Waals force etc… between the amino acids present in the active site and the substrate.

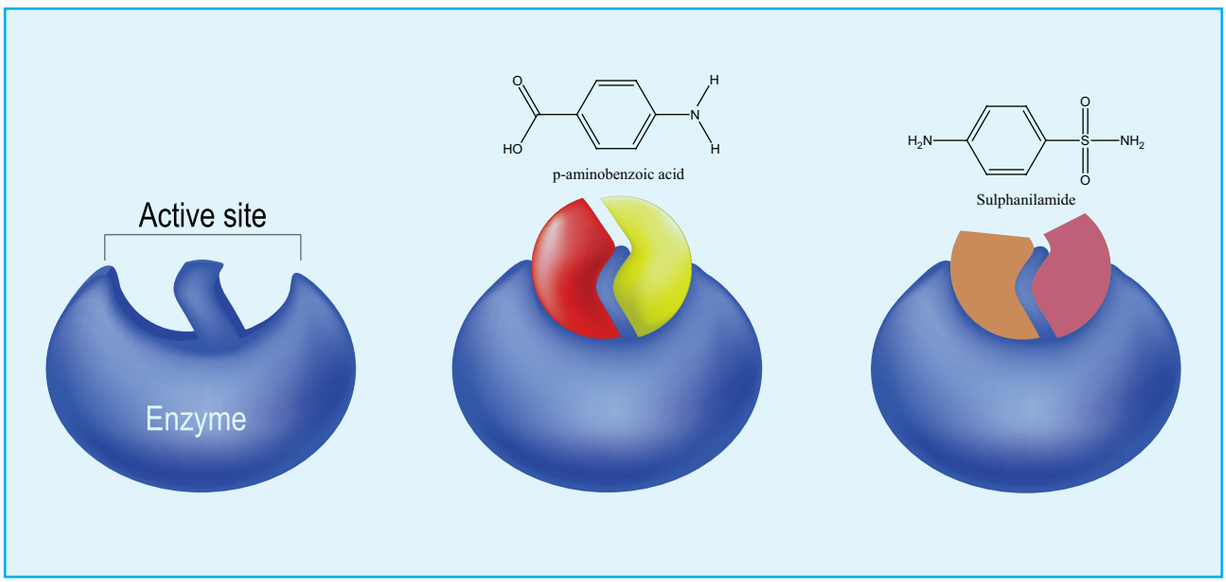
When a drug molecule that has a similar geometry (shape)as the substrate is administered, it can also bind to the enzyme and inhibit its activity.In other words, the drug acts as an inhibitor to the enzyme catalyst. These type of inhibitors are often called competitive inhibitors. For example the antibiotic sulphanilamide, which is structurally similar to *p*-aminobenzoic acid (PABA) inhibits the bacterial growth. Many bacteria need PABA in order to produce an important coenzyme, folic acid. When the antibiotic sulphanilamide is administered, it acts as a competitive inhibitor to the enzyme dihydropteroate synthase (DHPS) in the biosynthetic pathway of converting PABA into folic acid in the bacteria. It leads to the folic acid deficiency which retards the growth of the bacteria and can eventually kill them.



Sulphanilamide



p-aminobenzoic acid

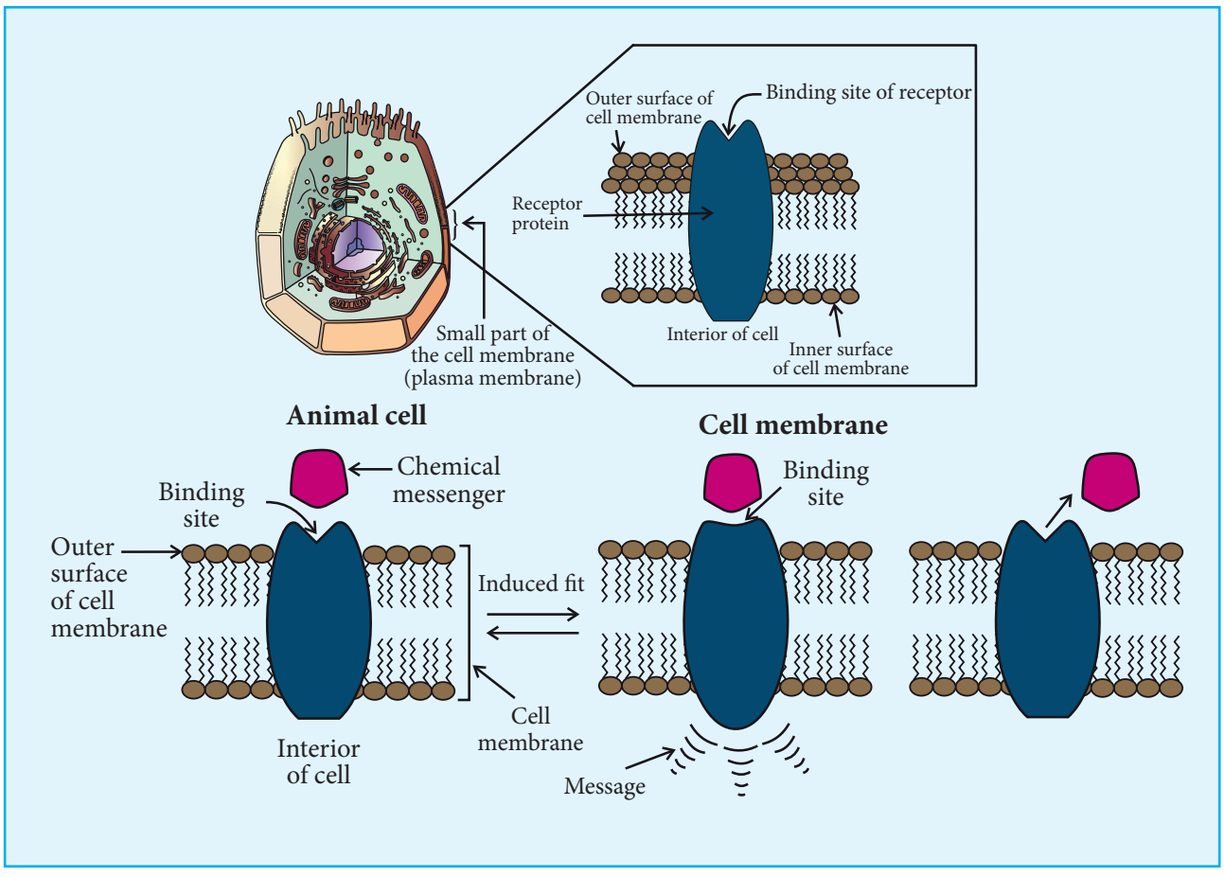


In certain enzymes, the inhibitor molecule binds to a different binding site, which is commonly referred to as allosteric site, and causes a change in its active site geometry (shape). As a result, the substrate cannot bind to the enzyme. This type of inhibitors are called allosteric inhibitors.

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Receptor as drug targets:

Many drugs exert their physiological effects by binding to a specific molecule called a receptor whose role is to trigger a response in a cell. Most of the receptors are integrated with the cell membranes in such a way that their active site is exposed to outside region of the cell membrane. The chemical messengers, the compounds that carry messages to cells, bind to the active site of these receptors. This brings about the transfer of message into the cell. These receptors show high selectivity for one chemical messenger over the others. If we want to block a message, a drug that binds to the receptor site should inhibit its natural function. Such drugs are called **antagonists**. In contrast, there are drugs which mimic the natural messenger by switching on the receptor. These type of drugs are called **agonists** and are used when there is lack of chemical messenger.

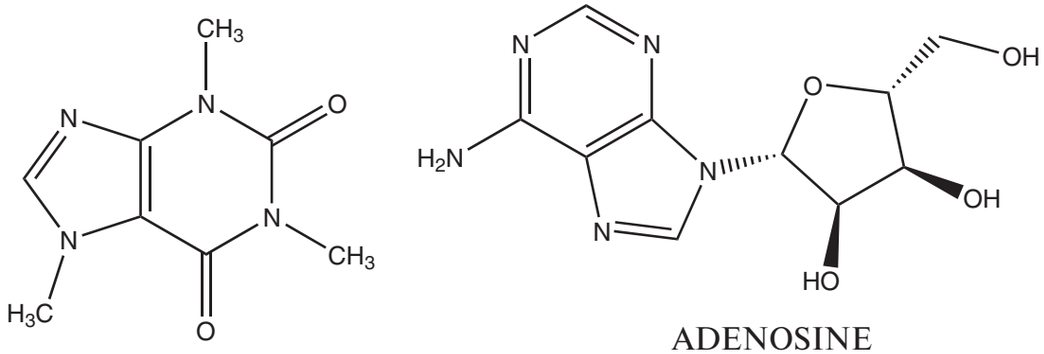


For example, when adenosine binds to the adenosine receptors, it induces sleepiness. On the other hand, the antagonist drug caffeine binds to the adenosine receptor and makes it inactive. This results in the reduced sleepiness (wakefulness).

The agonist drug, morphine, which is used as a pain killer, binds to the opioid receptors and activates them. This supress the neuro transmitters that causes pain.

Most receptors are chiral and hence different enantiomers of a drug can have different effect

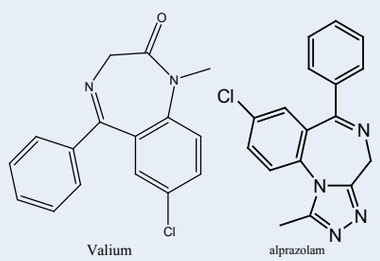
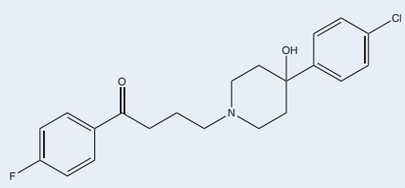
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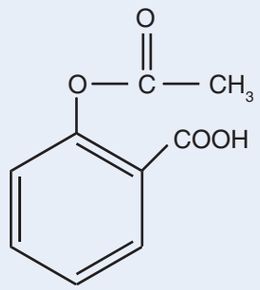
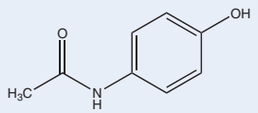
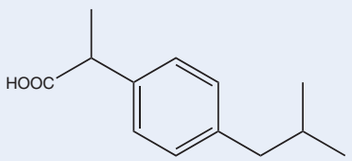
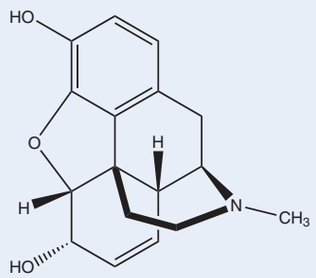
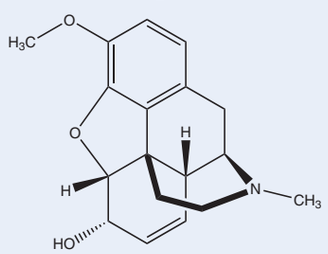
ADENOSINE

Therapeutic action of Different classes of Drugs:

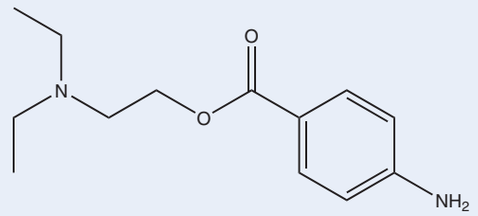
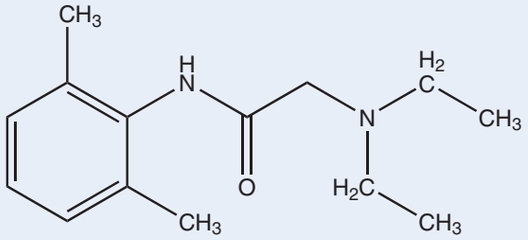
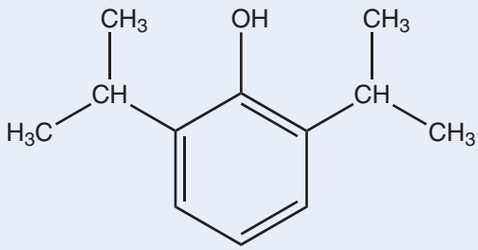
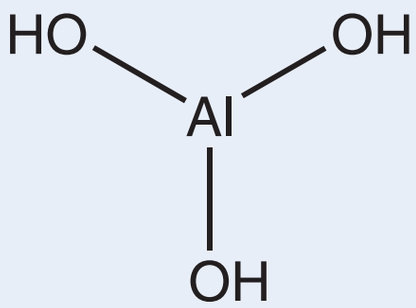
The developments in the field of biology allowed us to understand various biological process and their mechanism in detail. This enabled to develop new safer efficient drugs. For example, to treat acidity, we have been using weak bases such as aluminium and magnesium hydroxides. But these can make the stomach alkaline and trigger the production of much acid. Moreover, This treatment only relives the symptoms and does not control the cause. Detailed studies reveal that histamines stimulate the secretion of HCl by activating the receptor in the stomach wall. This findings lead to the design of new drugs such as cimetidine, ranitidine etc.. which binds the receptor and inactivate them. These drugs are structurally similar to histamine.In this section, we shall discuss the therapeutic action of a few important classes of drugs.

Class of Drugs	Mode of action	Chemical structure of some important structures
1) Tranquilizers They are neurologically active drugs. **i) Major tranquilizers:** Haloperidol, clozapine **ii) Minor tranquilizers:** Diazepam (Valium), alprazolam	Acts on the central nervous system by blocking the neurotransmitter dopamine in the brain **Uses** Treatment of stress, anxiety, depression, sleep disorders and severe mental diseases like schizophrenia	 Valium alprazolam  Haloperidol

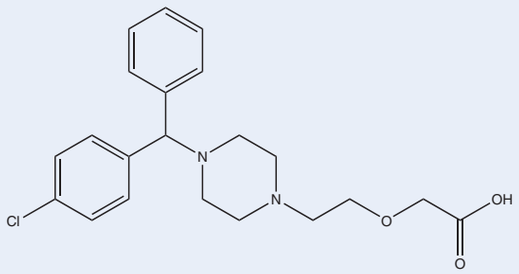
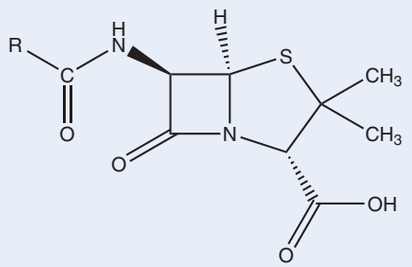
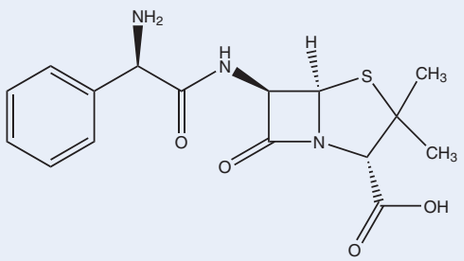
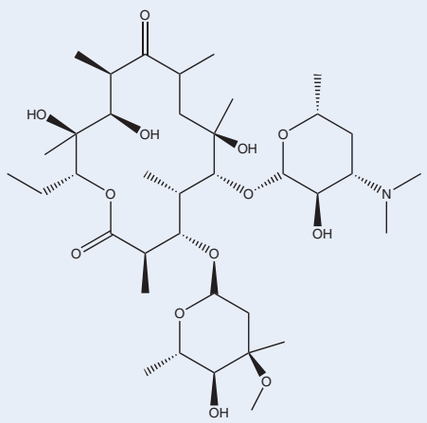
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2) Analgesics (Non – narcotic) Analgesics reduce the pain without causing impairment of consciousness. **i) Anti-inflammatory drugs** **Example** Acetaminophen or paracetamol, Ibuprofen, Asprin. **ii) Antipyretics** Example **Salicylates** Acetylsalicylic acid (aspirin), **Acetaminophen or Paracetamol** **iii) Nonsteroidal anti-inflammatory drugs (NSAIDs)** Ibuprofen	They alleviate pain by reducing local inflammatory responses **Uses** Used for short-term pain relief and for modest painlike headache, muscle strain, bruising, or arthritis. These drugs have many other effects such as reducing fever (antipyretic) and preventing platelet coagulation. Due to this property, aspirin finds useful in the prevention of heart attacks Reduces fever by causing the hypothalamus to override a prostaglandin-induced increase in temperature..	 Acetylsalicylic acid (aspirin)  Paracetamol  Ibuprofen
3) **Opioids (Narcotic Analgesics)** **Examples** Morphine, codeine	Relive pain and produce sleep. These drugs are addictive. In poisonous dose,these produce coma and ultimately death. **Uses** Used for either short-term or long-term relief of severe pain. Mainly used for post operative pain, pain of terminal cancer.	 Morphine  codeine

