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QUESTION BANK

HIGHER SECONDARY – SECOND YEAR

CHEMISTRY - VOLUME II – ENGLISH MEDIUM

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UNIT – 8 IONIC EQUILIBRIUM

I. Text Book Questions and Answers

1. What are Lewis acids and bases? Give two examples for each.

S.No	Lewis Acids	Lewis Bases
1	Species that accepts an electron pair	Species that donates an electron pair
2	Ex: BF_3, $AlCl_3$	Ex: NH_3, H_2O

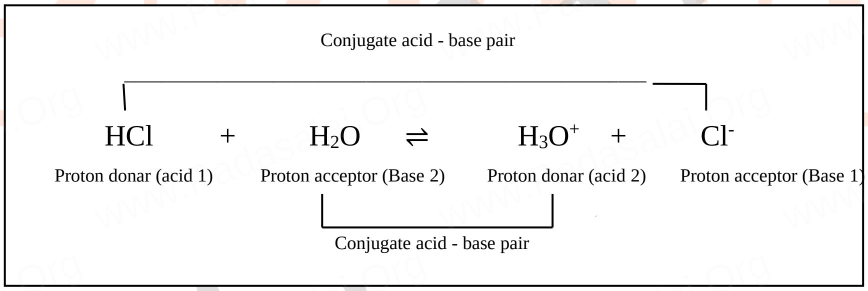
2. Discuss the Lowry-Bronsted concept of acids and bases .

- An acid is a proton donar.

  $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
- A base is a proton acceptor.

  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- 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 $_1$) .
- The species that remains after the acceptance of a proton is an acid (Acid$_2$) and is called the conjugate acid of the Bronsted base (Base$_2$) .
- Lowry – Bronsted (acid – base) reaction is represented as

  $\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$

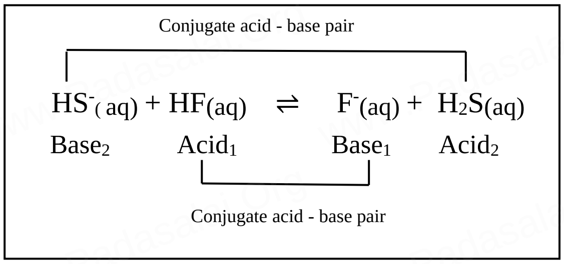


- In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.
- **Limitations of Lowry-Bronsted Theory**

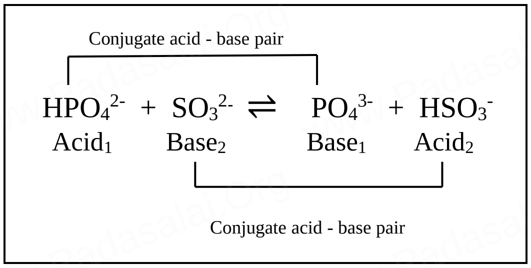
  Substance like BF_3, $AlCl_3$ do not have a proton but they are acids.

3. Identify the conjugate acid base pair for the following reaction in aqueous solution

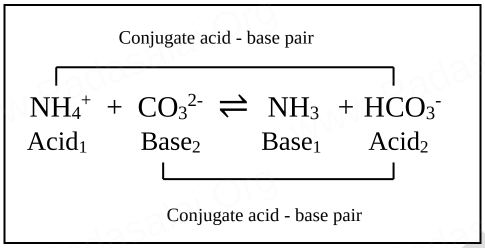
i) HS^- (aq) + HF $\rightleftharpoons$ F^- (aq) + H_2S (aq)



ii) $\mathbf{HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-}$



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



4. Account for the acidic nature of $HClO_4$ in terms of Bronsted – Lowry theory, identify its conjugate base.

$$\mathbf{HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-}$$

- The conjugate base of $HClO_4$ is ClO_4^-.
- When oxidation number of an element in an oxy acid increases then its acidic nature increases.
- The oxidation number of chlorine in $HClO_4$ is 7, which weakens the bond between O-H bond and increases the acidity.

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.

- In complexes, central metal ion act as a lewis acid which has a tendency to accept lone pair of electron from lewis base (ie) ligands.
- In the presence of a strong lewis base, the lewis acid (ie) the central metal ion undergoes ligand exchange reaction with weak lewis base.
- In the above equation, NH_3 replaces H_2O molecule to form the deep blue complex, so NH_3 is the strong 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.

GIVEN: $[OH^-] = 2.5 \times 10^{-6}$ M

$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log [2.5 \times 10^{-6}] \\ &= 6 - \log 2.5 = 6 - 0.3979 = 5.6021 \end{aligned}$$

pH = 14 - pOH

pH = 14 – 5.6021 = 8.3979.

pH = 8.3979. Since the pH is greater than 7, the solution is basic.

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas at 25 C^0 to get a solution with $[H_3O^+] = 4\times10^{-5}$ M. Is the solution neutral (or) acidic (or) basic.

GIVEN: $[H_3O^+] = 4 \times 10^{-5} M$

$$pH = -\log [H_3O^+]$$
$$= -\log [4 \times 10^{-5}]$$
$$= 5 - \log 4 = 5 - 0.6021 = 4.3979$$

pH = 4.3979. Since the pH is lesser than 7, the solution is acidic

8. Calculate the pH of 0.04 M HNO_3

GIVEN: $[H^+] = 0.04M$

$$pH = -\log[H^+] = -\log 0.04$$
$$= -\log [4 \times 10^{-2}]$$
$$= 2 - \log 4 = 2 - 0.6021 = 1.3979$$
$$\mathbf{pH = 1.3979}$$

9. Define Solubility Product.

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.

$$X_mY_n \rightleftharpoons mX^{n+} + nY^{m-}$$

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

10. Define Ionic product of water. Give its value at room temperature.

- The product of concentration of hydrogen ion and hydroxyl ion of pure water is known as ionic product of water (K_w).

$$\boxed{K_w = [H_3O^+][OH^-]}$$

$$K_w = 1 \times 10^{-7} \times 1 \times 10^{-7}$$

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

$$K_w = \text{Ionic product of water}$$

- At room temperature, the value of K_w is $1 \times 10^{-14} mol^2 dm^{-6}$

11. Explain Common Ion effect with an example.

- When the salt of the weak acid is added to the acid, the dissociation of the weak acid decreases. This is known as common ion effect.
- Ex. When sodium acetate is added to acetic acid, the dissociation of acetic acid decreases. Here CH_3COO^- is the common ion present.

12. Derive an expression for Oswald'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).

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

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

Content	CH_3COOH	CH_3COO^-	H^+
Initial number of moles	1	--	--
Number of moles Ionized	α	--	--
Number of moles remaining	1 − α	α	α
Equilibrium concentration	C (1 − α)	C α	C α

$$K_a \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} = \frac{C\alpha \text{ x } C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

When 1 >> α, the denominator can be neglected.

$$K_a = C\,\alpha^2$$

$$\boxed{\alpha = \sqrt{\frac{K_a}{C}}}$$

13. Define pH

pH is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solutions.