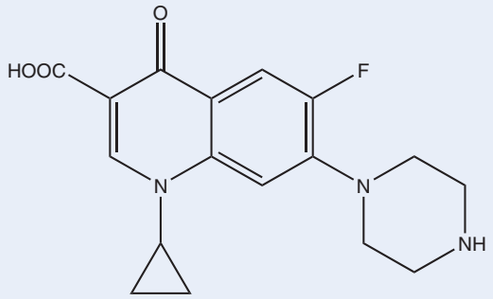
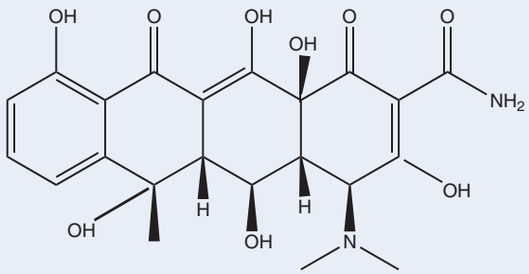
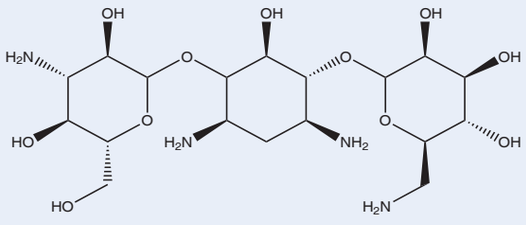
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4) Anaesthetics i) Local anaesthetics Examples **Ester-linked local anaesthetic** - Procaine **Amide-linked local anaesthetic** - Lidocaine	It causes loss of sensation, in the area in which it is applied without losing consciousness. They block pain perception that is transmitted via peripheral nerve fibres to the brain **Uses** They are often used during minor surgical procedures.	 Procaine  Lidocaine
ii) General anaesthetics Example **Intravenous general anaesthetics**– Propofol **Inhalational general anaesthetics**- Isoflurane	Cause a controlled and reversible loss of consciousness by affecting central nervous system **Uses** They are often used for major surgical procedures.	 Propofol
5) Antacids **Examples** Milk of Magnesia, Sodium bicarbonate, calcium bicarbonate, aluminium hydroxide Ranitidine, Cemitidine Omeprazole, rabeprazole	Neutralize the acid in the stomach that causes acidity. **Uses** To relieve symptoms such as burning sensation in the chest/ throat area (heart burns) caused by acid reflux.	 aluminium hydroxide

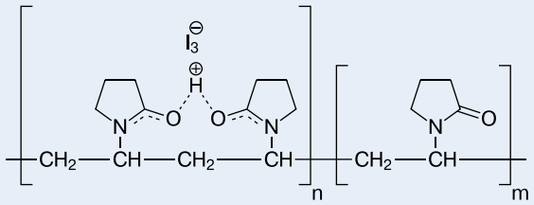
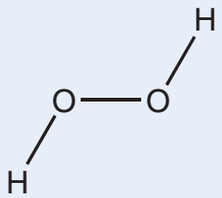
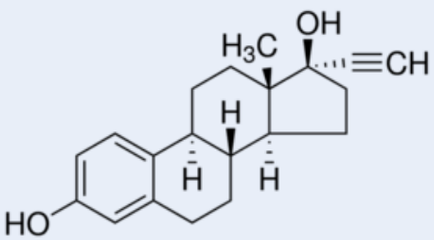
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6) Antihistamines Examples Cetirizine, levocetirizine, desloratadine, brompheniramine Terfenadine	Block histamine release from histamine-1 receptors **Uses** To provide relief from the allergic effects	 Cetirizine
7) Antimicrobials i) Beta-Lactams Examples Penicillins, ampicillin, cephalosporins, carbapenems, and monobactams	Inhibits bacterial cell wall biosynthesis **Uses** To treat skin infections, dental infections, ear infections, respiratory tract infections, pneumonia, urinary tract infections, and gonorrhoea	 Penicillins  Ampicillin
ii) Macrolides Examples Erythromycin, azithromycin	Targets bacterial ribosomes and prevent protein production **Uses** To treat respiratory tract infections, genital, gastrointestinal tractand skin infections	 Erythromycin

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iii) Fluoroquinolones Examples Clinafloxacin, ciprofloxacin, levofloxacin	Inhibits bacterial enzyme DNA gyrase **Uses** To treat urinary tract infections, skin infections, and respiratory infections (such as sinusitis, pneumonia, bronchitis), pulmonary infections in cystic fibrosis	 Ciprofloxacin
iv) Tetracyclines Examples Doxycycline, minocycline, oxytetracycline	Inhibit the bacterial protein synthesis via interaction with the 30S subunit of the bacterial ribosome **Uses** Used in the treatment of peptic ulcer disease, infections of the respiratory tract, cholera, acne vulgaris.	 Oxytetracycline
v) Aminoglycosides Examples Kanamycin, gentamicin, neomycin	Bind to the 30S subunit of the bacterial ribosome, thus stopping bacteria from making proteins **Uses** Used to treat infections caused by gram-negative bacteria	 Kanamycin

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8) Antiseptics Examples Hydrogen peroxide, povidone-iodine, benzalkonium chloride	Stop or slow down the growth of microorganisms – Applied to living tissue **Uses** To reduce the risk of infection during surgery and other procedures	 Povidone-iodine
9) Disinfectants Examples Chlorine compounds, alcohol, Hydrogen peroxide.	Stop or slow down the growth of microorganisms – Generally used on inanimate objects	 Hydrogen peroxide
10) Antifertility drugs **Example** **Synthetic oestrogen** - Ethynylestradiol, Menstranol **Synthetic Progesterone** - Norethindrone, Norethynodrel	These synthetic hormones that suppresses ovulation/ fertilisation. **Uses** Used in birth control pills.	 Ethynylestradiol

15.2 Food additives:

Have you ever noticed the ingredients that is printed on the cover of the packed food materials such as biscuits, chocolates etc...You might have noticed that emulsifiers such as 322, 472E, dough conditioners 223 etc… are used in the preparation, in addition to the main ingredients such as wheat flour, edible oil, sugar, milk solid etc… Do you think that these substances are necessary? Yes. These substances enhance the nutritive, sensory and practical value of the food. They also increase the shelf life of food. The substances which are not naturally a part of the food and added to improve the quality of food are called food additives.

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15.2.1 Important categories of food additives

- Aroma compounds
- Food colours
- Preservatives
- Stabilizers
- Artificial Sweeteners
- Antioxidants
- Buffering substances
- Vitamins and minerals

Advantages of food additives:

1. Uses of preservatives reduce the product spoilage and extend the shelf-life of food
2. Addition of vitamins and minerals reduces the mall nutrient
3. Flavouring agents enhance the aroma of the food
4. Antioxidants prevent the formation of potentially toxic oxidation products of lipids and other food constituents

15.2.2. Preservatives:

Preservatives are capable of inhibiting, retarding or arresting the process of fermentation, acidification or other decomposition of food by growth of microorganisms. Organic acids such as benzoic acid, sorbic acid and their salts are potent inhibitors of a number of fungi, yeast and bacteria. Alkyl esters of hydroxy benzoic acid are very effective in less acidic conditions. Acetic acid is used mainly as a preservative for the preparation of pickles and for preserved vegetables. Sodium metabisulphite is used as preservatives for fresh vegetables and fruits. Sucrose esters with palmitic and steric acid are used as emulsifiers. In addition that some organic acids and their salts are used as preservatives. In addition to chemical treatment, physical methods such as heat treatment (pasteurisation and sterilisations), cold treatment (chilling and freezing) drying (dehydration) and irradiation are used to preserve food.

15.2.3. Antioxidants:

Antioxidants are substances which retard the oxidative deteriorations of food. Food containing fats and oils is easily oxidised and turn rancid. To prevent the oxidation of the fats and oils, chemical BHT(butylhydroxy toluene), BHA(Butylated hydroxy anisole) are added as food additives. They are generally called antioxidants. These materials readily undergo oxidation by reacting with free radicals generated by the oxidation of oils, thereby stop the chain reaction of oxidation of food. Sulphur dioxide and sulphites are also used as food additives. They act as anti-microbial agents, antioxidants and enzyme inhibitors.

15.2.4 Sugar Substituents:

Those compounds that are used like sugars (glucose, sucrose) for sweetening, but are metabolised without the influence of insulin are called sugar substituents. Eg. Sorbitol, Xylitol, Mannitol.

15.2.5 Artificial sweetening agents:

Synthetic compounds which imprint a sweet sensation and possess no or negligible nutritional value are called artificial sweeteners. Eg. Saccharin, Aspartame, sucralose, alitame etc…

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15.3 Cleansing agents:

Soaps and detergents are used as cleansing agents. Chemically soap is the sodium or potassium salt of higher fatty acids. Detergent is sodium salt of alkyl hydrogen sulphates or alkyl benzene sulphonic acids.

15.3.1 Soaps:

Soaps are made from animal fats or vegetable oils. They contain glyceryl esters of long chain fatty acids. When the glycerides are heated with a solution of sodium hydroxide they become soap and glycerol. We have already learnt this reaction under the preparation of glycerol by saponification. Common salt is added to the reaction mixture to decrease the solubility of soap and it helps to precipitate out from the aqueous solution. Soap is then mixed with desired colours, perfumes and chemicals of medicinal importance.

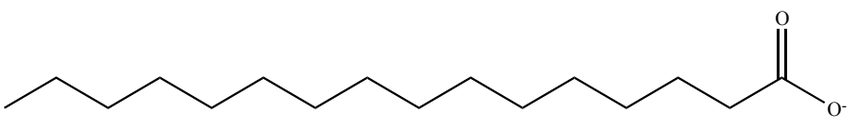
Total fatty matter:

The quality of a soap is described in terms of total fatty matter (TFM value). It is defined as the total amount of fatty matter that can be separated from a sample after splitting with mineral acids., Higher the TFM quantity in the soap better is its quality.

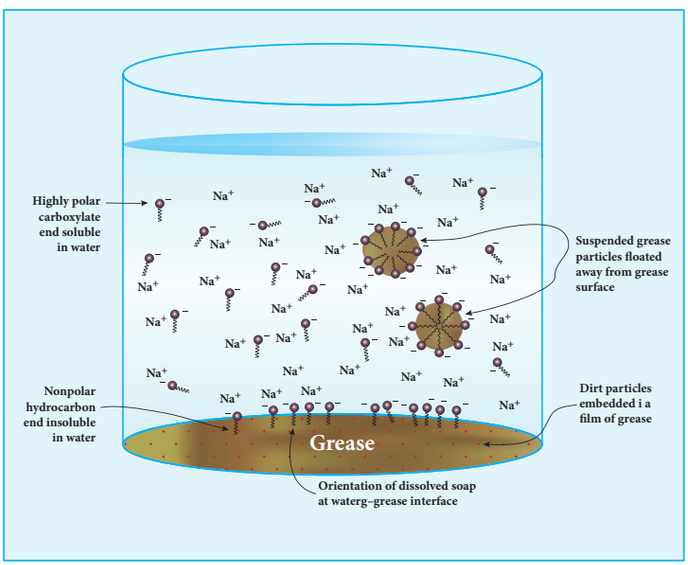
As per BIS standards, Grade-1 soaps should have 76% minimum TFM, while Grade-2 and 3 must have 70 and 60% , minimum respectively. The other quality parameters are lather, moisture content,mushiness, insoluble matter in alcohol etc..

The cleansing action of soap:

To understand how a soap works as a cleansing agent, let us consider sodium palmitate an example of a soap. The cleansing action of soap is directly related to the structure of carboxylate ions (palmitate ion) present in soap. The structure of palmitate exhibit dual polarity. The hydrocarbon portion is non polar and the carboxyl portion is polar.



The nonpolar portion is hydrophobic while the polar end is hydrophilic. The hydrophobic hydro carbon portion is soluble in oils and greases, but not in water. The hydrophilic carboxylate group is soluble in water. The dirt in the cloth is due to the presence of dust particles intact or grease which stick. When the soap is added to an oily or greasy part of the cloth, the hydrocarbon part of the soap dissolve in the grease, leaving the negatively charged carboxylate end exposed on the grease surface. At the

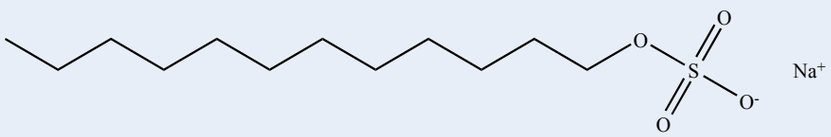
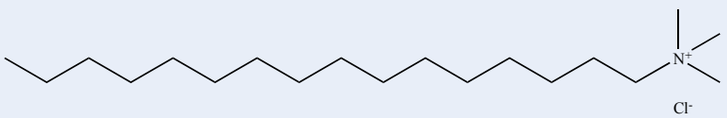
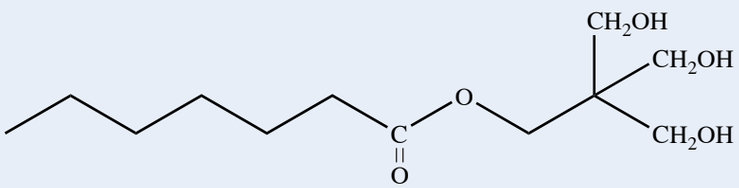


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same time the negatively charged carboxylate groups are strongly attracted by water, thus leading to the formation of small droplets called micelles and grease is floated away from the solid object. When the water is rinsed away, the grease goes with it. As a result, the cloth gets free from dirt and the droplets are washed away with water. The micelles do not combine into large drops because their surfaces are all negatively charged and repel each other. The cleansing ability of a soap depends upon its tendency to act as a emulsifying agent between water and water insoluble greases.

15.3.2 Detergents:

Synthetic detergents are formulated products containing either sodium salts of alkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonic acids. There are three types of detergents.

Detergent Type	Example
Anionic detergent	Sodium Lauryl sulphate (SLS) 
Cationic detergent	n-hexadecyltrimethyl ammonium chloride  *N,N,N*-trimethylhexadecan-1-aminium chloride
Non-ionic detergent	Pentaerythrityl stearate.  3-hydroxy-2,2-bis(hydroxymethyl)propyl heptanoate

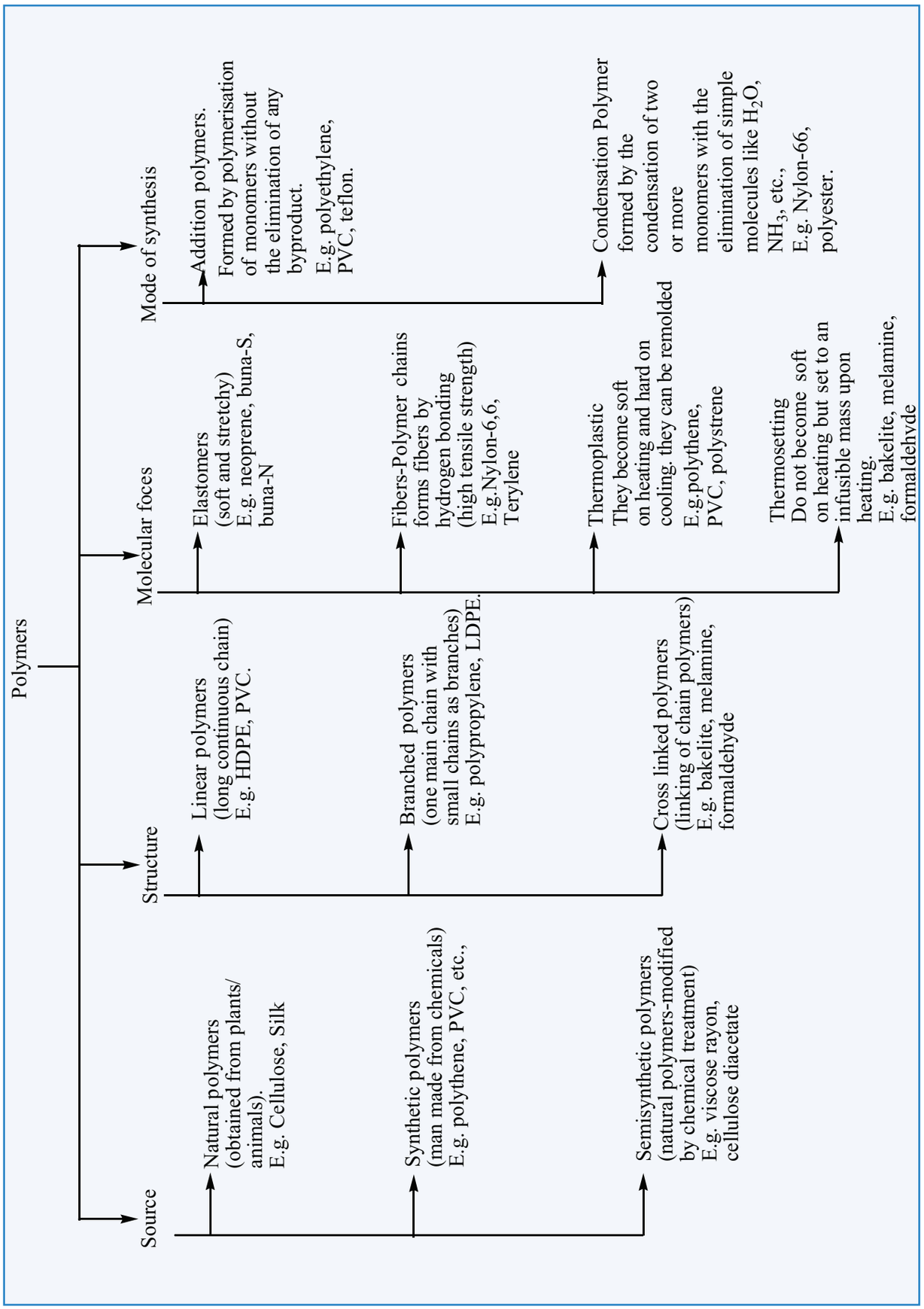
Detergents are superior to soaps as they can be used even in hard water and in acidic conditions. The cleansing action of detergents are similar to the cleansing action of soaps.