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

14. Calculate the pH of 1.5 x 10^{-3}M solution of $Ba(OH)_2$

$$\mathbf{Ba(OH)_2 \rightarrow Ba^{2+} + 2\,OH^-}$$

$$\text{Concentration of hydroxide ion} = 2[OH^-] = 2 \text{ x } 1.5 \text{ x } 10^{-3}M = 3 \text{ x } 10^{-3}M$$

$$pOH = -\log\ [OH^-]$$

$$= -\log(3 \text{ x } 10^{-3}) = 3 - \log 3 = 3 - 0.4771 = 2.5229$$

$$pH = 14 - pOH$$

$$pH = 14 - 2.5229 = 11.4771$$

$$\mathbf{pH = 11.4771}$$

15. 50ml of 0.05M HNO_3 is added to 50ml of 0.025M KOH . Calculate the pH of the resultant solution.

$$V_1M_1 - V_2M_2 = V_3M_3$$

$$(0.05 \text{ x } 50) - (0.025 \text{ x } 50) = 100M_3$$

$$2.5 - 1.25 = 100M_3$$
$$1.25 = 100M_3$$

$$M_3 = \frac{1.25}{100} = 1.25 \times 10^{-2}$$
$$pH = -\log[H^+] = -\log 1.25 \times 10^{-2}$$
$$= 2 - \log 1.25 = 2 - 0.0969 = 1.9031$$
$$\mathbf{pH = 1.9031}$$

16. The Ka value for HCN is 10^{-9} . What is the pH of 0.4 M HCN solution?

HCN is a weak acid.

$$[H^+] = \sqrt{K_a C} = \sqrt{4 \times 10^{-1} \times 10^{-9}} = \sqrt{4 \times 10^{-10}} = 2 \times 10^{-5}$$
$$pH = -\log[H^+] = -\log 2 \times 10^{-5}$$
$$= 5 - \log 2 = 5 - 0.3010 = 4.6990$$
$$\mathbf{pH = 4.6990}$$

17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate. Given that $K_a = K_b = 1.8 \times 10^{-5}$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 1.8 \times 10^{-10}}}$$
$$h = \sqrt{0.3086 \times 10^{-4}} = 0.5555 \times 10^{-2} = 5.555 \times 10^{-3}$$
$$\mathbf{h = 5.555 \times 10^{-3}}$$

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

If $K_a = K_b$, then, $pK_a = pK_b$

pH = = 7

pH = 7

18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base

Consider the reaction between strong acid and weak base

$$HCl_{(aq)} + NH_4OH_{(aq)} \rightleftharpoons NH_4Cl_{(aq)} + H_2O_{(l)}$$

The salt completely dissociates to give respective ions.

$$NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

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.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}$$

Here, $[H^+] > [OH^-]$ so the solution is acidic and the pH is less than 7.

Hydrolysis constant (K_h):

$$\begin{array}{cccc} NH_4^+{}_{(aq)} + H_2O_{(l)} & \rightarrow & NH_4OH_{(aq)} & + H^+{}_{(aq)} \\ C(1-h) & & Ch & Ch \end{array}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} ----(1) \qquad K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} ----(2)$$

Equ (1) x (2)

$$K_b \times K_h = K_w$$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_b}}}$$

Degree of hydrolysis: (h)

$$K_h = \frac{C\,h \times C\,h}{C(1-h)} = C\,h^2$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b C}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_b C}}}}$$

Concentration of hydrogen ion: $[H^+]$

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

$$\boxed{\mathbf{[H^+] = \sqrt{\frac{C\,K_w}{K_b}}}}$$

pH of the solution:

$$pH = -\log\ [H^+] = -\log\left[\frac{C\,K_w}{K_b}\right]^{\frac{1}{2}} = -\frac{1}{2}\log C - \frac{1}{2}\log\ K_w + \frac{1}{2}\log\ K_b$$

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

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

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?

$$\underset{(S)}{Ag_2CrO_4} \rightleftharpoons \underset{(2S)}{2Ag^+} + \underset{(S)}{CrO_4^{2-}}$$

$$\underset{0.01M}{AgNO_3} \rightarrow \underset{0.01\ M}{Ag^+} + \underset{0.01\ M}{NO_3^-}$$

Initial concentration of Ag^+ ion	2
Concentration of Ag^+ ion at equilibrium	2S
Change in concentration of Ag^+ ion after addition of $AgNO_3$	2S +0.01

$[Ag^+] = 2S + 0.01$; $(2S << 0.01)$; $[Ag^+] \cong 0.01$

$[Ag^+] = 0.01 = 1 \times 10^{-2}$; $[CrO_4^{2-}] = S$; $K_{sp} = 1 \times 10^{-12}$

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

$1 \times 10^{-12} = (1 \times 10^{-2})^2 \times S$

$S = \frac{1 \times 10^{-12}}{1 \times 10^{-4}} = 1 \times 10^{-8} M$

$\mathbf{S = 1 \times 10^{-8} M}$

20. Write the expression for the solubility product of $Ca_3(PO_4)_2$

$Ca_3(PO_4)_2 \rightleftharpoons 3 Ca^{2+} + 2 PO_4^{3-}$

S 3 S 2 S

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$K_{sp} = [3S]^3[2S]^2$

$K_{sp} = [27S^3] [4S^2] = 108 S^5$

$\mathbf{K_{sp} = 108 S^5}$

21. A saturated solution, prepared by dissolving CaF_2 (s) in water, has $[Ca^{2+}] = 3.3 \times 10^{-4}$ M .What is the Ksp of CaF_2 ?

$CaF_2 \rightleftharpoons Ca^{2+} + 2 F^-$

$[F^-] = 2[Ca^{2+}] = 2 \times 3.3 \times 10^{-4} = 6.6 \times 10^{-4}$ M

$K_{sp} = [Ca^{2+}] [F^-]^2$

$K_{sp} = 3.3 \times 10^{-4} \times (6.6 \times 10^{-4})^2 = 143.748 \times 10^{-12} = 1.44 \times 10^{-10}$

$\mathbf{K_{sp} = 1.44 \times 10^{-10}}$

22. Ksp of AgCl is 1.8×10^{-10} . Calculate molar solubility in 1 M $AgNO_3$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

S S

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

1M 1M 1M

Initial concentration of Ag^+ ion	1
Concentration of Ag^+ ion at equilibrium	S
Change in concentration of Ag^+ ion after addition of $AgNO_3$	S +1

$[Ag^+] = S + 1; (S << 1) ; [Ag^+] \cong 1$

$[Ag^+] = 1; [Cl^-] = S ; K_{sp} = 1.8 \times 10^{-10}$

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

$1.8 \times 10^{-10} = 1 \times S$

$\mathbf{S = 1.8 \times 10^{-10} M}$

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 Ksp for Ag_2CrO_4 ?

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 5 \times 10^{-5}$ M ; $[CrO_4^{2-}] = 4.4 \times 10^{-4}$ M

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = (5 \times 10^{-5})^2 (4.4 \times 10^{-4}) = 1.1 \times 10^{-12}$

$\mathbf{K_{sp} = 1.1 \times 10^{-12}}$

24. Write the expression for the solubility product of Hg_2Cl_2 .

$$\begin{array}{ccc} Hg_2Cl_2 & \rightleftharpoons Hg_2^{2+} + & 2Cl^- \\ S & S & 2S \end{array}$$

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = S(2S)^2 = 4S^3$

$\mathbf{K_{sp} = 4S^3}$

25. Ksp of Ag_2CrO_4 is 1.1×10^{-12} . What is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$$\begin{array}{ccc} Ag_2CrO_4 & \rightleftharpoons 2Ag^+ + & CrO_4^{2-} \\ S & 2\,S & S \end{array}$$

$$\begin{array}{cccc} K_2CrO_4 & \rightarrow 2K^+ & + & CrO_4^{2-} \\ 0.1M & 2 \times 0.1M & & 0.1M \end{array}$$

Initial concentration of CrO_4^{2-} ion	1
Concentration of CrO_4^{2-} ion at equilibrium	S
Change in concentration of CrO_4^{2-} ion after addition of K_2CrO_4.	S +0.1

$[CrO_4^{2-}] = S + 0.1$; $(S << 0.1)$; $[CrO_4^{2-}] \cong 0.1$

$[Ag^+] = 2S$; $[CrO_4^{2-}] = 0.1$; $K_{sp} = 1.1 \times 10^{-12}$

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

$1.1 \times 10^{-12} = (2S)^2(0.1)$

$1.1 \times 10^{-12} = 4S^2 \times 0.1$

$S^2 = \frac{1.1 \times 10^{-12}}{4 \times 0.1} = 2.75 \times 10^{-12}$

$S = \sqrt{2.75 \times 10^{-12}} = 1.658 \times 10^{-6}$

$\mathbf{S = 1.658 \times 10^{-6} M}$

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? Ksp ($PbCl_2$)=1.2 × 10^{-5}

The concentration of Pb^{2+} and Cl^- in the mixture is different from the concentration of individual solutions . The total volume (0.150 + 0.100 = 0.250L) changes on mixing.

$$\begin{array}{cccc} Pb(NO_3)_2 & \rightleftharpoons Pb^{2+} & + & 2NO_3^- \\ 0.1M & 0.1M & & 0.2M \end{array}$$

Number of moles of Pb^{2+} = molarity x volume of solution in litres = 0.1 x 0.15 = 0.015

Molarity of Pb^{2+} in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$[Pb^{2+}]_{mix} = \frac{0.015}{0.25} = 0.06M$

$$\begin{array}{llll} NaCl & \rightleftharpoons & Na^{+} + & Cl^{-} \\ 0.2M & & 0.2M & 0.2M \end{array}$$

Number of moles of Cl^{-} = molarity x volume of solution in litres = 0.1 x 0.2 = 0.02

Molarity of Cl^{-} in the mixture = $\frac{\text{Number of moles}}{\text{Volume}}$

$[Cl^{-}]_{mix} = \frac{0.02}{0.25} = 0.08M$

Ionic Product = $[Pb^{2+}][Cl^{-}]^2 = (0.06)\,(0.08)^2 = 3.84 \times 10^{-4}$

Solubility product = 1.2×10^{-5}

Ionic Product > Solubility product

$PbCl_2$ is precipitated.

27. Ksp of $Al(OH)_3$ is $1x\ 10^{-15}$M . At what pH does 1.0×10^{-3} M Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3(OH^{-})$
$K_{sp} = [Al^{3+}]\,[OH^{-}]^3$

$Al(OH)_3$ precipitates when $[Al^{3+}]\,[OH^{-}]^3 > K_{sp}$

$[Al^{3+}]\,[OH^{-}]^3 > 1x\ 10^{-15}$
$(1x\ 10^{-3})\,[OH^{-}]^3 > 1x\ 10^{-15}$
$[OH^{-}]^3 > 1x\ 10^{-12}$
$[OH^{-}] > 1x\ 10^{-4}$
$[OH^{-}] = 1x\ 10^{-4}M$

$pOH = -\log\,[OH^{-}] = -\log\,(1 \times 10^{-4})$
$= 4 - \log 1 = 4$
$pH = 14 - pOH = 14 - 4 = 10$

$Al(OH)_3$ precipitates at a pH above 10

II EVALUATE YOURSELF:

1. Classify the following as acids (or) base using Arrhenius concept.
i) HNO_3 ii) $Ba(OH)_2$ iii) H_3PO_4 iv) CH_3COOH

HNO_3	Acid
$Ba(OH)_2$	Base
H_3PO_4	Acid
CH_3COOH	Acid

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

i) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

Conjugate acid - base pair

$$\underset{Acid_1}{NH_4^+} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Base_1}{NH_3} + \underset{Acid_2}{H_3O^+}$$

Conjugate acid - base pair

ii) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$

Conjugate acid - base pair

$$\underset{Acid_1}{H_2SO_4} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Base_1}{HSO_4^-} + \underset{Acid_2}{H_3O^+}$$

Conjugate acid - base pair

iii) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Conjugate acid - base pair

$$\underset{Acid_1}{CH_3COOH} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Base_1}{CH_3COO^-} + \underset{Acid_2}{H_3O^+}$$

Conjugate acid - base pair

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

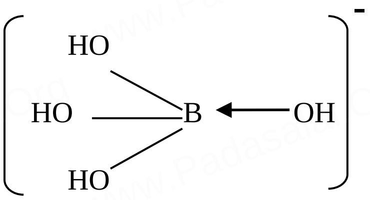
i) $CaO + CO_2 \rightarrow CaCO_3$

ii) $CH_3{-}O{-}{-}CH_3 + AlCl_3 \rightarrow (CH_3)_2O{\rightarrow}AlCl_3$

	Compound	Lewis Acid	Lewis Base
1	$CaCO_3$	CO_2	CaO
2.	$(CH_3)_2O{\rightarrow}AlCl_3$	$AlCl_3$	$(CH_3)_2O$

4. H_3BO_3 accepts hydroxide ion from water as shown below
$H_3BO_{3(aq)} + H_2O_{(l)} \rightarrow [B(OH)_4]^- + H^+$. Predict the nature of H_3BO_3 using Lewis concept.

H_3BO_3 is a Lewis acid. It accepts an electron pair from H_2O as follows.



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 $[OH^-]$

Since the solution is neutral, $[H_3O^+] = [OH^-]$. Let their concentration be x

$$K_w = [H_3O^+]\ [OH^-]$$
$$4 \times 10^{-14} = (x).(x)$$
$$x^2 = 4 \times 10^{-14}$$
$$x = \sqrt{4 \times 10^{-14}} = 2 \times 10^{-7}$$
$$\mathbf{[H_3O^+] = [OH^-] = 2 \times 10^{-7}}$$

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

Given: $[H^+]$= 2 x Concentration of H_2SO_4 = 2×10^{-8}M

$[H_3O^+] = 10^{-7}$ (from water) + 2×10^{-8} (from H_2SO_4)
$= 10 \times 10^{-8} + 2 \times 10^{-8} = (10 + 2) \times 2 \times 10^{-8}$
$= 12 \times 10^{-8}$ M
pH = $-\log(12 \times 10^{-8}) = 8 - \log 12 = 8 - 1.0792 = 6.9208$
pH= 6.9208

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

Given: pH = 5.4.