15.4 Polymers

The term Polymer is derived from the Greek word 'polumeres' meaning "having many parts". The constitution of a polymer is described in terms of its structural units called monomers. Polymers consists of large number of monomer units derived from simple molecules. For example: PVC(Poly Vinyl Chloride). is a polymer which is obtained from the monomer vinyl chloride. Polymers can be classified based on the source of availability, structure, molecular forces and the mode of synthesis. The following chart explain different classification of polymers.

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15.4.1 Classification of Polymers:



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15.4.2 Types of polymerisation

The process of forming a very large, high molecular mass polymer from small structural units i.e., monomer is called polymerisation. Polymerisation occurs in the following two ways

i. Addition polymerisation or chain growth polymerisation
ii. Condensation polymerisation or step growth polymerisation

Addition polymerisation

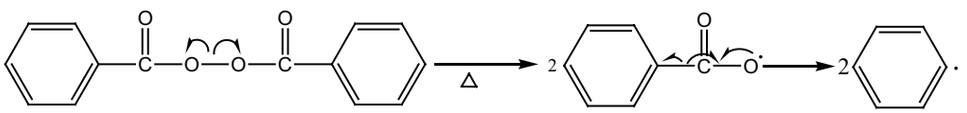
Many alkenes undergo polymerisation under suitable conditions. The chain growth mechanism involves the addition of the reactive end of the growing chain across the double bond of the monomer. The addition polymerisation can follow any of the following three mechanisms depending upon the reactive intermediate involved in the process.

i. Free radical polymerisation
ii. Cationic polymerisation
iii. Anionic polymerisation

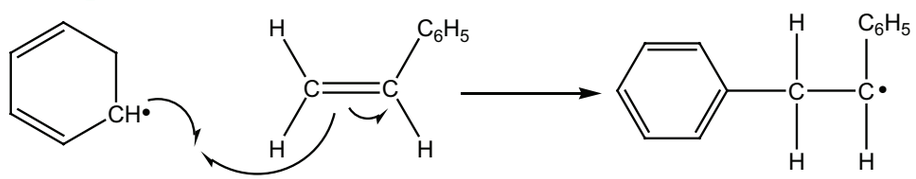
Free radical polymerisation

When alkenes are heated with free radical initiator such as benzoyl peroxide, they undergo polymerisation reaction. For example styrene polymerises to polystyrene when it is heated to ionic with a peroxide initiator. The mechanism involves the following steps.

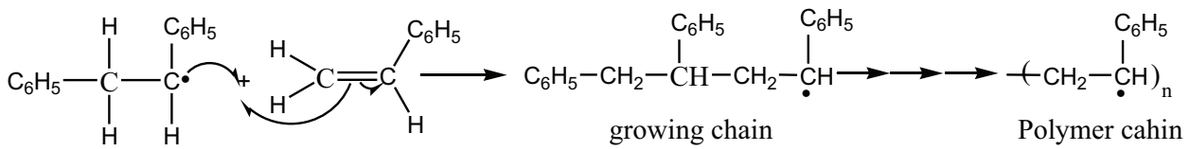
1. initiation – formation of free radical



2. Propagation step



The stabilized radical attacks another monomer molecule to give an elongated radical

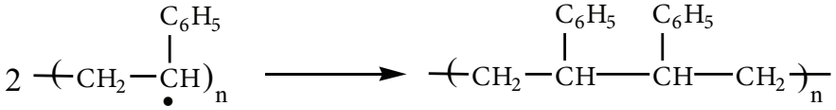


Chain growth will continue with the successive addition of several thousands of monomer units.

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Termination

The above chain reaction can be stopped by stopping the supply of monomer or by coupling of two chains or reaction with an impurity such as oxygen.



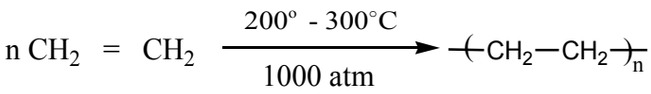
15.4. 3 Preparation of some important addition polymers

1. Polythene

It is an addition polymer of ethene. There are two types of polyethylene i) HDPE (High Density Polyethylene) ii) LDPE (Low Density polyethylene).

LDPE

It is formed by heating ethene at 200° to 300° C under oxygen as a catalyst. The reaction follows free radical mechanism. The peroxides formed from oxygen acts as a free radical initiator.



ethene Polythene

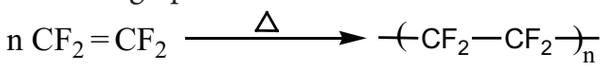
It is used as insulation for cables, making toys etc…

HDPE

The polymerization of ethylene is carried out at 373K and 6to7 atm pressure using Zeiglar – Natta catalyst $[TiCl_4+(C_2H_5)_3Al]$ HDPE has high density and melting point and it is used to make bottles, pipe etc..,

Preparation of Teflon (PTFE)

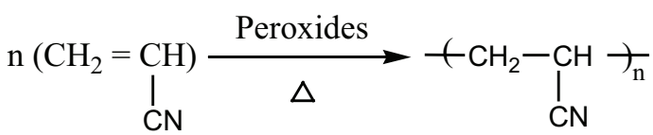
The monomer is tetrafluroethylene. When the monomer is heated with oxygen (or) ammonium persulphate under high pressure, Teflon is obtained.



It is used for coating articles and preparing non – stick utensils.

I. Preparation of Orlon (polyacrylonitrile – PAN)

It is prepared by the addition polymerisation of vinylcyanide (acrylonitrile) using a peroxide initiator.



Prop - 2-enenitrile PAN

It is used as a substitute of wool for making blankets, sweaters etc…

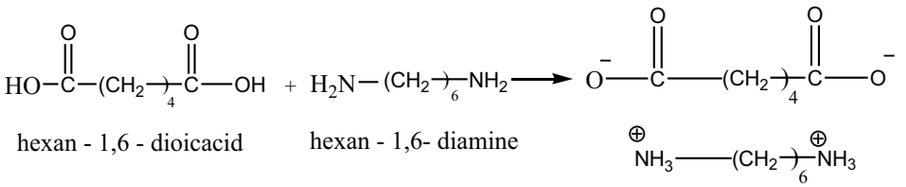
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Condensation polymerisation

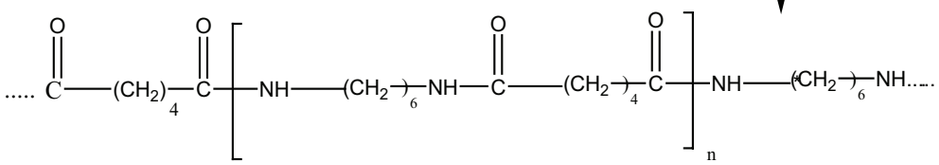
Condensation polymers are formed by the reaction between functional groups an adjacent monomers with the elimination of simple molecules like H_2O, NH_3 etc…. Each monomer must undergo at least two substitution reactions to continue to grow the polymer chain i.e., the monomer must be at least bi functional. Examples : Nylon– 6,6, terylene….

Nylon – 6,6

Nylon – 6,6 can be prepared by mixing equimolar adipic acid and hexamethylene – diamine to form a nylon salt which on heating eliminate a water molecule to form amide bonds.



hexan - 1,6 - dioicacid hexan - 1,6- diamine Nylon salt

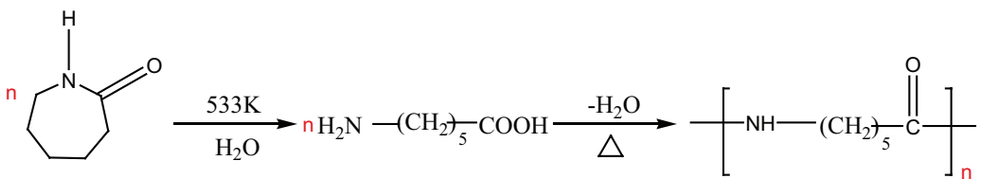


Poly (hexamethyleneadipamide)
Nylon 6,6

It is used in textiles, manufacture of cards etc…

Nylon – 6

Capro lactam (monomer) on heating at 533K in an inert atmosphere with traces of water gives ϵ- amino carproic acid which polymerises to give nylon – 6



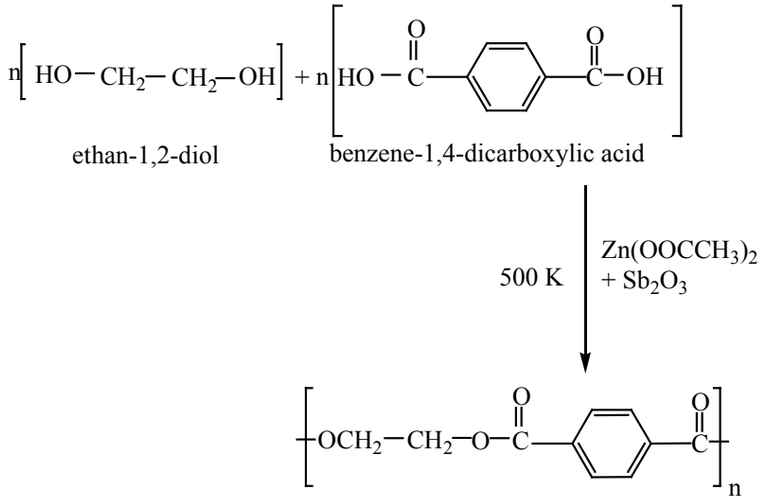
Nylon -6

It is used in the manufacture of tyrecards fabrics etc….

II. Preparation of terylene (Dacron)

The monomers are ethylene glycol and terepathalic acid (or) dimethylterephthalate. When these monomers are mixed and heated at 500K in the presence of zinc acetate and antimony trioxide catalyst, terylene is formed.

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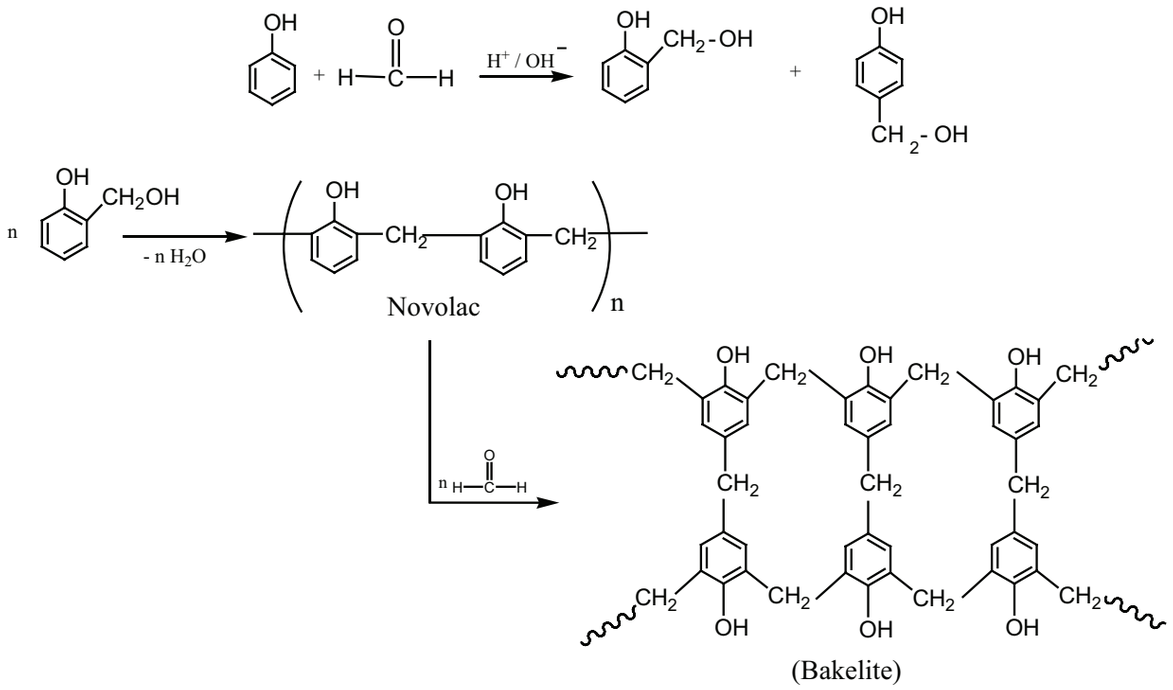


It is used in blending with cotton or wool fibres and as glass reinforcing materials in safety helmets.

Preparation of Bakelite

The monomers are phenol and formaldehyde. The polymer is obtained by the condensation polymerization of these monomers in presence of either an acid or a base catalyst.

Phenol reacts with methanal to form ortho or para hydroxyl methylphenols which on further reaction with phenol gives linear polymer called novolac. Novalac on further heating with formaldehyde undergo cross linkages to form bakelite.



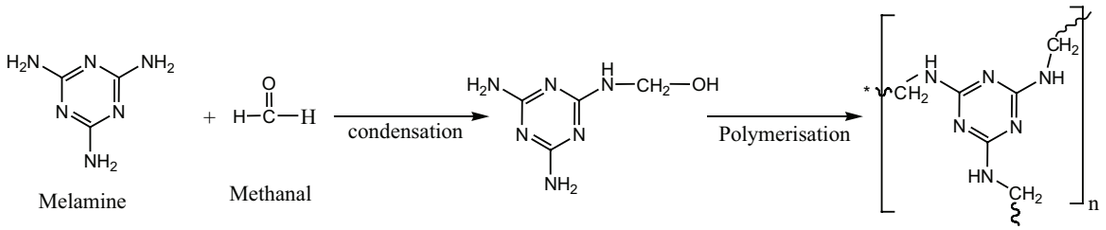
Uses:

Navolac is used in paints. Soft bakelites are used for making glue for binding laminated wooden planks and in varinishes, Hard bakelites are used to prepare combs, pens etc..

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Melamine (Formaldehyde melamine):

The monomers are melamine and formaldehyde. These monomers undergo condensation polymerisation to form melamine formaldehyde resin.