$[H_3O^+]$ = antilog (-pH)
= antilog (-5.4)
= antilog (-5.4 +6 -6)
= antilog (-6 +0.6)
= 3.981×10^{-6}

$[H_3O^+] = 3.981 \times 10^{-6}$M

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

$$V_1M_1 - V_2M_2 = V_3M_3$$

$$(50 \text{ x } 0.2) - (50 \text{ x } 0.1) = 100M_3$$

$10 - 5 = 100M_3$
$5 = 100M_3$

$$M_3 = \frac{5}{100} = 5 \text{ x } 10^{-2}$$

$$pH = -\log[H^+] = -\log(5 \text{ x } 10^{-2})$$

$$= 2 - \log 5 = 2 - 0.6990 = 1.3010$$

$$\mathbf{pH = 1.3010}$$

7. **K_b for NH_4OH is 1.8 x 10^{-5}. Calculate the percentage of ionization of 0.06M ammonium hydroxide solution.**
Given: K_b= 1.8 x 10^{-5} , C = 0.06M

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.8 \text{ x } 10^{-5}}{0.06}}$$

$$= \sqrt{\frac{1.8 \text{ x } 10^{-5}}{6 \text{ x } 10^{-2}}} = \sqrt{0.3 \text{ x } 10^{-3}}$$

$$= \sqrt{3 \text{ x } 10^{-4}} = \sqrt{3} \text{ x } 10^{-2} = 1.732 \text{ x } 10^{-2}$$

Degree of ionisation (α) = $\mathbf{1.732 \text{ x } 10^{-2}}$

Percentage of ionization = 1.732 x 10^{-2} x 100 = 1.732%

Percentage of ionization = 1.732%

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

Consider the buffer action in a solution containing NH_4OH and NH_4Cl. The dissociation of buffer components occur below.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$NH_4Cl_{(s)} \xrightarrow{H_2O(l)} NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

If a base is added to this mixture, it will be consumed by the conjugate acid NH_4^+ to form the undissociated weak base i.e. the increases in the concentration of OH^- does not reduce the pH significantly.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_4OH_{(aq)}$$

If an acid is added, it will be neutralised by OH^-, and the ammonium hydroxide is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

$$NH_4OH_{(aq)} \overset{H_2O(l)}{\Longleftrightarrow} NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

$$H^+_{(aq)} + NH_4OH_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + H_2O_{(l)}$$

b) Calculate the pH of the 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 solution. Assume that the addition of HCl causes negligible change in the volume. Given K_a = 1.8 x 10^{-5}

pH of the buffer solution:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $CH_3COONa \rightarrow CH_3COO^- + Na^+$

0.4 α α 0.4 – α α α

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

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a(0.4 - \alpha\,)}{(0.4 + \alpha)}$$

α<< 0.4, therefore [0.4 – α = 0.4] and [0.4 – α = 0.4]

$$[H^+] = \frac{K_a(0.4)}{(0.4)} = K_a$$

$$[H^+] = 1.8 \text{ x } 10^{-5}$$

$$pH = -\log[H^+] = -\log 1.8 \text{ x } 10^{-5}$$

$$= 5 - \log 1.8 = 5 - 0.2553 = 4.7447$$

$$\mathbf{pH} = \mathbf{4.7447}$$

Calculation pH after adding 0.01 mol of HCl to 500ml of buffer.

$$\text{Added } [H^+] = \frac{0.01 \text{ mol}}{500 \text{ ml}} = 0.02M$$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $CH_3COONa \rightarrow CH_3COO^- + Na^+$

0.4 – α α α 0.4 α α

$CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$

0.02 0.02 0.02 0.02

0.02 mol HCl is added with 0.02 mol acetate ion and produce 0.02 mol acetic acid. Therefore

$[CH_3COOH]$ = (0.4 – α) +(0.02)= 0.42 –α = 0.42

$[CH_3COO^-]$ = (0.4 +α) – (0.02)= 0.38 –α = 0.38

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

$$[H^+] = \frac{(1.8 \text{ x } 10^{-5})(0.42)}{(0.38)} = 1.99 \text{ x} 10^{-5}$$

$$pH = -\log[1.99 \text{ x} 10^{-5}]$$

$$= 5 - \log 1.99 = 5 - 0.2989 = 4.7011$$

$$\mathbf{pH = 4.7011}$$

The addition of strong acid 0.01 mol HCl increased the pH only slightly ie., from 4.7447 to 4.7011. So the buffer action is verified.

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. ($pK_b = 4.7$)

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

$$pH + pOH = 14$$

$$9 + pOH = 14$$

$$pOH = 14 - 9 = 5$$

$$5 = 4.7 + \log\frac{[NH_4Cl]}{[NH_4OH]}$$

$$0.3 = \log\frac{[NH_4Cl]}{0.1}$$

$$\frac{[NH_4Cl]}{0.1} = \text{antilog of } (0.3)$$

$$[NH_4Cl] = 0.1\text{M x } 1.995 = 0.2\text{M}$$

Amount of NH_4Cl required to prepare 1 litre of 0.2M solution

= Strength x molar mass of NH_4Cl = 0.2 x 53.5 = 10.70g

Amount of NH_4Cl required to prepare 1 litre of 0.2M solution= 10.70g

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 (pK_a = 3.75)

$$pH = pK_a + \log\frac{[\text{sodium formate}]}{[\text{formic acid}]}$$

$$[\text{sodium formate}] = 0.6 \text{ x } V$$

$$[\text{formic acid}] = 0.8 \text{ x } 100 = 80$$

$$4 = 3.75 + \log\frac{[0.6\ V]}{[80]}$$

$$4 - 3.75 = \log\frac{[0.6\ V]}{[80]}$$

$$\text{antilog of } 0.25 = \frac{[0.6\ V]}{[80]}$$

$$0.6V = 1.778 \text{ x } 80 = 142.24$$

$$V = \frac{142.24}{0.6} = 237.08$$

Volume required = 237.08 mL

10. Calculate the i) hydrolysis constant ii) degree of hydrolysis and iii) pH of 0.05M sodium carbonate (pK_a= 10.26)

pK_a= 10.26
pK_a= -log K_a
K_a= antilog (-pK_a) = antilog (-10.26)
= antilog (-10.26 +11 -11)
= antilog (-11 + 0.74) = 5.495 x 10^{-11}

i) hydrolysis constant (K_h)

$$K_h = \frac{K_w}{K_a} = \frac{1 \text{ x} 10^{-14}}{5.5 \text{ x} 10^{-11}} = 1.8 \text{ x } 10^{-4}$$

hydrolysis constant (K_h) = $1.8 \text{ x } 10^{-4}$

ii) degree of hydrolysis (h)

$$h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{1 \text{ x } 10^{-14}}{5.5 \text{ x } 10^{-11} \text{ x } 0.05}} = \sqrt{\frac{1 \text{ x } 10^{-3}}{0.275}} = \sqrt{3.63 \text{ x } 10^{-3}} = \sqrt{36.3 \text{ x } 10^{-4}} = 6.025 \text{ x } 10^{-2}$$

degree of hydrolysis (h) = $6.025 \text{ x } 10^{-2}$

iii) pH of the solution:

$$\text{pH} = 7 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log C = 7 + \frac{10.26}{2} + \frac{\log 0.05}{2} = 7 + 5.13 - 0.6505 = 11.4795$$

pH= 11.4795

III TEXT BOOK EXAMPLES:

Example: 1 (page no 8)

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

Given: [H_3O^+] = 2 x 10^{-3}M

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

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \text{ x } 10^{-14}}{2 \text{ x } 10^{-3}} = 5 \text{ x } 10^{-12} \text{ M}$$

2 x 10^{-3} >> 5 x 10^{-12} i.e. [H_3O^+] >>[OH^-], **hence the juice is acidic in nature.**

Example: 2 (page no 11)

Calculate the pH of 0.001M HCl solution.

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

pH = 3

Example:3 (page no 11)

Calculate the pH of 10 $^{-7}$M HCl solution

Given: Concentration of HCl = 10^{-7}

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

$= 10^{-7} + 10^{-7} = (1 + 1) \times 10^{-7} = 2 \times 10^{-7}$

$$\text{pH} = -\log\ [H_3O^+] = -\log\ (2 \times 10^{-7}) = 7 - \log 2 = 7 - 0.3010 = 6.699 = 6.70$$

pH= 6.70

Example: 4 (page no 14)

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

$$\textbf{Given: } \alpha = 1.20\% = \frac{1.20}{100} = 1.2 \times 10^{-2}$$

$$K_a = \alpha^2 C = (1.2 \times 10^{-2})^2\ (0.1) = 1.44 \times 10^{-4} \times 10^{-1} = 1.44 \times 10^{-5}$$

Example:5 (page no 15)

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

Given: $K_a = 1.8 \times 10^{-5}$, C = 0.1M

For weak acids, $[H^+] = \sqrt{K_a \times C}$

$$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1} = \sqrt{1.8 \times 10^{-6}}$$

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

pH = -log (1.34 x 10^{-3})

= 3 – log 1.34

= 3- 0.1271 = 2.8729

pH= 2.8729

Example:6 (page no 19)

Find the pH of the buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. K_a = 1.8 x 10^{-5}

Given: $K_a = 1.8 \times 10^{-5}$, [acid] = 0.18 mole per litre, [salt] = 0.20 mole per litre

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

$$= 4.7447 + \log\frac{0.20}{0.18}$$

$$= 4.7447 + \log\frac{10}{9}$$

$$= 4.7447 + \log 10 - \log 9 = 4.7447 + 1 - 0.9542$$

$$= 4.7905$$

pH= 4.7905

Example:7 (page no 20)

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

$$\text{pH} = \text{p}K_a + \log\frac{[\text{sodium acetate}]}{[\text{acetic acid}]}$$

$$\mathrm{pK_a} = 4.7447$$

$$\text{Number of moles of sodium acetate} = \frac{\text{mass}}{\text{molar mass}} = \frac{8.2}{82} = 0.1\text{mole}$$

$$[\text{sodium acetate}] = \frac{\text{number of moles}}{\text{volume of soluition}} = \frac{0.1}{0.5} = 0.2\text{M}$$

$$\text{Number of moles of acetic acid} = \frac{\text{mass}}{\text{molar mass}} = \frac{6}{60} = 0.1\text{mole}$$

$$[\text{acetic acid}] = \frac{\text{number of moles}}{\text{volume of soluition}} = \frac{0.1}{0.5} = 0.2\text{M}$$

$$\mathrm{pH} = 4.7447 + \log\frac{0.2}{0.2}$$
$$= 4.7447$$

pH= 4.7447

Example: 8 (page no 24)

Calculate the i) hydrolysis constant ii) degree of hydrolysis and iii) pH of 0.1M sodium acetate (pK $_a$ of acetic acid= 4.74)

pK $_a$= 4.74

pK $_a$= -log K$_a$

K$_a$= antilog (-pK $_a$) = antilog (-4.74)

= antilog (-4.74 +5 -5)
= antilog (-5 + 0.26) = 1.8 x 10^{-5}

i) hydrolysis constant (K$_h$)

$$\mathrm{K_h} = \frac{K_w}{K_a} = \frac{1\ \mathrm{x}10^{-14}}{1.8\ \mathrm{x}\ \mathrm{x}10^{-5}} = 5.6\mathrm{x}\ 10^{-10}$$

hydrolysis constant (K$_h$) = $\mathbf{5.6x\ 10^{-10}}$

ii) degree of hydrolysis (h)

$$\mathrm{h} = \sqrt{\frac{\mathrm{K_w}}{K_a\mathrm{C}}} = \sqrt{\frac{1\ \mathrm{x}\ 10^{-14}}{1.8\ \mathrm{x}\ 10^{-5}\ \mathrm{x}\ 0.1}} = \sqrt{\frac{1\ \mathrm{x}\ 10^{-8}}{1.8}} = \sqrt{0.5555\mathrm{x}\ 10^{-8}} = 0.75\ \mathrm{x}\ 10^{-4}$$

degree of hydrolysis (h) = $\mathbf{7.5\ x\ 10^{-5}}$

iii) pH of the solution:

$$\mathrm{pH} = 7 + \frac{1}{2}\mathrm{p\ K_a} + \frac{1}{2}\log\mathrm{C} = 7 + \frac{4.74}{2} + \frac{\log 0.1}{2} = 7 + 2.37 - 0.5 = 8.87$$

pH= $\mathbf{8.87}$

Example:9 (page no 25)

Find out whether lead chloride gets precipitated or not when 1mL of 0.1M lead nitrate and

0.5mL of 0.2M NaCl solution are mixed? K_{sp} of $PbCl_2$= 1.2 x 10^{-5}

The concentration of Pb^{2+} and Cl^- in the mixture is different from the concentration of individual solutions . The total volume (0.1 + 0.5 = 1.5mL) changes on mixing.

$$\underset{0.1M}{Pb(NO_3)_2} \rightleftharpoons \underset{0.1M}{Pb^{2+}} + \underset{0.2M}{2NO_3^-}$$

Number of moles of Pb^{2+} = molarity x volume of solution in litres = 0.1 x 1 x 10^{-3} = 10^{-4}

$$\text{Molarity of } Pb^{2+} \text{ in the mixture} = \frac{\text{Number of moles}}{\text{Volume}}$$

$$[Pb^{2+}]_{mix} = \frac{10^{-4}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-2}\ M$$

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

Number of moles of Cl^- = molarity x volume of solution in litres = 0.2 x 0.5 x 10^{-3}= 10^{-4}

$$\text{Molarity of } Cl^- \text{ in the mixture} = \frac{\text{Number of moles}}{\text{Volume}}$$

$$[Cl^-]_{mix} = \frac{10^{-4}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-2}\ M$$

Ionic Product = $[Pb^{2+}][Cl^-]^2 = (6.7 \times 10^{-2})(6.7 \times 10^{-2})^2 = 3.01 \times 10^{-4}$

Solubility product = 1.2 × 10^{-5}

Ionic Product > Solubility product

$PbCl_2$ is precipitated.

Example: 10 (page no 26)

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

a) $BaSO_4$

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

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

$K_{sp} = S^2$

b) Ag_2CrO_4

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2S)^2(S) = 4S^3$

$K_{sp} = 4S^3$

IV ADDITIONAL QUESTIONS AND ANSWERS:

1. Discuss Arrhenius concept of acids and bases with suitable example. Give its limitations.

- An acid is a substance that dissociates to give hydrogen ion in water. Ex: HCl, H_2SO_4
- A base is a substance that dissociates to give hydroxyl ion in water. Ex: NaOH, KOH

Limitations:

- It does not explain the behavior of acids and bases in non aqueous solvents like acetone, tetrahydrofuran etc..
- It does not account the basicity of the substance like ammonia which do not posses hydroxyl group.