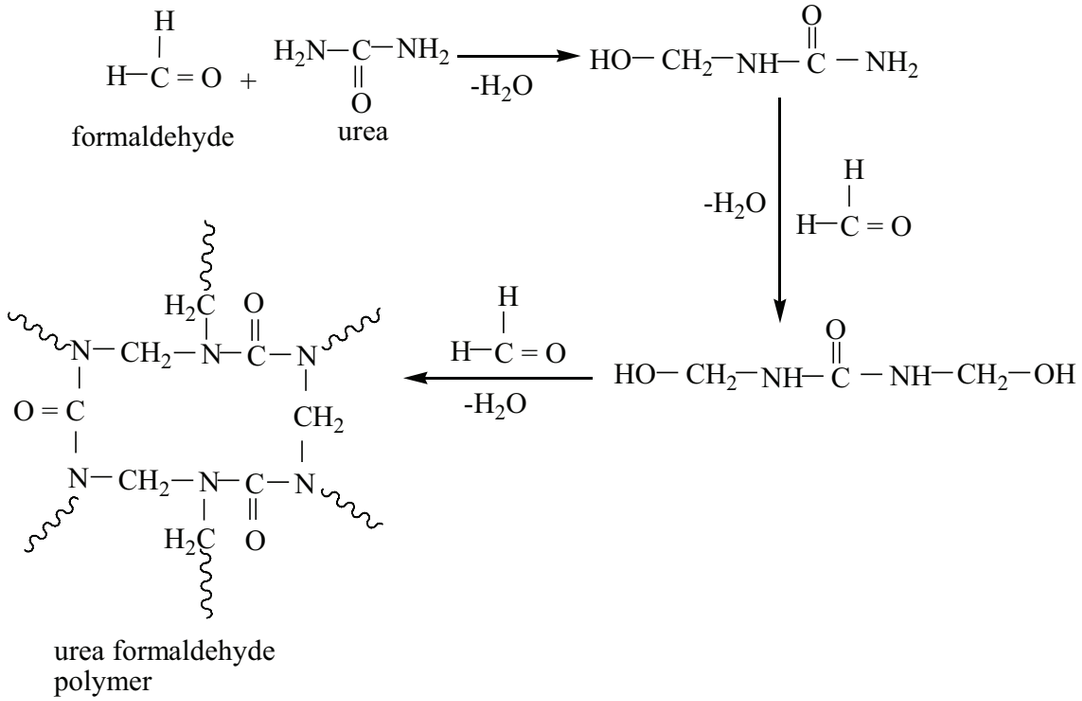


Uses: It is used for making unbreakable crockery

Melamine-formaldehyde polymer

Urea formaldehyde polymer:

It is formed by the condensation polymerisation of the monomers urea and formaldehyde.



urea formaldehyde polymer

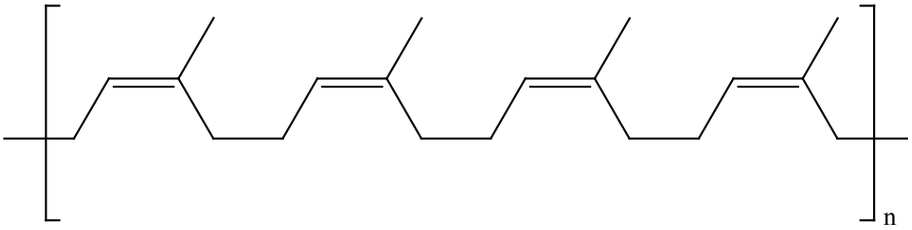
15.4.4 Co-polymers:

A polymer containing two or more different kinds of monomer units is called a co-polymer. For example, SBR rubber(Buna-S) contains styrene and butadiene monomer units. Co-polymers have properties quite different from the homopolymers.

15.4.5 Natural and Synthetic rubbers:

Rubber is a naturally occurring polymer. It is obtained from the latex that excludes from cuts in the bark of rubber tree (Ficus elastic). The monomer unit of natural rubber is cis isoprene (2-methyl buta-1,3-diene). Thousands of isoprene units are linearly linked together in natural rubber. Natural rubber is not so strong or elastic. The properties of natural rubber can be modified by the process called vulcanization.

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cispolyisoprene

Vulcanization: Cross linking of Rubber

In the year 1839, Charles Good year accidently dropped a mixture of natural rubber and sulphur onto a hot stove. He was surprised to find that the rubber had become strong and elastic. This discovery led to the process that Good year called vulcanization.

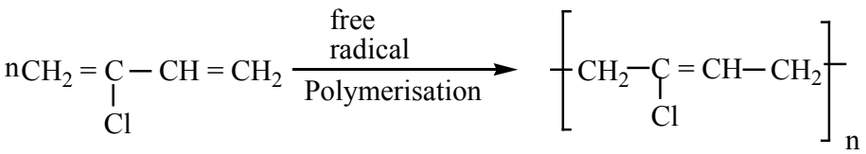
Natural rubber is mixed with 3-5% sulphur and heated at 100-150˚C causes cross linking of the cis-1,4-polyisoprene chains through disulphide (-S-S-) bonds. The physical properties of rubber can be altered by controlling the amount of sulphur that is used for vulcanization. In sulphur rubber, made with about 1 to 3% sulphur is soft and stretchy. When 3 to 10% sulphur is used the resultant rubber is somewhat harder but flexible.

Synthetic rubber:

Polymerisation of certain organic compounds such as buta-1,3-diene or its derivatives gives rubber like polymer with desirable properties like stretching to a greater extent etc., such polymers are called synthetic rubbers.

Preparation of Neoprene:

The free radical polymeristion of the monomer, 2-chloro buta-1,3-diene(chloroprene) gives neoprene.

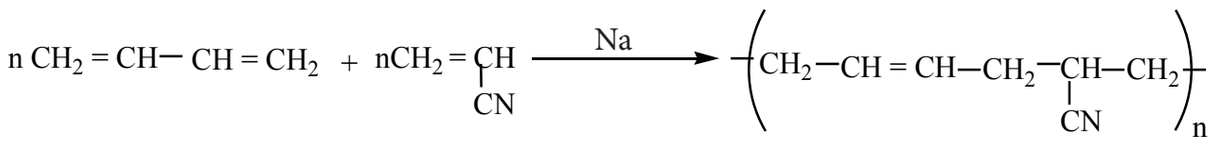


It is superior to rubber and resistant to chemical action.

Uses: It is used in the manufacture of chemical containers, conveyer belts.

Preparation of Buna-N:

It is a co-polymer of acrylonitrile and buta-1,3-diene.



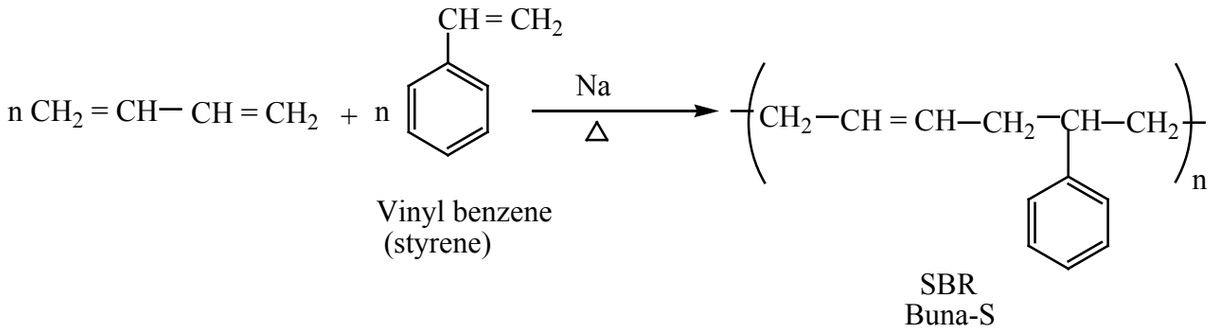
Vinyl cyanide Buna-N

It is used in the manufacture of hoses and tanklinings.

Preparation of Buna-S:

It is a co-polymer. It is obtained by the polymerisation of buta-1,3-diene and styrene in the ratio 3:1 in the presence of sodium.

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15.4.6 Biodegradable Polymers

The materials that are readily decomposed by microorganisms in the environment are called biodegradable. Natural polymers degrade on their own after certain period of time but the synthetic polymers do not. It leads to serious environmental pollution. One of the solution to this problem is to produce biodegradable polymers which can be broken down by soil micro organism.

Examples:

Polyhydroxy butyrate (PHB)

Poly(3 hydroxy butyrate-co-3-hydroxy valerate) (PHBV)

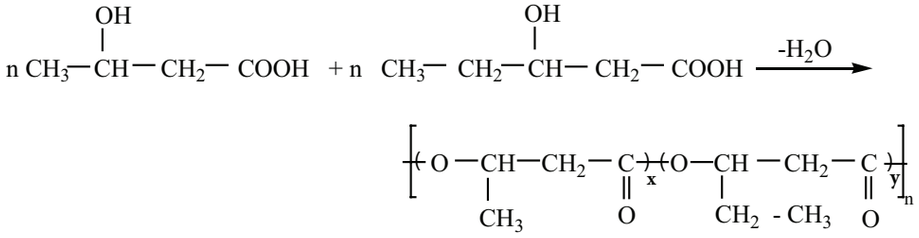
Polyglycolic acid (PGA), Polylactic acid (PLA)

Poly (∈ caprolactone) (PCL)

Biodegradable polymers are used in medical field such as surgical sutures, plasma substitute etc… these polymers are decomposed by enzyme action and are either metabolized or excreted from the body.

Preparation of PHBV

It is the co – polymer of the monomers 3 – hydroxybutanoic acid and 3-hydroxypentanoic acid. In PHBV, the monomer units are joined by ester linkages.

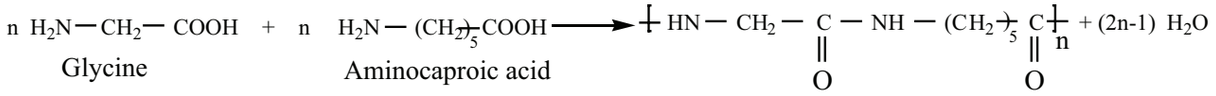


Uses : It is used in ortho paedic devices, and in controlled release of drugs.

Nylon– 2-Nylon -6

It is a co – polymer which contains polyamide linkages. It is obtained by the condensation polymersiation of the monomers, glycine and E - amino caproic acid.

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Nylon -2-nylon - 6

EVALUATION

8WNHC

Choose the correct answer:

1. Which of the following is an analgesic?

   a) Streptomycin b) Chloromycetin c) Aspirin d) Penicillin

2. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statement is not true.

   a) dilute solutions of boric acid and hydrogen peroxide are strong antiseptics.

   b) Disinfectants harm the living tissues.

   c) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.

   d) Chlorine and iodine are used as strong disinfectants.

3. Drugs that bind to the receptor site and inhibit its natural function are called

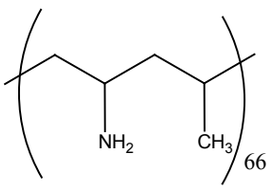
   a) antagonists b) agonists c) enzymes d) molecular targets

4. Aspirin is a/an

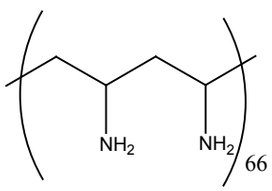
   a) acetylsalicylic acid b) benzoyl salicylic acid c) chlorobenzoic acid d) anthranilic acid

5. Which one of the following structures represents nylon 6,6 polymer?

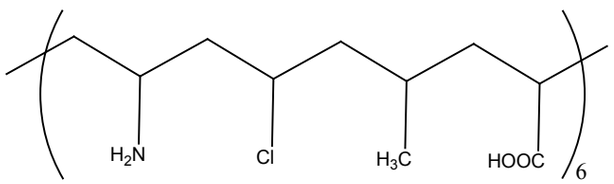
(a)



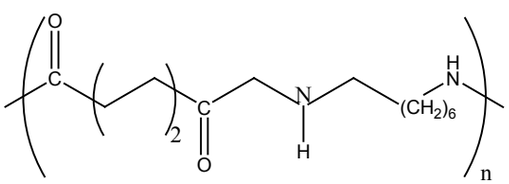
(b)



(c)



(d)



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6. Natural rubber has

a) alternate cis- and trans-configuration b) random cis- and trans-configuration

c) all cis-configuration d) all trans-configuration

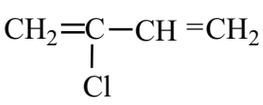
7. Nylon is an example of

a) polyamide b) polythene c) polyester d) poly saccharide

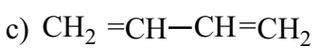
8. Terylene is an example of

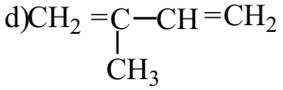
a) polyamide b) polythene c) polyester d) polysaccharide

9. Which is the monomer of neoprene in the following?

a) 

b) 

c) 

d) 

10. Which one of the following is a bio-degradable polymer?

a) HDPE b) PVC c) Nylon 6 d) PHBV

11. Non stick cook wares generally have a coating of a polymer, whose monomer is

a) ethane b) prop-2-enenitrile c) chloroethene d) 1,1,2,2-tetrafluoroethane

12. Assertion: 2-methyl-1,3-butadiene is the monomer of natural rubber

Reason: Natural rubber is formed through anionic addition polymerisation.

a) If both assertion and reason are true and reason is the correct explanation of assertion.

b) if both assertion and reason are true but reason is not the correct explanation of assertion.

c) assertion is true but reason is false. d) both assertion and reason are false.

13. Which of the following is a co-polymer?

a) Orlon b) PVC c) Teflon d) PHBV

14. The polymer used in making blankets (artificial wool) is

a) polystyrene b) PAN c) polyester d) polythene

15. Regarding cross-linked or network polymers, which of the following statement is incorrect? (NEET)

a) Examples are Bakelite and melamine

b) They are formed from bi and tri-functional monomers

c) They contain covalent bonds between various linear polymer chains

d) They contain strong covalent bonds in their polymer chain

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Short Answer Questions

1. What are antibiotics?
2. Name one substance which can act as both analgesic and antipyretic
3. Write a note on synthetic detergents
4. How do antiseptics differ from disinfectants?
5. What are food preservatives?
6. What are drugs? How are they classified
7. How the tranquilizers work in body.
8. Write the structural formula of aspirin.
9. Explain the mechanism of cleansing action of soaps and detergents
10. Which sweetening agent are used to prepare sweets for a diabetic patient?
11. What are narcotic and non – narcotic drugs. Give examples
12. What are anti fertility drugs? Give examples.
13. Write a note on co –polymer
14. What are bio degradable polymers? Give examples.
15. How is terylene prepared?
16. Write a note on vulcanization of rubber
17. Classify the following as linear, branched or cross linked polymers

    a) Bakelite b) Nylon-6,6 c) LDPE d) HDPE

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VOLUME II

ANSWERS

UNIT 8

MCQ

1. $Ag_2C_2O_4 \rightleftharpoons 2Ag^+ + C_2O_4^{2-}$

$[Ag^+] = 2.24\times10^{-4} \text{ mol } L^{-1}$

$[C_2O_4^{2-}] = \frac{2.24\times10^{-4}}{2} \text{ mol } L^{-1}$

$= 1.12\times10^{-4} \text{ mol } L^{-1}$

$K_{sp} = [Ag^+]^2 [C_2O_4^{2-}]$

$= (2.24\times10^{-4} \text{ mol } L^{-1})^2 (1.12\times10^{-4} \text{ mol } L^{-1})$

$= 5.619\times10^{-12} \text{ mol}^3 L^{-3}$

[Option (d)]

2. iii) 75 ml $\frac{M}{5}$ HCl + 25ml $\frac{M}{5}$ NaOH

No of moles of HCl = $0.2\times75\times10^{-3} = 15 \times 10^{-3}$

No of moles of NaOH = $0.2 \times 25 \times 10^{-3} = 5 \times 10^{-3}$

No of moles of HCl after mixing = $15 \times 10^{-3} - 5 \times 10^{-3}$

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

$\therefore$ concentration of HCl = $\frac{\text{No of moles of HCl}}{\text{Vol in litre}}$

$= \frac{10\times10^{-3}}{100\times10^{-3}} = 0.1M$

for (iii) solution, pH of 0.1M HCl = $-\log_{10}(0.1)$

$= 1.$

[Option (d)].

3. $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = (s)\ (s)$

$K_{sp} = (s)^2$

$= (2.42\times10^{-3} \text{ g } L^{-1})^2$

$= \left(\frac{2.42\times10^{-3} \text{ g } L^{-1}}{233 \text{g mol}^{-1}}\right)^2$

$= (0.01038\times10^{-3})^2$

$= (1.038\times10^{-5})^2$

$= 1.077\times10^{-10}$

$= 1.08\times10^{-10} \text{ mol}^2 \text{ } L^{-2}$

[Option (c)]

4. $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

Given that pH=9

pOH=14-9=5

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

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

$[OH^-] = 10^{-5} \text{ M}$

$K_{sp} = [Ca^{2+}][OH^-]^2$

$= \frac{10^{-5}}{2} \times (10^{-5})^2$

$= 0.5\times10^{-15}$

[Option (a)]

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5. $\underset{\text{acid 1}}{H_2O} + \underset{\text{base 1}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 2}}{OH^-}$

$\underset{\text{acid 1}}{HF} + \underset{\text{base 1}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 2}}{F^-}$

$\therefore$ Conjugate bases are OH^- and F^- respectively

i.e.,[Option (c)]

6. Basic buffer is the solution which has weak base and its salt

$$\underset{200\,ml}{NH_4OH} + \underset{100\,ml}{HCl} \longrightarrow \underset{Salt}{NH_4Cl} + H_2O + \underset{(100\,ml\ weak\ base)}{NH_4OH}$$

i.e.,[Option (c)]

7. $BF_3 \rightarrow$ elctron deficient $\rightarrow$ Lewis acid

$PF_3 \rightarrow$ electron rich $\rightarrow$ lewis base

$CF_4 \rightarrow$ neutral $\rightarrow$ neither lewis acid nor base

$SiF_4^- \rightarrow$ neutral $\rightarrow$ neither lewis acid nor base

[option (b)]

8. $BF_3 \rightarrow$ elctron deficient $\rightarrow$ Lewis acid

$PF_3 \rightarrow$ electron rich $\rightarrow$ lewis base

$CO \rightarrow$ having lone pair of electron $\rightarrow$ lewis base

$F^- \rightarrow$ unshared pair of electron $\rightarrow$ lewis base

[option (a)]

9. $HCOONa + H\cdot OH \rightleftharpoons \underset{\text{strong base}}{NaOH} + \underset{\text{weak acid}}{H\text{-}COOH}$

Basic in nature.

$$C_6H_5NH_3Cl^- + H\cdot OH \rightleftharpoons \underset{acidic}{H_3O^+} + C_6H_5\text{-}NH_2 + Cl^-$$

$$KCN + H - OH \rightleftharpoons \underset{\text{strong base}}{KOH} + \underset{\text{weak acid}}{HCN}$$

basic

[option (b)] basic, acidic, basic is correct.