2. Distinguish Lewis acids and Lewis bases.

Lewis acids	**Lewis bases**
Electron deficient molecules . Ex: BF_3, $AlCl_3$	Molecules with one or more lone pairs of electrons. Ex: NH_3, H_2O
All metal ions or atoms. Ex: Fe^{2+}, Fe^{3+}, Cr^{3+}	All anions. Ex: F^-,Cl^-, CN^-
Molecules with polar double bond. Ex: SO_2, CO_2	Molecules with carbon – carbon double bond Ex: $CH_2=CH_2$, $CH \equiv CH$
Molecules in which the central atom can expand its octet due to the availability of empty d-orbitals. Ex: SiF_4, SF_4	All metal oxides. Ex: CaO, MgO
Carbonium ion. Ex: $(CH_3)_3C^+$	Carbanion. Ex: CH_3^-

3.What are strong acids and bases. Give examples.

S.No	**Strong Acids**	**Strong Bases**
1.	A strong acid is one that is almost completely dissociated in water	A strong base is one that is almost completely dissociated in water
2.	Ex: HCl,HNO_3	Ex: NaOH, KOH

4.What are weak acids and bases. Give examples

S.No	**Weak Acids**	**Weak Bases**
1.	A weak acid is one which are partially dissociated in water.	A weak base is one which are partially dissociated in water.
2.	Ex: CH_3COOH	Ex: NH_4OH

5. The K_a value of Acid (A) is 2×10^6 and Acid (B) is 1.8×10^{-5} at 25^0C. Identify the strong acid.

K_a is called the ionization constant or dissociation constant of the acid. It measures the strength of the acid. Higher the K_a value, stronger the acid is. So Acid (A) is stronger than Acid (B).

6. Conjugate base of a strong acid is a weak base. Justify your answer

Consider the dissociation of HCl in aqueous solution.

$$\underset{Acid_1}{HCl} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Acid_2}{H_3O^+} + \underset{Base_1}{Cl^-}$$

Due to complete dissociation, the equilibrium lies almost to the right i.e., the Cl^- ion has only a negligible tendency to accept proton from H_3O^+. It means that conjugate base of a strong acid is a weak base.

7. At 25^0C, the value of K_w is 1.00 x 10^{-14} and at 40^0C, it is 2.71 x 10^{-14}. Why such variation in K_w value is observed?

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

8. Aqueous solution of NaCl is neutral. Comment on it.

In aqueous solution of NaCl, both Na^+ and Cl^- do not undergo hydrolysis. So the concentration of both H_3O^+ and OH^- are equal. Hence the solution is neutral.

9. Aqueous solution of HCl is acidic and solution of NaOH is basic. Why?

The following equilibrium exist in aqueous solution of HCl.

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

HCl molecules also produces H_3O^+ by donating proton to water and so $[H_3O^+] > [OH^-]$. Hence, aqueous solution of HCl is acidic. Similarly, in basic solutions, $[OH^-] > [H_3O^+]$. Hence, aqueous solution of NaOH is basic.

10. Express the concentration of H_3O^+ and OH^- present in a solution, when concentration of acid and base is less than 10^{-6}.

If the concentration of acid and base is less than 10^{-6}, then the concentration of H_3O^+ produced due to the auto ionisation of water cannot be neglected.

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

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

11. From Ostwald dilution law, how the concentration of H^+(H_3O^+) can be calculated from K_a value.

$$[H^+] = \alpha C$$

$$[H^+] = \sqrt{\frac{K_a}{C}} \text{ x } C = \sqrt{K_a \ C}$$

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

12 What are buffer solution? What are its types.?

- Buffer solution is a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid.
- It resists drastic changes in its pH upon addition of a small amount of acids or bases.
- There are two types of buffer solutions.
  1. Acidic buffer solution: a solution containing weak acid and its salt. Ex: solution containing acetic acid and sodium acetate.
  2. Basic buffer solution : a solution containing weak base and its salt. Ex: solution containing ammonium hydroxide and ammonium chloride.

13. Explain the buffer action in a acidic buffer containing equimolar acetic acid and sodium acetate.

Consider the buffer action in a solution containing CH_3COOH and CH_3COONa. The dissociation of buffer components occur below.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$CH_3COONa_{(s)} \xrightarrow{H_2O(l)} Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

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 increases in the concentration of H^+ does not reduce the pH significantly.

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

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

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

$$CH_3COOH_{(aq)} \overset{H_2O(l)}{\Longleftrightarrow} H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$OH^-_{(aq)} + CH_3COOH_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

14. What is 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.

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

15. Derive Henderson – Hasselbalch equation to calculate pH of acidic buffer.

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.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]}$$

Due to common ion effect and very less extent of dissociation, the concentration of weak acid is nearly equal to the initial concentration of unionized acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of added salt.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]}$$

Taking logarithm on both sides of the equation

$$\log [H_3O^+] = \log K_a + \log \frac{[acid]}{[salt]}$$

Reverse the sign on both sides,

$$-\log [H_3O^+] = -\log K_a - \log \frac{[acid]}{[salt]}$$

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

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

16 What is salt hydrolysis?

Salts completely dissociates in aqueous solution to give their constituent ions. The ions so produced are hydrated by water. In certain cases, cations , anions or both react with water and the reaction is called salt hydrolysis.

17. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of weak acid and strong base

Consider the reaction between weak acid and strong base

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightleftharpoons CH_3COONa_{(aq)} + H_2O_{(l)}$$

The salt completely dissociates to give respective ions.

$$CH_3COONa_{(s)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

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

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Here, $[OH^-] > [H^+]$ so the solution is basic and the pH is greater than 7.

Hydrolysis constant (K_h):

$$\begin{array}{cccc} CH_3COO^-_{(aq)} & + H_2O_{(l)} \rightarrow & CH_3COOH_{(aq)} & + OH^-_{(aq)} \\ C(1-h) & & Ch & Ch \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} ----(1) \qquad K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} ----(2)$$

Equation (1) x (2)

$$K_a \text{ x } K_h = K_w$$

$$\boxed{\mathbf{K_h = \frac{K_w}{K_a}}}$$

Degree of hydrolysis: (h)

$$K_h = \frac{Ch \text{ x } Ch}{C(1-h)} = Ch^2$$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a C}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_a C}}}}$$

Concentration of hydroxide ion: $[\mathrm{OH^-}]$

$$[\mathrm{OH^-}] = \mathrm{C\,h} = \mathrm{C}\sqrt{\frac{\mathrm{K_w}}{\mathrm{K_a C}}} = \sqrt{\frac{\mathrm{C\,K_w}}{\mathrm{K_a}}}$$

$$\boxed{[\mathbf{OH^-}] = \sqrt{\frac{\mathbf{C\,K_w}}{\mathbf{K_a}}}}$$

pH of the solution:

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 + \log[\mathrm{OH^-}] = 14 + \log\left[\frac{\mathrm{C\,K_w}}{\mathrm{K_a}}\right]^{\frac{1}{2}} = 14 + \frac{1}{2}\log \mathrm{C} + \frac{1}{2}\log \mathrm{K_w} - \frac{1}{2}\log \mathrm{K_a}$$

$$= 14 - 7 + \frac{1}{2}\log \mathrm{C} - \frac{1}{2}\log \mathrm{K_a} = 7 + \frac{1}{2}\log \mathrm{C} + \frac{1}{2}\mathrm{pK_a}$$

$$\boxed{\mathbf{pH = 7 + \frac{1}{2}\log C + \frac{1}{2}pK_a}}$$

18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of weak acid and weak base

Consider the reaction between weak acid and weak base

$$\mathrm{CH_3COOH_{(aq)} + NH_4OH_{(aq)} \rightleftharpoons CH_3COO\,NH_{4\,(aq)} + H_2O_{(l)}}$$

The salt completely dissociates to give respective ions.

$$\mathrm{CH_3COO\,NH_{4\,(s)} \rightarrow NH_4^+{}_{(aq)} + CH_3COO^-{}_{(aq)}}$$

In this case, both the cation and anion have the tendency to react with water.

$$\mathrm{CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-{}_{(aq)}}$$
$$\mathrm{NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}}$$

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

Hydrolysis constant (K_h):

$$\mathrm{CH_3COO^-{}_{(aq)} + H_2O_{(l)} \rightarrow CH_3COOH_{(aq)} + OH^-{}_{(aq)}}$$

C (1-h) C h C h

$$\mathrm{NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow NH_4OH_{(aq)} + H^+{}_{(aq)}}$$

C (1-h) C h C h

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} ----(1) \qquad K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} ----(2)$$

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_4OH]} ----(3)$$

Equations (1) x (2) x (3)

K_a x K_b x K_h = K_w

$$\boxed{\mathbf{K_h = \frac{K_w}{K_a K_b}}}$$

Degree of hydrolysis: (h)

$$\underset{C(1-h)}{CH_3COO^-_{(aq)}} + \underset{C(1-h)}{NH_4{}^+_{(aq)}} + H_2O_{(l)} \rightarrow \underset{Ch}{CH_3COOH_{(aq)}} + \underset{Ch}{NH_4OH_{(aq)}}$$

$$K_h = \frac{Ch \text{ x } Ch}{C^2(1-h)^2} = h^2$$

$$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$\boxed{\mathbf{h = \sqrt{\frac{K_w}{K_a K_b}}}}$$

Concentration of hydrogen ion: $[H^+]$

$$[H^+] = K_a h = K_a\sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w\ K_a}{K_b}}$$

$$\boxed{\mathbf{[H^+] = \sqrt{\frac{K_w\ K_a}{K_b}}}}$$

pH of the solution:

$$pH = -\log[H^+] = -\log\left[\frac{K_w\ K_a}{K_b}\right]^{\frac{1}{2}} = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log K_b$$

$$= pK_w + \frac{1}{2}\,p\,K_a - \frac{1}{2}\,p\,K_b$$

$$\boxed{\mathbf{pH = 7 + \frac{1}{2}\,p\,K_a - \frac{1}{2}\,p\,K_b}}$$

19. How is solubility product is used to decide the precipitation of ions?

Ionic product > K_{sp}	Precipitation occurs.	Solution is super saturated
Ionic product < K_{sp}	No precipitation	Solution is unsaturated
Ionic product = K_{sp}	Equilibrium exist	Solution is saturated

20. What is molar solubility?

The maximum number of moles of solute that can be dissolved in one litre of the solution.

UNIT – 9 ELECTRO CHEMISTRY

I. Text book question and answer.

1. Define anode and cathode.

Anode: The electrode at which the oxidation occurs is called the anode.

Cathode: The electrode at which the reduction occurs is called the cathode.

2. Why does conductivity of a solution decrease on dilution of the solution.

Conductivity of a solution decreases on dilution because the number of ions per unit volume that carry the current in a solution decreases on dilution.

3. State Kohlrausch Law. How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution.

Kohlrausch 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.

The molar conductance of CH_3 COOH, can be calculated using the experimentally determined molar conductivities of strong electrolytes HCl, NaCl and CH_3 COONa.

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

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

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

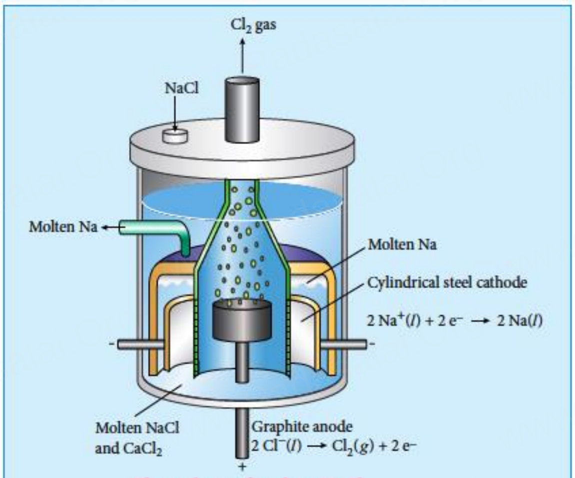
Equation (1) + Equation (2) – Equation (3) gives,

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

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

4. Describe the electrolysis of molten NaCl using inert electrodes.

- ⇨ The electrolytic cell consists of two iron electrodes dipped in molten sodium chloride and they are connected to an external DC power supply via a key.
- ⇨ The electrode which is attached to the negative end of the power supply is called the cathode, and the one which 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.



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)

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

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

Anode (oxidation)

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

The overall reaction is,

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

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.

5. State Faraday's Laws of electrolysis.

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.

$m \ \alpha \ Q$

$m = Z It$

Faraday's Second Law

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.

6. Describe the construction of Daniel cell. Write the cell reaction.

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.

Reduction half cell

A copper strip that dips into an aqueous solution of copper sulphate taken in a beaker.

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 a agar-agar gel mixed with an inert electrolytes such as KCl, Na_2SO_4 etc.,

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.

Anodic oxidation

The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation takes place at zinc electrode, i.e., zinc is oxidised to Zn^{2+} ions by losing its electrons.

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

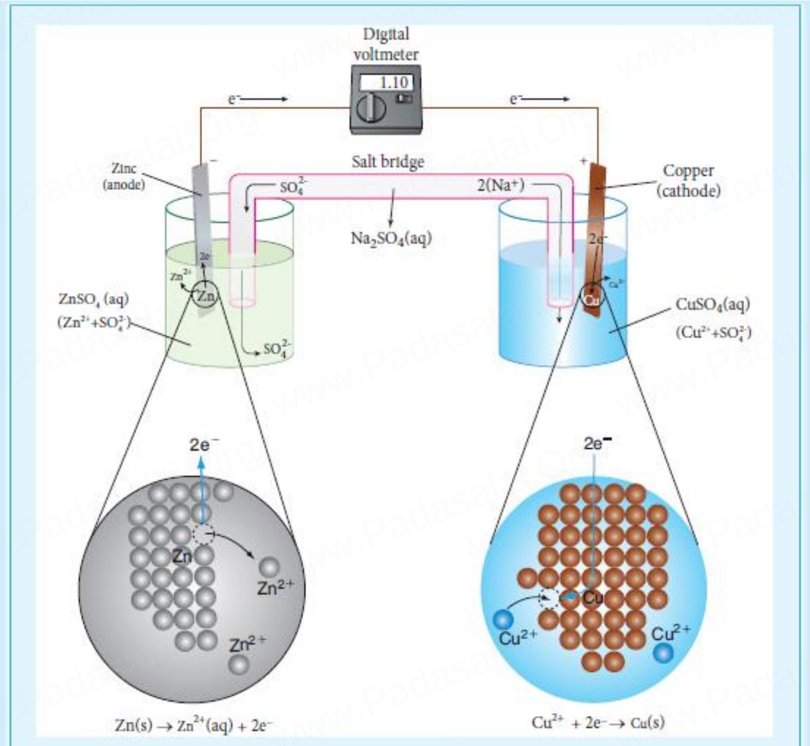
Cathodic reduction

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.