10. $C_5H_5N + H\text{-}OH \rightleftharpoons C_5H_5\overset{+}{N}H + OH^-$

$$\frac{\alpha^2 C}{1-\alpha} = K_b$$

$$\alpha^2 C \approx K_b$$

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7\times10^{-9}}{0.1}}$$

$$= \sqrt{1.7}\times10^{-4}$$

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Percentage of dissociation $= \sqrt{1.7 \times 10^{-4}} \times 100$

$= 1.3 \times 10^{-2} = 0.013\ \%$

[Option (b)]

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

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

Let the volume be x mL

$V_1M_1 + V_2M_2 + V_3M_3 = VM$

$\therefore$ x mL of 10^{-1}M + x mL of 10^{-2}M + x mL of 10^{-3} M

= 3x mL of $[H^+]$

$$\therefore [H^+] = \frac{x[0.1+0.01+0.001]}{3x}$$

$$= \frac{0.1+0.01+0.001}{3}$$

$$= \frac{0.111}{3}$$

$= 0.037$

$= 3.7 \times 10^{-2}$

[Option (a)]

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

$\underset{0.1\ M}{NaCl} \longrightarrow \underset{0.1\ M}{Na^+} + \underset{0.1\ M}{Cl^-}$

$K_{sp} = 1.6 \times 10^{-10}$

$K_{sp} = [Ag^+][Cl^-]$

$K_{sp} = (s)(s+0.1)$

$0.1 >>> s$

$\therefore s + 0.1 \simeq 0.1$

$$\therefore S = \frac{1.6 \times 10^{-10}}{0.1} = 1.6 \times 10^{-9}$$

[Option (b)]

13. $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

$K_{sp} = (s)(2s)^2$

$3.2 \times 10^{-8} = 4s^3$

$$s = \left(\frac{3.2 \times 10^{-8}}{4}\right)^{1/3}$$

$= (8 \times 10^{-9})^{1/3}$

$= 2 \times 10^{-3}$M [Option (a)]

14. Addition of salt KY (having a common ion Y^-) decreases the solubility of MY and NY_3 due to common ion effect.

Option (a) and (b) are wrong.

For salt MY , $MY \rightleftharpoons M^+ + Y^-$

$K_{sp} = (s)(s)$

$6.2 \times 10^{-13} = s^2$

$\therefore s = \sqrt{6.2 \times 10^{-13}} \simeq 10^{-7}$

for salt NY_3,

$NY_3 \rightleftharpoons N^{3+} + 3Y^-$

$K_{sp} = (s)(3s)^3$

$K_{sp} = 27s^4$

$$s = \left(\frac{6.2 \times 10^{-13}}{27}\right)^{1/4}$$

$s. \simeq 10^{-4}$

The molar solubility of MY in water is less than of NY_3

[Option (d)]

15. x ml of 0.1 M NaOH + x ml of 0.01 M HCl

No of moles of NaOH = $0.1 \times x \times 10^{-3} = 0.1x \times 10^{-3}$

No of moles of HCl = $0.01 \times x \times 10^{-3} = 0.01x \times 10^{-3}$

No of moles of NaOH after mixing = $0.1x \times 10^{-3} - 0.01x \times 10^{-3}$

$= 0.09x \times 10^{-3}$

$$\text{Concentration of NaOH} = \frac{0.09x \times 10^{-3}}{2x \times 10^{-3}} = 0.045$$

$[OH^-] = 0.045$

$P^{OH} = -\log(4.5 \times 10^{-2})$

$= 2 - \log 4.5$

$= 2 - 0.65 = 1.35$

$pH = 14 - 1.35 = 12.65$

[Option (d)]

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16. $K_a = 1 \times 10^{-3}$

$pH = 4$

$\frac{[salt]}{[Acid]} = ?$

$pH = pK_a + \log \frac{[Salt]}{[Acid]}$

$4 = -\log_{10}(1 \times 10^{-3}) + \log \frac{[Salt]}{[Acid]}$

$4 = 3 + \log \frac{[Salt]}{[Acid]}$

$1 = \log_{10} \frac{[Salt]}{[Acid]}$

$\Rightarrow \frac{[Salt]}{[Acid]} = 10^1$

i.e., $\frac{[Acid]}{[Salt]} = \frac{1}{10}$

1:10

[Option (d)]

17. $\underset{10^{-5}m}{KOH} \rightarrow \underset{10^{-5}m}{K^+} + \underset{10^{-5}m}{OH^-}$

$[OH^-] = 10^{-5}M.$

$pH = 14 - pOH$

$pH = 14 - \left(-\log \left[OH^-\right]\right)$

$= 14 + \log [OH^-]$

$= 14 + \log 10^{-5}$

$= 14 - 5$

$= 9.$

[Option (a)]

18. $\underset{\text{acid 1}}{H_3PO_4} + \underset{\text{base 1}}{H - OH} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 2}}{H_2PO_4^-}$

$\therefore H_2PO_4^-$ is the conjugate base of H_3PO_4

[Option (c)]

19. HPO_4^{2-} can have the ability to accept a proton to form $H_2PO_4^-$.

It can also have the ability to donate a proton to form PO_4^{-3}

[Option (c)]

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

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

$= 10^0 = 1$

$[H^+] = 1M$

The solution is strongly acidic

[Option (b)]

21. According to Henderson equation

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

ie. $-\log [H^+] = -\log K_a + \log \frac{[salt]}{[acid]}$

$-\log[H^+] = \log \frac{[salt]}{[acid]} \times \frac{1}{K_a}$

$\log \frac{1}{[H^+]} = \log \frac{[salt]}{[acid]} \times \frac{1}{K_a}$

$\therefore [H^+] = K_a \frac{[acid]}{[salt]}$

[option (a)]

22. $h = \sqrt{\frac{K_h}{K_a . K_b}}$

[Option (c)]

23. $K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$

$= 0.55 \times 10^{-9}$

$= 5.5 \times 10^{-10}$

[option (b)]

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Key answer for short answer question

8. Concentration of HNO_3 = 0.04M

$[H_3O^+]$=0.04 mol dm^{-3}

$pH=-\log[H_3O^+]$

$=-\log(0.04)$

$=-\log(4\times10^{-2})$

$=2-\log4$

$=2-0.6021$

$=1.3979 = 1.40$

14. $Ba(OH)_2 \rightarrow Ba^{2+}+2OH^-$

1.5×10^{-3}M $\qquad 2\times1.5\times10^{-3}$M.

$[OH^-] = 3\times10^{-3}$M

[$\because$ pH+pOH=14]

pH= 14-pOH

pH= 14- $\left(-\log [OH^-]\right)$

$= 14+ \log [OH^-]$

$=14+\log(3\times10^{-3})$

$=14 + \log 3 + \log 10^{-3}$

$= 14+ 0.4771-3$

$=11+0.4771$

pH=11.48

15. Number of moles of $HNO_3 = 0.05 \times 50 \times 10^{-3}$

$=2.5 \times 10^{-3}$

Number of moles of $KOH = 0.025 \times 50 \times 10^{-3}$

$= 1.25 \times 10^{-3}$

Number of moles of HNO_3 after mixing

$= 2.5 \times 10^{-3} - 1.5 \times 10^{-3}$

$= 1.25 \times 10^{-3}$

$\therefore$ concentration of $HNO_3 = \dfrac{\text{Number of moles of } HNO_3}{\text{Volume is litre}}$

After mixing, total volume = 100 ml = 100×10^{-3}L

$\therefore [H^+]=\dfrac{1.25\times10^{-3}\text{moles}}{100\times10^{-3}\text{L}}$

$=1.25\times10^{-2}$ moles L^{-1}

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

$pH = -\log(1.25\times10^{-2}) = 2-0.0969$

$= 1.9031$

16. Given

$K_a=10^{-9}$

c=0.4M

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

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

$=\sqrt{10^{-9}\times0.4}$

$=2\times10^{-5}$

$\therefore pH= -\log(2\times10^{-5})$

$=5-\log2$

$=5-0.3010$

$=4.699.$

17. $h = \sqrt{K_h} = \sqrt{\dfrac{K_W}{K_aK_b}} = \sqrt{\dfrac{1\times10^{-14}}{1.8\times10^{-5}\times1.8\times10^{-5}}}$

$= \dfrac{1}{1.8}\times10^{-2}$

$= 5.556\times10^{-3}$

$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

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

if $K_a = K_b$, then, $pK_a = pK_b$

$\therefore pH = \frac{1}{2}pK_w = \frac{1}{2}(14) = 7$

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19. Given that $K_{sp} = 1 \times 10^{-12}$

$$\underset{s}{Ag_2CrO_4}(s) \rightleftharpoons \underset{2s}{2Ag^+_{(aq)}} + \underset{s}{CrO_4^{-2}}(aq)$$

$$\underset{0.01M}{AgNO_3}(s) \rightleftharpoons \underset{0.01M}{Ag^+_{(aq)}} + \underset{0.01M}{NO_3^-}(aq)$$

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$

$$\begin{bmatrix} [Ag^+] = 2s + 0.01 \\ 0.01 >> 2S \\ \therefore\ [Ag^+] = 0.01M \\ [CrO_4^{2-}] = s \end{bmatrix}$$

$$1 \times 10^{-12} = (0.01)^2\ (s)$$

$$(s) = \frac{1 \times 10^{-12}}{(10^{-2})^2} = 1 \times 10^{-8}\,M$$

20. $Ca_3(PO_4)_2 \rightleftharpoons \underset{3s}{3Ca^{2+}} + \underset{2s}{2PO_4^{3-}}$

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$K_{sp} = (3s)^3(2s)^2$

$K_{sp} = 27s^3.4s^2$

$K_{sp} = 108s^5$

21. $CaF_2(s) \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-(aq)$

$[F^-] = 2\,[Ca^{2+}] = 2 \times 3.3 \times 10^{-4}M$

$= 6.6 \times 10^{-4}M$

$K_{sp} = [Ca^{2+}][F^-]^2$

$= (3.3 \times 10^{-4})(6.6 \times 10^{-4})^2$

$= 1.44 \times 10^{-10}$

22. $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

x= solubility of AgCl in 1M $AgNO_3$

$$\underset{1M}{AgNO_3}(aq) \rightleftharpoons Ag^+(aq) + \underset{1M}{NO_3^-}(aq)$$

$[Ag^+] = x + 1 \simeq 1M \qquad (\because x << 1)$

$[Cl^-] = x$

$K_{sp} = [Ag^+][Cl^-]$

$1.8 \times 10^{-10} = (1)(x)$

$x = 1.8 \times 10^{-10}\,M$

23. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}(aq)$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$= (5 \times 10^{-5})^2(4.4 \times 10^{-4})$

$= 1.1 \times 10^{-12}$

24. $Hg_2Cl_2 \rightleftharpoons \underset{s}{Hg_2^{2+}} + \underset{2s}{2Cl^-}$

$K_{sp} = [Hg_2^{2+}][Cl^-]^2$

$= (s)(2s)^2$

$K_{sp} = 4s^3$

25. $\underset{x}{Ag_2CrO_4} \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$

x is the solubility

of Ag_2CrO_4 in 0.1M K_2CrO_4

$$\underset{0.1M}{K_2CrO_4} \rightleftharpoons \underset{0.2\ M}{2K^+} + \underset{0.1\ M}{CrO_4^{2-}}$$

$[Ag^+] = 2x$

$[CrO_4^{2-}] = (x + 0.1) \approx 0.1 \qquad \because x << 0.1$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$1.1 \times 10^{-12} = (2x)^2(0.1)$

$1.1 \times 10^{-12} = 0.4x^2$

$$x^2 = \frac{1.1 \times 10^{-12}}{0.4}$$

$$x = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}}$$

$$x = \sqrt{2.75 \times 10^{-12}}$$

$x = 1.65 \times 10^{-6}M$

26. When two are more solution are mixed, the resulting concentrations are differnet from the original.

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Total volume = 0.250L

$$\underset{0.1\ M}{Pb(NO_3)_2} \rightleftharpoons \underset{0.1\ M}{Pb^{2+}} + \underset{0.2\ M}{2NO_3^-}$$

Number of moles

Pb^{2+} = molarity × Volume of the solution in lit

$= 0.1 \times 0.15$

$$[Pb^{2+}]_{mix} = \frac{0.1 \times 0.15}{0.25} = 0.06\ M$$

$$\underset{0.2\ M}{NaCl} \rightleftharpoons \underset{0.2\ M}{Na^+} + \underset{0.2\ M}{Cl^-}$$

No.of moles $Cl^- = 0.2 \times 0.1$

$$[Cl^-]_{mix} = \frac{0.2 \times 0.1}{0.25} = 0.08\ M$$

Precipitation of $PbCl_2$ (s) occurs if

$[Pb^{2+}][Cl^-]^2 > K_{sp}$

$[Pb^{2+}][Cl^-]^2 = (0.06)(0.08)^2$

$= 3.84 \times 10^{-4}$

Since ionic product $[Pb^{2+}][Cl^-]^2 > K_{sp}$, $PbCl_2$ is precipitated

27. $Al(OH)_3 \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$

$K_{sp} = [Al^{3+}][OH^-]^3$

$Al(OH)_3$ precipitates when

$[Al^{3+}][OH^-]^3 > K_{sp}$

$(1 \times 10^{-3})[OH^-]^3 > 1 \times 10^{-15}$

$[OH]^3 > 1 \times 10^{-12}$

$[OH^-] > 1 \times 10^{-4} M$

$[OH^-] = 1 \times 10^{-4} M$

$POH = -\log_{10}[OH^-] = -\log(1 \times 10^{-4}) = 4$

pH = 14-4= 10

Thus, $Al(OH)_3$ precipitates at a pH of 10

Evaluate yourself

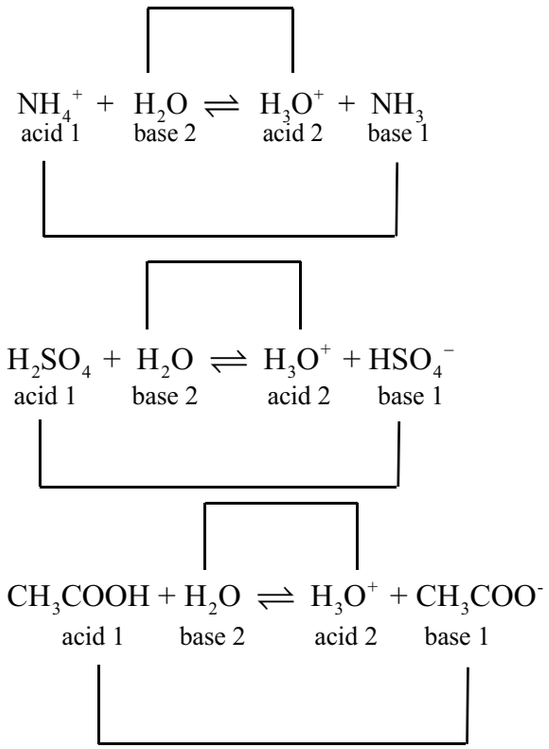
Key

Evaluate yourself – 1

acid : (i) HNO_3 iii) H_3PO_3 iv) CH_3COOH

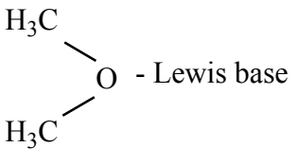
base : ii) $Ba(OH)_2$

Evaluate yourself – 2



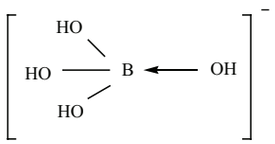
Evaluate yourself – 3

i) CaO - Lewis base ; CO_2 -Lewisacid

ii)  - Lewis base

$AlCl_3$ - Lewis acid

Evaluate yourself – 4

 ; electron pair acceptor - Lewis acid

Evaluate yourself – 5

Given solution is neutral

$\therefore [H_3O^+] = [OH^-]$ Let $[H_3O^+] = x$; then $[OH^-] = x$

$K_w = [H_3O^+][OH^-]$

$4 \times 10^{-14} = x \cdot x$

$x^2 = 4 \times 10^{-14}$

$x = \sqrt{4 \times 10^{-14}} = 2 \times 10^{-7}$

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Evaluate yourself – 6

a) Answer

$$\underset{10^{-8}\ M}{H_2SO_4} \xrightarrow{H_2O} \underset{2\times10^{-8}}{2H_3O^+} + \underset{10^{-8}\ M}{SO_4^{2-}}$$

In this case the concentration of H_2SO_4 is very low and hence $[H_3O^+]$ from water cannot be neglected

$\therefore [H_3O^+] = 2\times10^{-8}$ (from H_2SO_4) + 10^{-7} (from water)

$=10^{-8}(2+10)$

$=12\times10^{-8} = 1.2 \times10^{-7}$

$pH = -\log_{10}[H_3O^+]$

$= -\log_{10}(1.2\times10^{-7})$

$=7 - \log_{10}1.2$

$=7 - 0.0791 = 6.9209$

b) Answer

pH of the solution = 5.4

$[H_3O^+]$ = antilog of (-pH)

= anitlog of (-5.4)

= antilog of $(-6 + 0.6) = \bar{6}.6$

$= 3.981\times10^{-6}$

i.e., 3.98×10^{-6} mol dm^{-3}

c) Answer

No of moles of HCl $= 0.2\times 50 \times 10^{-3} = 10 \times 10^{-3}$

No of moles of NaOH $= 0.1 \times 50 \times 10^{-3} = 5 \times 10^{-3}$

No of moles of HCl after mixing $= 10 \times 10^{-3} - 5 \times 10^{-3}$

$= 5 \times 10^{-3}$

after mixing total volume = 100mL

$\therefore$ Concentration of HCl in moles per litre = $\frac{5\times10^{-3}\text{mole}}{100 \times 10^{-3}\text{L}}$

$[H_3O^+]=5\times10^{-2}$ M

$pH = -\log(5 \times 10^{-2})$

$= 2 - \log 5$

$= 2 - 0.6990$

$= 1.30$

Evaluate yourself - 7

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.8\times10^{-5}}{6\times10^{-2}}}$$

$= \sqrt{3 \times 10^{-4}}$

$= 1.732 \times 10^{-2}$

$= \frac{1.732}{100} = 1.732\%$

Evaluate yourself – 8

a) Answer

Dissociation of buffer components

$$NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl \rightarrow NH_4^+ + Cl^+$$

Addition of H+

The added H^+ ions are neutralized by NH_4OH and there is no appreciable decrease in pH.

$$NH_4OH(aq) + H^+ \rightarrow NH_4^+(aq) + H_2O(l)$$

Addition of OH^-

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_4OH\ (aq)$$

The added OH^- ions react with NH_4^+ to produce unionized NH_4OH. Since NH_4OH is a weak base, there is no appreciable increase in pH

b) Answer

pH of buffer

$$\underset{0.4-\alpha}{CH_3COOH(aq)} \rightleftharpoons \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.4}{CH_3COONa(aq)} \longrightarrow \underset{0.4}{CH_3COO^-(aq)} + \underset{0.4}{Na^+(aq)}$$

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

$[CH_3COOH] = 0.4 - \alpha \simeq 0.4$

$[CH_3COO^-] = 0.4 + \alpha \simeq 0.4$

$$\therefore [H^+] = \frac{K_a(0.4)}{(0.4)}$$

$[H^+] = 1.8\times10^{-5}$

$\therefore pH = -\log(1.8\times10^{-5}) = 4.74$

Addition of 0.01 mol HCl to 500ml of buffer

$$\text{Added } [H^+] = \frac{0.01\text{ mol}}{500\text{ mL}} = \frac{0.01\text{ mol}}{\frac{1}{2}\text{L}}$$

$= 0.02M$

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$$\underset{0.4-\alpha}{CH_3COOH(aq)} \rightleftharpoons \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.4}{CH_3COONa} \rightarrow \underset{0.4}{CH_3COO^-} + \underset{0.4}{Na^+}$$

$$\underset{(0.02)}{CH_3COO^-} + \underset{0.02}{HCl} \rightarrow \underset{0.02}{CH_3COOH} + \underset{0.02}{Cl^-}$$

$\therefore$ $[CH_3COOH] = 0.4 - \alpha + 0.02 = 0.42 - \alpha \simeq 0.42$

$[CH_3COO^-] = 0.4 + \alpha - 0.02 = 0.38 + \alpha \simeq 0.38$

$$[H^+] = \frac{(1.8 \times 10^{-5})(0.42)}{(0.38)}$$

$[H^+] = 1.99 \times 10^{-5}$

$pH = - \log (1.99 \times 10^{-5})$

$= 5 - \log 1.99$

$= 5 - 0.30$

$= 4.70$

Evaluate yourself – 9

a) answer

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

We know that

$pH + pOH = 14$

$\therefore 9 + pOH = 14$

$\Rightarrow pOH = 14 - 9 = 5$

$$5 = 4.7 + \log \frac{[NH_4Cl]}{[NH_4OH]}$$

$$0.3 = \log \frac{[NH_4Cl]}{0.1}$$

$$\frac{[NH_4Cl]}{0.1} = \text{antilog of } (0.3)$$

$[NH_4Cl] = 0.1M \times 1.995$

$= 0.1995\ M$

$= 0.2M$

Amount of NH_4Cl required to prepare 1 litre 0.2M solution = Strength of NH_4Cl × molar mass of NH_4Cl

$= 0.2 \times 53.5$

$= 10.70\ g$

10.70 g ammonium chloride is dissolved in water and the solution is made up to one litre to get 0.2M solution. On mixing equal volume of the given NH_4OH solution and the prepared NH_4Cl solution will give a buffer solution with required pH value (pH = 9).

b)answer

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

$$4 = 3.75 + \log \frac{[\text{sodium formate}]}{[\text{formic acid}]}$$

[Sodium formate] = number of moles of HCOONa

$= 0.6 \times V \times 10^{-3}$

[formic acid] = number of moles of HCOOH

$= 0.8 \times 100 \times 10^{-3}$

$= 80 \times 10^{-3}$

$$4 = 3.75 + \log \frac{0.6V}{80}$$

$$0.25 = \log \frac{0.6V}{80}$$

$$\text{antilog of } 0.25 = \frac{0.6V}{80}$$

$0.6V = 1.778 \times 80$

$= 1.78 \times 80$

$= 142.4$

$$V = \frac{142.4\ mL}{0.6} = 237.33mL$$

Evaluate yourself - 10

Sodium carbonate is a salt of weak acid, H_2CO_3 and a strong base, NaOH, and hence the solution is alkaline due to hydrolysis.

$$Na_2CO_3(aq) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^- + OH^-$$

i) $$h = \sqrt{\frac{K_w}{K_a \times C}}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{5.5 \times 10^{-11} \times 0.05}}$$

$h = 6.03 \times 10^{-2}$

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Given that $pK_a = 10.26$

$pK_a = -\log K_a$

i.e., K_a = antilog of $(-pK_a)$

= antilog of (-10.26)

= antilog of (-11 + 0.74)

$= 10^{-11} \times 5.5$

[antilog of 0.74 = 5.49 $\simeq$ 5.5]

ii) $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{5.5 \times 10^{-11}}$

$= 1.8 \times 10^{-4}$

iii) $pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$

$= 7 + \frac{10.26}{2} + \frac{\log 0.05}{2} = 7 + 5.13 - 0.65$

$= 11.48$

Unit 9 Electro Chemistry

1. 1F = 96500 C = 1 mole of e^- = 6.023×10^{23} e^-

$\therefore$ 9650 C = $\frac{6.22 \times 10^{23}}{96500} \times 9650 = 6.022 \times 10^{22}$

Option (C)

2. $Mn^{2+} + 2e^- \rightarrow Mn\ (E^\circ_{red}) = -1.18V$

$2\left[Mn^{2+} \rightarrow Mn^{3+} + e^-\right] (E^\circ_{ox}) = -1.51V$

$3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ $E^\circ_{cell} = ?$

$E^\circ_{cell} = (E^\circ_{ox}) + (E^\circ_{red})$

$= -1.51 - 1.18$ and non spontaneous

$= -2.69V$

Since E° is –ve ΔG is +ve and the given

forward cell reaction is non – spontaneous.

(Option (b))

3. Anodic oxidation: (Reverse the given reaction)

$(E^\circ_{ox}) = 0.76V$ cathodic reduction

$\therefore$ $E^\circ_{cell} = (E^\circ_{ox}) + (E^\circ_{red})$

= 0.76 + 0.34 = 1.1V

(Option (c))

4. $\Lambda = \frac{\kappa}{M} \times 10^{-3}$ mol^{-1} m^3

$= \frac{5.76 \times 10^{-3}\ S\ c\ m^{-1} \times 10^{-3}}{0.5} mol^{-1}\ m^3$

$= \frac{5.76 \times 10^{-3} \times 10^{-3} \times 10^6}{0.5}$ $S\ cm^{-1} mol^{-1}\ cm^3$.

$= 11.52\ S\ cm^2\ mol^{-1}$

(Option (b))

5. $(\Lambda_\infty)_{HoAC} = \left[(\Lambda^\circ)_{HCl} + (\Lambda^\circ)_{NaOAC}\right] - (\Lambda^\circ)_{NaCl}$

$= (426.2 + 91) - (126.5)$

$= 390.7$

(Option (c))

6. 1F = 96500 C = charge of 1 mole of e^- = $charge\ of\ 6.022 \times 10^{23}$ e^-

(Option (b))

7. $7MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

5 moles of electrons i.e., 5F charge is required.

(Option (a))

8. m=ZIt

$= \frac{40 \times 3.86 \times 2500}{2 \times 96500}$

= 2g

41min 40sec = 2500 seconds

$Z = \frac{m}{n \times 96500} = \frac{40}{2 \times 96500}$

(Option (b))

9. m=ZIt (mass of 1 mole of Cl_2 gas = 71)

$t = \frac{m}{ZI}$ ($\therefore$ mass of 0.1mole of Cl_2 gas = 7.1 g mol^{-1})

$= \frac{7.1}{\frac{71}{2 \times 96500} \times 3} (2\ Cl^- \rightarrow Cl_2 + 2e^-)$

$= \frac{2 \times 96500 \times 7.1}{71 \times 3}$

$= 6433.33 sec$

$= 107.2$ min

(Option (b))

10. $Q = It$

$= 1A \times 60S$

$96500\ C\ \text{charge} \equiv 6.022 \times 10^{23}\ \text{electrons}$

$60\ C\ \text{charge} \equiv \frac{6.022 \times 10^{23}}{96500} \times 60$

$= 3.744 \times 10^{20}\ \text{electrons}$

(Option (C))

11. In general, specific conductance of an electrolyte decreases with dilution. So, 0.002N solution has least specific conductance.

(Option (b))

12. Charging : anode : $PbSO_4(s) + 2e^- \rightarrow Pb\ (s) + SO_4^{-2}(aq)$

Cathode : $PbSO_4(s) + 2H_2O\ (l) \rightarrow PbO_2\ (s) + SO_4^{-2}(aq) + 2e^-$

(Option (C))

13. Option (a) I and IV

14. $E^o_{Zn^{2+}|Zn} = -0.76V$ and $E^o_{Fe^{2+}|Fe} = -0.44V$ Zinc has higher negative electrode potential than iron, iron cannot be coated on zinc.

Option (d)

15. Both are false

i) Dry air has no reaction with iron

ii) Rust has the composition $Fe_2O_3 . x\ H_2O$

(Option (d))

16. (Option (a))

17. $\alpha = \frac{\Lambda}{\Lambda_o} = \frac{6}{400}$

$K_a = \alpha^2 C$

$= \frac{6}{400} \times \frac{6}{400} \times \frac{1}{36}$

$= 6.25 \times 10^{-6}$

Option (b)

18. $R = \rho . \frac{l}{A}$

$\text{cell constant} = \frac{R}{\rho}$

$= \kappa . R \left(\frac{1}{\rho} = \kappa \right)$

$= 1.25 \times 10^{-3}\ \Omega^{-1} cm^{-1} \times 800\ \Omega$

$= 1\ cm^{-1}$

Option (c)

19. Option (d)

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20. $E_{cell}=E^{o}_{cell}-\frac{0.0591}{2}\log\frac{[zn^{2+}]}{[Cu^{2+}]}$

$E_1=E^{o}_{cell}-\frac{0.0591}{2}\log\frac{10^{-2}}{1}$

$E_1=E^{o}_{cell}+0.0591.....(1)$

$Zn(s) \rightarrow Zn^{2+}(aq)+2e^{-}$

$Cu^{2+}(aq)+2e^{-} \rightarrow Cu(s)$

$Zn(s)+Cu^{2+}(aq) \rightarrow Zn^{2+}(aq)+Cu(s)$

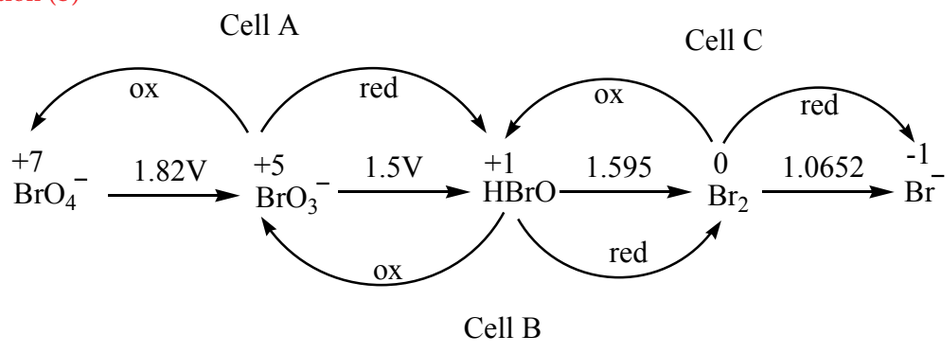
$E_2=E^{o}_{cell}-\frac{0.0591}{2}.\log\frac{1}{10^{-2}}$

$E_2=E^{o}_{cell}-0.0591.....(2)$

$\therefore E_1>E_2$

Option (b)

21.



$(E_{cell})_A=-1.82+1.5=-0.32V$

$(E_{cell})_B=-1.5+1.595=+0.095V$

$(E_{cell})_c=-1.595+1.0652=-0.529V$

$\therefore$ The species undergoing disproportionation is $HBrO$ (Option D)

Short answer

8. Given

$C = 0.01M$ $\quad \lambda^{o}_{cation} = 248.2\ S\ cm^2\ mol^{-1}$

$K= 1.5\times10^{-4}\ S\ cm^{-1}$ $\quad \lambda^{o}_{anion} = 51.8\ S\ cm^2\ mol^{-1}$.

1. Molar conductivity

$\Lambda^{\circ}_{m} = \frac{K(sm^{-1})\times10^{-3}}{C\ (in\ M)}\ mol^{-1}\ m^3$ $\quad K = 1.5\times10^{-4}S\ cm^{-1}$

$= \frac{1.5\times10^{2}\times10^{-3}}{0.01}\ S\ mol^{-1}\ m^2$ $\quad 1\ cm^{-1} = 10^{2}m^{-1}$

$= 1.5\times10^{-3}\ S\ m^2\ mol^{-1}$ $\quad = 1.5\times10^{2}$

2. Degree of dissociation $\alpha = \frac{\Lambda^{\circ}}{\Lambda^{\circ}_{\infty}}$

$\Lambda^{o}_{\infty}=\lambda^{o}_{cation}+\lambda^{o}_{anion}$

$= (248.2+51.8)\ S\ cm^2\ mol^{-1}$

$= 300\ S\ cm^2\ mol^{-1}$

$= 300\times10^{-14}\ s\ m^2\ mol^{-1}$

$$\alpha = \frac{1.5\times10^{-3}\ S\ m^2\ mol^{-1}}{300\times10^{-4}\ S\ m^2\ mol^{-1}}$$

$$\alpha = 0.05$$

$$K_a = \frac{\alpha^2 c}{1-\alpha}$$

$$= \frac{(0.05)^2(0.01)}{1-0.05}$$

$$= \frac{25\times10^{-4}\times10^{-2}}{95\times10^{-2}}$$

$$= 0.26\times10^{-4}$$

$$= 2.6\times10^{-5}.$$

13. Given

$I = 1.608A$; $t = 50\ min = 50\times60 = 3000S$

$V = 250\ mL$

$C = 0.5\ M$

$\eta = 100\%$

Calculate the number of faradays of electricity passed through the $CuSO_4$ solution

$\Rightarrow Q = It$

$Q = 1.608\times3000$

$Q = 4824C$

$\therefore$ number of Faradays of electicity $= \frac{4824\ C}{96500\ C} = 0.05F$

Electrolysis of $CuSO_4$

$Cu^{2+}(aq)+2e^- \rightarrow Cu(s).$

The above equation shows that 2F electricity will deposit 1 mole of Cu^{2+} to Cu.

$\therefore$ 0.05F electricity will

deposit $\frac{1mol}{2F}\times0.05F = 0.025\ mol$

Initial number of molar of Cu^{2+} in 250 ml of solution $= \frac{0.5}{1000\ mL}\times250mL$

$= 0.125\ mol$

$\therefore$ number of moles of Cu^{2+} after electrolysis $= 0.125 - 0.025$

$= 0.1\ mol$

$\therefore$ Concentration of $Cu^{2+} = \frac{0.1\ mol}{250\ mL}\times1000\ mL$

$= 0.4\ M$

14. Required half cell reaction

$2\ Br^- \rightarrow Br_2 + 2e^-$ $\quad (E^\circ_{ox}) = -1.09V$

$2\ Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$ $\quad (E^\circ_{red}) = +0.771V$

$2Fe^{3+} + 2Br^- \rightarrow 2Fe^{2+} + Br_2$ $\quad (E^\circ_{cell}) = ?$

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$$E^{\circ}_{cell} = \left(E^{\circ}_{ox}\right) + \left(E^{\circ}_{red}\right)$$
$$= -1.09 + 0.771$$
$$= -0.319V$$

E°_{cell} is – ve; ΔG is +ve and the cell reaction is non spontaneous. Hence Fe^{3+} cannot oxidises Br^{-} to Br_2 .

15. $\left(E^{\circ}_{ox}\right)_{Fe|Fe^{2+}} = 0.44V$ and $\left(E^{\circ}_{red}\right)_{Cu^{2+}|Cu} = 0.34V$.

These +ve emf values shows that iron will oxidise and copper will get reduced i.e., the vessel will dissolve. Hence it is not possible to store copper sulphate in an iron vessel.

16. Metals having higher oxidation potential will liberate H_2 from H_2SO_4 . Hence, the metal M_1 having $+ xV,$ oxidation potential will liberate H_2 from H_2SO_4 .
17. oxidation potential of M_1 is more +ve than the oxidation potential of Fe which indicates that it will prevent iron from rusting
18. Cell reactions:

Oxidation at anode: $Cd\,(s) \rightarrow Cd^{2+}(aq) + 2e^{-}$ $\qquad \left(E^{\circ}_{ox}\right)_{Cd|Cd^{2+}} = 0.4V$

Reduction at cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu\,(s)$ $\qquad \left(E^{\circ}_{red}\right)_{Cu^{2+}|Cu} = 0.34V$

$$Cd(s) + 2e^{-} \rightarrow Cd^{2+}(aq) + Cu(s)$$
$$E^{\circ}_{cell} = \left(E^{\circ}_{ox}\right) + \left(E^{\circ}_{red}\right)_{cathode}$$
$$= 0.4 + 0.34$$
$$= 0.74V.$$

emf is +ve, so ΔG is (-)ve, the reaction is feasible.

19. Oxidation at anode:

$$2H_2(g) + 4OH^{-}(aq) \rightarrow 4H_2O\,(l) + 4e^{-}$$

1 mole of hydrogen gas produces 2 moles of electrons at 25^0C and 1 atm pressure, 1 mole of hydrogen gas occupies = 22.4 litres

$$\therefore \text{ no. of moles of hydrogen gas produced} = \frac{1 \text{ mole}}{22.4 \text{ litres}} \times 44.8 \text{ litres}$$
$$= 2 \text{ moles of hydrogen}$$

$\therefore$ 2 of moles of hydrogen produces 4 moles of electron i.e., 4F charge.

We know that $Q = It$

$$I = \frac{Q}{t}$$
$$= \frac{4F}{10 \text{ mins}}$$
$$= \frac{4 \times 96500 \text{ C}}{10 \times 60 \text{ s}}$$
$$I = 643.33 \text{ A}$$

Electro deposition of copper

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

2F charge is required to deposit

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1 mole of copper i.e., 63.5 g
If the entire current produced in the fuel cell ie., 4 F is utilised for electrolysis, then
2× 63.5 i.e., 127.0 g copper will be deposited at cathode.

20. $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni\ (s)$

$Cr^{2+}(aq)+3e^{-} \rightarrow Cr\ (s)$

The above reaction indicates that 2F charge is required to deposit 58.7g of Nickel form nickel nitrate and 3F charge is required to deposit 52g of chromium.

Given that 2.935 gram of Nickel is deposited

$\therefore$ The amount of charge passed through the cell $= \frac{2F}{58.7g} \times 2.935g$

$= 0.1F$

$\therefore$ if 0.1F charge is passed through chromium nitrate the amount of chromium deposited

$= \frac{52g}{3F} \times 0.1F$

$= 1.733g$

21. Given that

$\left[Cu^{2+}\right] = 0.1M$

$E^{\circ}_{Cu^{2+}|Cu} = 0.34$

$E_{cell} = ?$

Cell reaction is

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu\ (s)$

$$E_{cell} = E^{o} - \frac{0.0591}{n} \log \frac{[Cu]}{\left[Cu^{2+}\right]}$$

$$= 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$= 0.34 - 0.0296$$

$$= 0.31V$$

22. oxidation at anode

$Mg \rightarrow Mg^{2+} + 2e^{-}$ .....(1) $\left(E^{o}_{ox}\right) = 2.37V$

Reduction at cathode

$Ag^{+} + e^{-} \rightarrow Ag$ ..... (2) $\left(E^{o}_{red}\right) = 0.80V$

$\therefore\ E^{o}_{cell} = \left(E^{o}_{ox}\right)_{anode} + \left(E^{o}_{red}\right)_{cathode}$

$= 2.37 + 0.80$

$= 3.17V$

Overall reaction

Equation (1) + 2 × equation $(2) \Rightarrow$

$Mg + 2Ag^{+} \rightarrow Mg^{2+} + 2Ag$

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$\Delta G^\circ = -nFE^\circ$

$= -2 \times 96500 \times 3.17$

$= -611810$ kJ

$\Delta G^o = -6.12 \times 10^5$ J

$W = 6.12 \times 10^5$ J

$\Delta G^o = -2.303\ RT \log^K C$

$\Rightarrow \log K_c = \dfrac{6.12 \times 10^5}{2.303 \times 8.314 \times 298}$

K_c = Antilog of (107.2)

23. Electrolysis of water

At anode:

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$.....(1)

At cathode:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall reaction $6H_2O \rightarrow 4H^+ + 4OH^- + 2H_2 + O_2$

(or)

Equation (1) +(2) $\times 2 \Rightarrow 2H_2O \rightarrow 2H_2 + O_2$

$\therefore$ According to faradays Law of electrolysis, to electrolyse two mole of Water $(36g \simeq 36\ mL\ of\ H_2O)$, 4F charge is required alternatively, when 36 mL of water is electrolysed, the charge generated = 4×96500 C.

$\therefore$ When the whole water which is available on the lake is completely electrolysed the amount of charge generated is equal to $\dfrac{4 \times 96500\ C}{36\ mL} \times 9 \times 10^{12} L$

$= \dfrac{4 \times 96500 \times 9 \times 10^{12}}{36 \times 10^{-3}} C$

$= 96500 \times 10^{15}$ C

$\therefore$ Given that in 1 second, 2×10^6 C is generated therefore, the time required to generate

96500×10^{15} C is $= \dfrac{1\ S}{2 \times 10^6 C} \times 96500 \times 10^{15} C$

$= 48250 \times 10^9$ S

$\therefore$ Number of years $= \dfrac{48250 \times 10^9}{365 \times 24 \times 60 \times 60}$

$= 1.5299 \times 10^6$ years

1 year = 365 days

$= 365 \times 24$ hours

$= 365 \times 24 \times 60$ min

$= 365 \times 24 \times 60 \times 60$ sec.

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Unit 10 Surface Chemistry

S.No.	Answers		
1.	(c) $\frac{x}{m}=k.p^{1/n}$ $\Rightarrow \log(\frac{x}{m})=\log k+\frac{1}{n}\log p$ $y=c+mx$ $\quad m=\frac{1}{n}$ and $c=\log k$		
2.	The incorrect statement is option (b) Physisorption is an exothermic process. Hence increase in temperature decreases the physisorption.		
3.	(d) Adsorption leads to decrease in randomness (entropy).i.e. $\Delta S< 0$ for the adsorption to occur, ΔG should be -ve. We know that $\Delta G=\Delta H-T\Delta S$ if ΔS is -ve, $T\Delta S$ is +ve. It means that ΔG will become negative only when ΔH is -ve and $\Delta H>T\Delta S$		
4.	(c) dispersion medium-gas dispersed phase-liquid	13.	pyroxylin(nitro cellulose)
5.	(a) (Hardy-Schulze rule)	14.	(d) Both reactant and catalyst are in same phase. i.e(l)
6.	(b)	15.	(a)
7.	(b) Emulsion dispersed phase Dispersion medium -liquid	16.	(a) coagulating power $\alpha \frac{1}{\text{coagulation value}}$
8.	(b) Gel-butter	17.	(d) ΔS is -ve
9.	(d) As_2S_3 is a -vely charged colloid. It will be most effectively coagulated by the cation with greater valency. i.e., Al^{3+}.	18.	(d)
10.	(b)	19.	(a)
11.	(d) Tyndall effect-scattering of light	20.	(d)
12.	(b)		

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Unit 11 Alcohols and Ethers

Key answer

1. $2\ R - OH + 2Na \rightarrow 2\ RONa + H_2\uparrow$ 2 moles of alcohol gives 1 mole of H_2 which occupies 22.4L at 273K and 1 atm

$$\therefore \text{ number of moles of alcohol} = \frac{2 \text{ moles of R - OH}}{22.4\,L \text{ of } H_2} \times 560 \text{ mL}$$

$$= 0.05 \text{ moles}$$

$$\therefore \text{ no. of moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$\Rightarrow \text{ molar mass} = \frac{3.7}{0.05} = 74 \text{ g mol}^{-1}$$

General formula for R - OH $C_n\ H_{2n+1}$ - OH

$$\therefore n(12) + (2n+1)(1) + 16+1=74$$

$$14n = 74 - 18$$

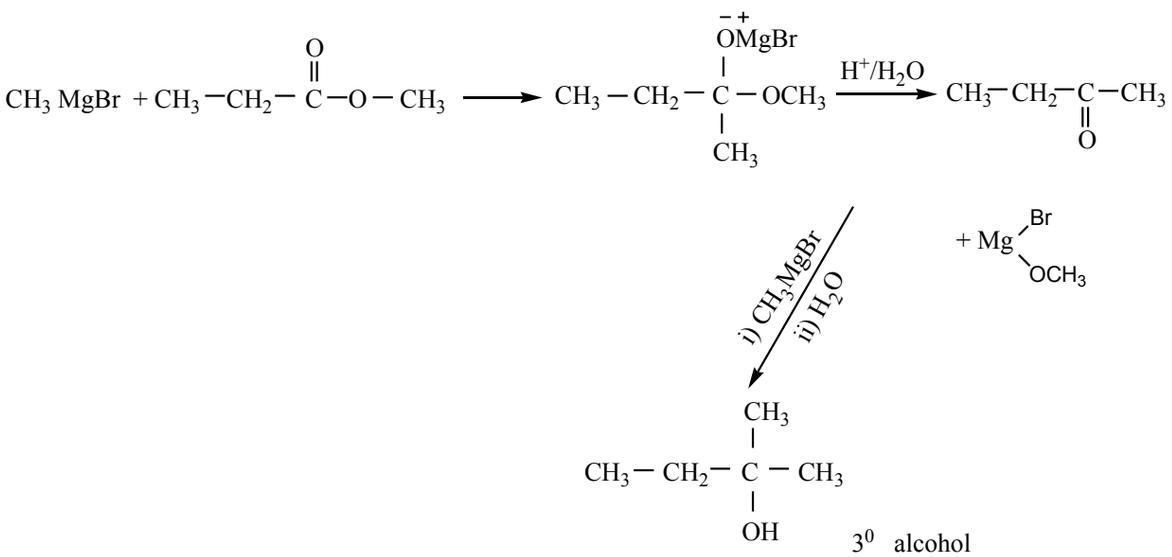
$$14n = 56$$

$$\therefore n = \frac{56}{14} = 4$$

The 2° alcohol which contains 4 carbon is $CH_3CH(OH)CH_2CH_3$

Option (a)

2.



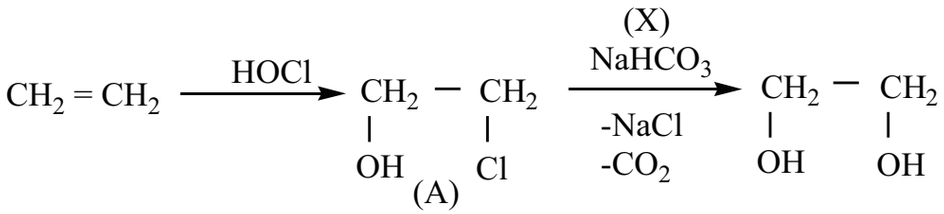
Option (c)

3. Hydro boration – Anti markownikoft product i.e., $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$

Option (a)

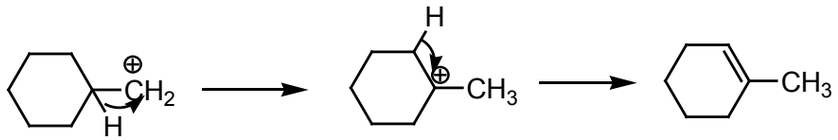
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4.



5. (c) 4 – nitrophenol

6. Option (b) saytzeff rule

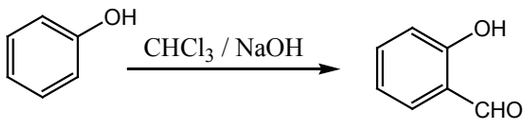


major product

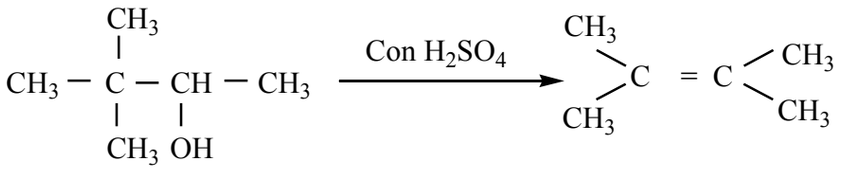
7. Carbolic acid is

a) phenol

8. Riemer – Tiemann reaction (option (c))



9.



Option (b)

10. Option (a)

11. Option (a)

12. $CH_3 - CH_2 - OH \xrightarrow{PCl_5} CH_3 - CH_2 - Cl \xrightarrow{ale.KOH} CH_2 = CH_2 \xrightarrow{H_2SO_4/H_2O} CH_3 - CH_2 - OH$

(Z) ethanol

13. Cyclic alcohol → sodium cyclic alkoxide → williamson ether synthesis option (c)

14. Option (d) phenol

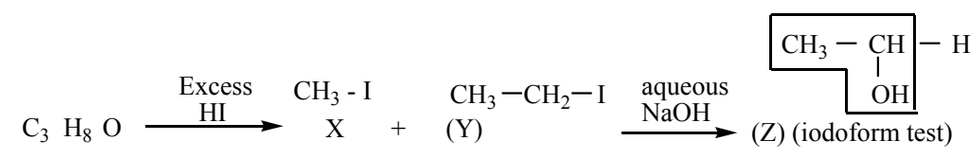
15. Option (a)

16. Option (c)

17. Option (d)

18. Option (c)

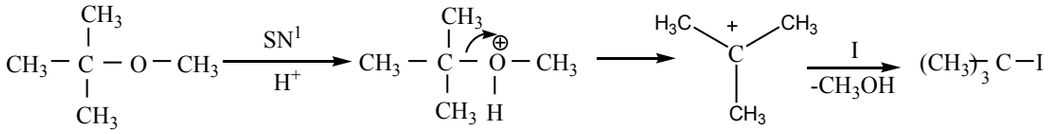
19.



Option (d)

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20.

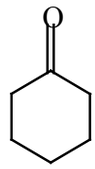


option (a)

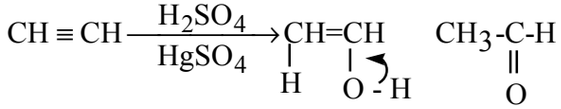
21. Option (b) SN^2 reaction
22. Violet color option (b)

Unit 12 Carbonyl Compounds and Carboxylic Acids

Key Answers



1. Option (b)
2. (d)
3. (c)
4. (b)



(X)

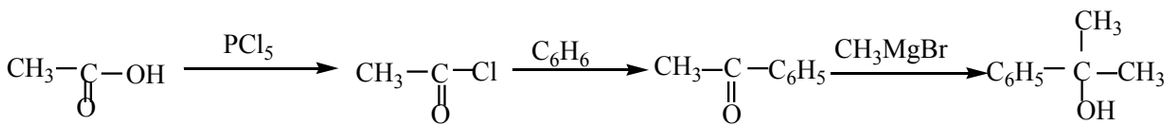
(x) reduces tollens reagent and Fehling solution and it also answers iodoform test.

5) (c)

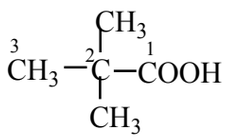
X-HCHO

$Y\text{-}(CH_2)_6N_4$

6) option (a)



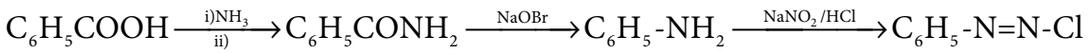
7) option (a)



8) (b)

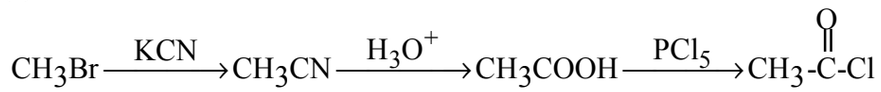
-I effect increases the acidity. If electronegativity is high, -I effect is also high.

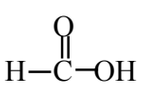
9) (c)



(A) (B)

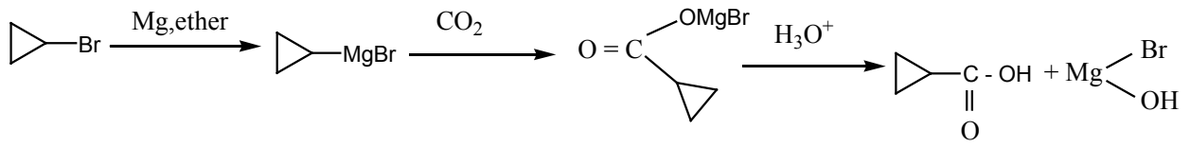
10. (c)
11. (a)

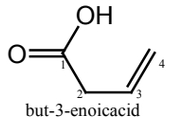


12. (a) formic acid 

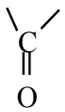
Answers.indd 316 16-12-2022 19:29:28

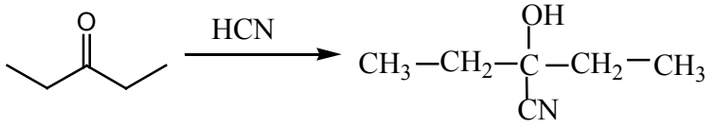
13. (b)

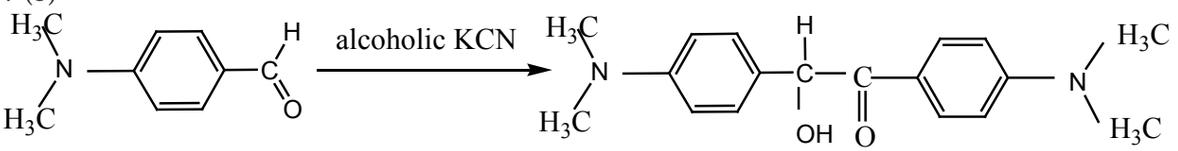


14. (a) 

but-3-enoicacid

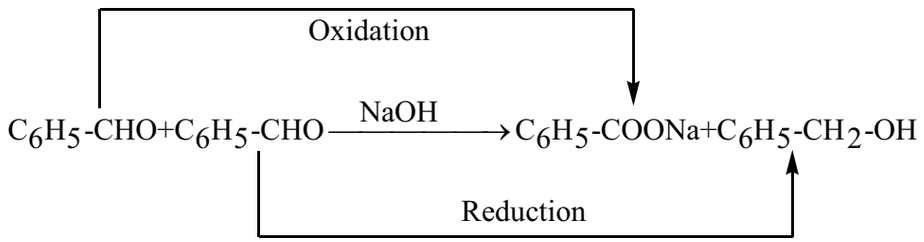
15. (d)  group is reduced to CH_2 - (Wolff-kishner reduction)

16. (a) 

17. (b) 

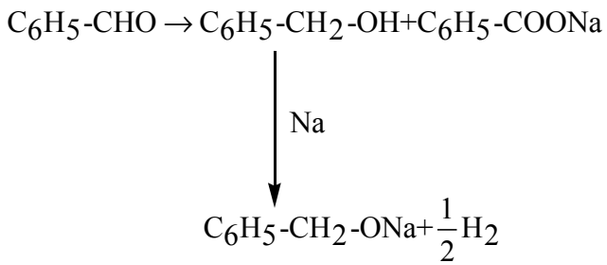
18. (b) Cannizaro reaction

19 (a)

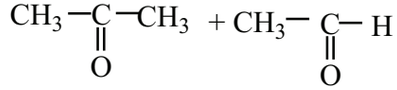


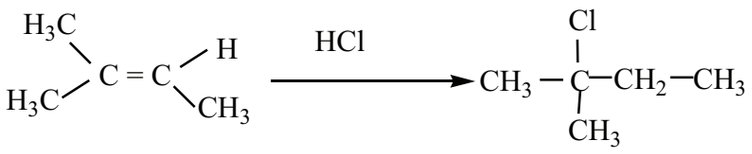
20(b). Fehling's solution

21. (c)



22. (d) Wolf kisher reduction

23. (c) 

alkene 

24.(d) formation of intermolecular H-bonding

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Unit – 13 Organic Nitrogen compounds

1. Option (a)
2. Option (b)
3. Option (a) only primary amides undergo hoffmann bromamide reaction
4. Option (d) both are wrong
5. $CH_3CH_3Br \xrightarrow{\text{aq NaOH}} CH_3CH_2\text{-}OH \xrightarrow{KMnO_4} CH_3\text{-}COOH \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3\text{-}NH_2$

   Option (c)
6. Option (c) 3° nitroalkane
7. Option (c)
8. Option (c) Suhiff's base
9. Option (b) p – nitrosation takes places, the product is $(CH_3)_2N$–C$_6$H$_4$–NO

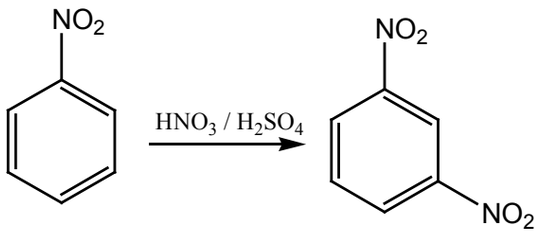
10. $C_6H_5NH_2 + CH_3COOCOCH_3 \longrightarrow C_6H_5NHCOCH_3$

    acetanilide

    Option (d)
11. Option (d)
12. Option (a)
13. Option (a)

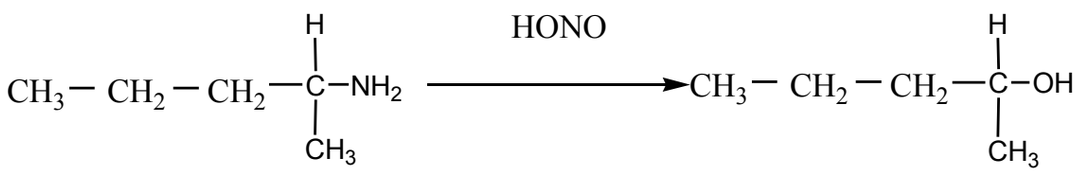
$$C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow{NaNO_2\ /\ HCl} C_6H_5\text{-}N_2Cl \xrightarrow{H_2O} C_6H_5\text{-}OH + N_2\uparrow + HCl$$

14. (d)



1,3 - dinitrobenzene

15. (b)



16. Option (b) blue solution

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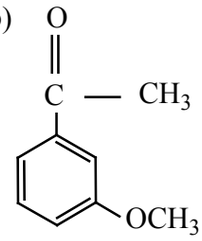
17. (d) triethyl amine (3° amine)

18. Option (b) CH_3 is a+I group, all other – I group. +I group increase the electron density on NH_2 and hence increases the basic nature.

19. Option (a) Ethanol, ammonium hydroxide

20. Option (d)

21. b)



22. (b) $C_6H_5COONH_4 \xrightarrow[\text{Heat}]{P_2O_5} C_6H_5\text{-}C \equiv N \xrightarrow{LiAlH_4} C_6H_5CH_2NH_2 \xrightarrow{HNO_2} C_6H_5CH_2OH$

23. Option (a)

Unit 9 Electro chemistry

1. (c) 2. (b) 3. (c) 4. (b) 5. (c) 6. (b) 7. (a) 8. (b) 9. (b) 10. (c) 11. (b) 12. (c)
13. (a) 14. (d) 15.(d) 16. (a) 17. (b) 18. (c) 19.(d) 20. (b) 21.(d) 22. (a) 23. (b) 24. (a)
25. (a)

Unit 10 – Surface Chemistry

1. (c) 2.(b) 3.(d) 4. (c) 5. (a) 6. (b) 7. (b) 8.(b) 9.(d) 10.(b) 11. (d) 12. (b)
13. (d) 14. (d) 15. (a) 16. (a) 17. (d) 18. (d) 19. (a) 20. (d)

Unit – 11 – Alcohols and Ethers

1. (a) 2. (c) 3. (a) 4. (c) 5. (c) 6.(b) 7.(a) 8.(c) 9.(b) 10.(a) 11.(a) 12.(d)
13. (c) 14. (d) 15. (a) 16.(c) 17.(d) 18.(c) 19.(d) 20.(a) 21.(b) 22. (b)

Unit – 12 Carbonyl Compounds and Carboxylic Acids

1. (b) 2. (d) 3. (c) 4. (b) 5. (c) 6. (a) 7.(a) 8.(b) 9. (c) 10. (c) 11. (a) 12.(a)
13. (b) 14. (a) 15. (d) 16. (a) 17.(b) 18.(b) 19. (a) 20.(b) 21. (c) 22. (d) 23.(c) 24. (d)

Unit – 13 Organic Nitrogen compounds

1. (a) 2. (b) 3. (a) 4. (d) 5. (c) 6. (c) 7.(c) 8.(c) 9. (b) 10. (d) 11. (d) 12.(a)
13. (a) 14. (d) 15. (b) 16. (b) 17.(d) 18.(b) 19. (a) 20.(d) 21. (b) 22.(b) 23.(a) 24. (b)
25. (b)

Unit – 14 Bio molecules

1. (c) 2. (d) 3. (b) 4. (a) 5. (a) 6. (c) 7. (a) 8. (c) 9. (d) 10. (d) 11. (d) 12. (d)
13. (a) 14. (c) 15. (c) 16. (d) 17. (d) 18. (d) 19. (c) 20. (b) 21. (a) 22. (c) 23. (b)
24. (d) 25. (d)

Unit – 15 Chemistry in Action

1. (c) 2. (a) 3. (a) 4. (a) 5.(d) 6.(c) 7. (a) 8. (c) 9. (a) 10.(d) 11. (d) 12. (c)
13.(d) 14.(b) 15. (d)

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Glossary - கலைச்சொற்கள்

Absorption	உட்கவர்தல்
Acid Anhydride	அமில நீரிலி
Active Sites	கிளர்வு மையங்கள்
Acylation	அசைலேற்றம்
Adhesives	ஒட்டும் தன்மையுடைய பொருள்
Adsorbate	பரப்பு கவரப்பட்ட பொருள்
Adsorbent	பரப்பு கவர்பொருள்
Adsorption	பரப்பு கவர்தல்
Aldol Condensation	ஆல்டால் குறுக்கம்
Alkylation	ஆல்கைலேற்றம்
Analgesic	வலி நிவாரணி
Anesthetic	மயக்க மருந்து
Anode	நேர்மின் முனை
Antacid	அமில நீக்கி
Antagonists	எதிர்வினையூக்கி
Antibiotics	எதிர்உயிரிகள்
Antiseptic	புரை தடுப்பான்
Anxiety	பதற்றம்
Auto Catalyst	தன் வினைவேகமாற்றி
Basicity	காரத் தன்மை
Benzoylation	பென்சாயிலேற்றம்
Biological Specimen	உயிரியல் மாதிரிகள்
Bromination	புரோமினேற்றம்
Carrier Proteins	கடத்து புரதங்கள்
Catalytic Poison	வினைவேகமாற்றியின் நச்சு
Cataphoresis	மின்முனைக் கவர்ச்சி
Cathode	எதிர்மின் முனை
Cell Constant	கலமாறிலி
Cell Membrane	செல்சவ்வு

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Chemisorption	வேதிப்பரப்பு கவர்ச்சி
Cinnamon	லவங்கப் பட்டை
Coagulation	கூழ்ம வீபடிவாதல்
Coal Tar	நிலக்கரித்தார்
Co-Enzyme	நொதிசெயல் உயர்த்தி
Concentration Cell	செறிவு மின்கலன்
Conductance	மின் கடத்துத்திறன்
Convulsions	வலிப்பு
Coupling Reaction	இணைப்பு வினை
Current Efficiency	மின்னாற் வீழ்படிவாக்குத்திறன்
Decarboxylation	கார்பாக்ஸில் நீக்கம்
Dehydration	நீர் நீக்கம்
Dehydrogenation	ஹைட்ரஜன் நீக்கம்
Denaturation	இயல்பு நீக்கம்
Desorption	பரப்பு நீக்குதல்
Detergents	அழுக்கு நீக்கிகள்
Dialysis	கூழ்மபிரிப்பு
Diazotisation	டையசோஆக்கல்
Disinfectant	தொற்றுநீக்கி
Double Decomposition	இரட்டைச் சிதைவு
Drugs	பலபடிகள்
Electrochemical Equivalent	மின்வேதிச் சமானநிறை
Electrochemical Series	மின்வேதி வரிசை
Electrode	மின்முனை
Electrode Potential	மின்முனை மின்னழுத்தம்
Electrolysis	மின்னாற்பகுத்தல்
Electrolyte	மின்பகுளி
Electromotive Force	மின்னியக்குவிசை
Electrophilic Substitution	எலக்ட்ரான் கவர்பதிலீடு
Electroplating	மின்முலாம்பூசுதல்
Emulsions	பால்மங்கள்

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Enzymes	நொதிகள்
Equivalent Conductance	சமான கடத்துத்திறன்
Esterification	எஸ்டராக்கல்
Fatty Acids	கொழுப்பு அமிலங்கள்
Fermentation	நொதித்தல்
Filterability	வடிபடும்தன்மை
Flavoring Agents	வாசனைப் பொருள்
Food Preservatives	உணவு பாதுகாப்பான்
Gel	களிமம் (களி)
Genetic Information	மரபுவழி தகவல்
Half-Cell Reaction	அரைக் கலவினை
Heterogeneity	பலபடித்தான தன்மை
Heterogeneous Catalyst	பலபடித்தான வினைவேகமாற்றி
Homogeneous Catalyst	ஒருபடித்தான வினைவேகமாற்றி
Induced Catalyst	தூண்டப்பட்ட வினைவேகமாற்றி
Infinite Dilution	முடிவிலா நீர்த்தல்
Inhibitor	வினைவேகதளர்த்தி
Isotherm	சமவெப்பநிலைக்கோடு
Lyophilic Sol	கரைப்பான் விரும்பும்கூழ்மங்கள்
Lyophobic Sol	கரைப்பான் வெறுக்கும்கூழ்மங்கள்
Miscelles	இணைவுக் கூழ்மம்
Mixed Ethers	கலப்பினஈதர்கள்
Molar Conductance	மோலார் கடத்துத்திறன்
Nitration	நைட்ரோஏற்றம்
Non-Spontaneous Process	தன்னிச்சையற்ற செயல்முறை
Nucleophilic Addition	கருகவர்சேர்ப்பு
Nucleophilic Substitution	கருகவர்பதிலீடு
Ozonolysis	ஓசோனேற்றம்
Peptisation	கூழ்மமாக்கல்
Perfumes	வாசனை திரவியங்கள்
Physisorption	இயற்பரப்புக் கவர்ச்சி

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Potential Gradient	மின்னழுத்த வேறுபாடு
Primary Amine	ஓரிணைய அமீன்
Primary Cell	முதன்மை மின்கலன்
Promoter	வினைவேக உயர்த்தி
Receptors	உணர்வேற்பி
Redox Reaction	ஆக்ஸிஜனேற்ற ஒடுக்கவினை
Resins	பிசின்
Resistance	மின்தடை
Rusting	துருப்பிடித்தல்
Sacrificial Protection	தன்னிழப்பு பாதுகாப்பு
Salt Bridge	உப்புப்பாலம்
Scattering Of Light	ஒளிச்சிதறல்
Secondary Amine	ஈரிணைய அமீன்
Secondary Cell	இரண்டாம்நிலை மின்கலன்
Sedimentation	படிவாதல்
Silver Mirror	வெள்ளிஆடி சோதனை
Solvation	கரைபானேற்றம்
Specific Conductance	நியமகடத்துத்திறன்
Specific Resistance	நியமமின்தடை
Spectator Ions	மின்வேதி வினையுறா அயனிகள்
Spontaneous Process	தன்னிச்சை செயல்முறை
Stress	மன உளைச்சல்
Stupor	மதி மயக்கம்

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