Cu^{2+} (aq) + $2e^-$ → Cu(S) (gain of electron - reduction)

Salt bridge

- The electrolytes present in two half cells are connected using a salt bridge.
- 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.



Daniel cell

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 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.

Daniel cell is represented as

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

7. Why is anode in galvanic cell considered to be negative and cathode positive electrode?

At anode, oxidation occurs and electrons are liberated. Hence it is negative (-ve). At cathode, reduction occurs and electrons are consumed. Hence it is positive (+ve).

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

$\lambda^{\circ}_{cation} = 248.2 \text{ S cm}^{2} \text{ mol}^{-1}$

$\lambda^{\circ}_{anion} = 51.8 \text{ S cm}^{2} \text{ mol}^{-1}$

Answer:

Given

$C = 0.01M$ $\lambda^{o}_{cation} = 248.2 \text{ S cm}^{2} \text{ mol}^{-1}$

$K = 1.5\times10^{-4} \text{ S cm}^{-1}$ $\lambda^{o}_{anion} = 51.8 \text{ S cm}^{2} \text{ mol}^{-1}$.

1. Molar conductivity

$$\Lambda^{\circ}_{m} = \frac{\mathbf{k}\ (\text{sm}^{-1})\times10^{-3}}{C\ (\text{in M})} \text{mol}^{-1} \text{ m}^{3} \qquad \mathbf{k} = 1.5\times10^{-4}\text{S cm}^{-1}$$

$$= \frac{1.5\times1\bar{0}^{2}\times10^{-3}}{0.01} \text{ S mol}^{-1} \text{ m}^{2} \qquad 1 \text{ cm}^{-1} = 10^{2}\text{m}^{-1}$$

$$= 1.5\times10^{-3} \text{ S m}^{2} \text{ mol}^{-1} \qquad = 1.5\times1\bar{0}^{2}$$

2. Degree of dissociation $\alpha = \dfrac{\Lambda^{\circ}}{\Lambda^{\circ}_{\infty}}$

$$\Lambda^{o}_{\infty} = \lambda^{o}_{cation} + \lambda^{o}_{anion}$$

$$= (248.2 + 51.8) \text{ S cm}^{2} \text{ mol}^{-1}$$

$$= 300 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$= 300\times10^{-4} \text{ s m}^{2} \text{ mol}^{-1}$$

$$\alpha = \frac{1.5\times10^{-3} \text{ S m}^{2} \text{ mol}^{-1}}{300\times10^{-4} \text{ S m}^{2} \text{ mol}^{-1}}$$

$$\alpha = 0.05$$

$$K_{a} = \frac{\alpha^{2}c}{1-\alpha}$$

$$= \frac{(0.05)^{2}(0.01)}{1-0.05}$$

$$= \frac{25\times10^{-4}\times10^{-2}}{95\times10^{-2}}$$

$$= 0.26\times10^{-4}$$

$$= 2.6\times10^{-5}.$$

9. Which of 0.1M HCl and 0.1 M KCl do you expect to have greater $\overset{0}{\Lambda}_{m}$ and why?

0.1M HCl have greater molar conductance when compared to 0.1M KCl.

(i) This is because, H^{+} ion in aqueous solution being smaller size than K^{+} ion, H^{+} ion have greater mobility than K^{+} ion.

(ii) When mobility of the ion increases, conductivity of that ions also increases.

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

⇨ specific conductance ∝ concentration

⇨ when concentration decreases, specific conductance also decrease.

⇨ ∴ decreasing order of specific conductance 0.5M KCl > 0.25M KCl > 0.1M KCl > 0.01M KCl > 0.005M KCl.

11. Why is AC current used instead of DC in measuring the electrolytic conductance?

- ⇨ 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.

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.

- ⇨ Specific conductance $k=\frac{1}{R}\frac{l}{A}$

  ∴ specific conductance ∝ cell constant
- ⇨ When cell constant value increases then specific conductance also increases.
- ⇨ ∴ The cell with cell constant value 0.5cm^{-1} 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 Cu2+ after electrolysis assuming volume to be constant and the current efficiency is 100%.

Answer:

Given

$I = 1.608A; t = 50 \text{ min} = 50 \times 60 = 3000S$

$\eta = 100\%$

$V = 250 \text{ mL}$

$C = 0.5 \text{ M}$

Calculate the number of faradays of electricity passed through the $CuSO_4$ solution

$\Rightarrow Q = It$

$Q = 1.608 \times 3000$

$Q = 4824C$

$\therefore$ number of Faradays of electicity $= \frac{4824 \text{ C}}{96500 \text{ C}} = 0.05F$

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 .

$\therefore$ 0.05F electicity will

deposit $\frac{1\text{mol}}{2F} \times 0.05F = 0.025 \text{ mol}$

Initial number of moles of Cu^{2+} in 250 ml of solution $= \frac{0.5}{1000 \text{ mL}} \times 250\text{mL}$

$= 0.125 \text{ mol}$

$\therefore$ number of moles of Cu^{2+} after electrolysis $= 0.125 - 0.025$

$= 0.1 \text{ mol}$

$\therefore$ Concentration of $Cu^{2+} = \frac{0.1 \text{ mol}}{250 \text{ mL}} \times 1000 \text{ mL}$

$= 0.4 \text{ M}$

14. Can Fe^{3+} oxidises bromide to bromine under standard conditions?

Given: $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.771$

$E^\circ_{Br_2|Br^-} = 1.09V.$

Answer:

Required half cell reaction

$$2\,Br^- \rightarrow Br_2 + 2e^- \qquad (E^o_{ox}) = -1.09V$$

$$2\,Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \qquad (E^o_{red}) = +0.771V$$

$$2Fe^{3+} + 2Br^- \rightarrow 2Fe^{2+} + Br_2 \qquad (E^o_{cell}) = ?$$

$$E^o_{cell} = (E^o_{ox}) + (E^o_{red})$$

$$= -1.09 + 0.771$$

$$= -0.319V$$

E°_{cell} is – ve; ΔG is +ve and the cell reaction is non spontaneous. Hence Fe^{3+} cannot oxidises Br^- to Br_2

15. 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 $E^\circ_{Fe^{2+}|Fe} = -0.44V$.

Answer:

$(E^o_{ox})_{Fe|Fe^{2+}} = 0.44V$ and $(E^o_{red})_{Cu^{2+}|Cu} = 0.34V$.

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. Two metals M1 and M2 have reduction potential values of -xV and +yV respectively. Which will liberate H_2 and H_2SO_4.

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 fromH_2 SO_4.

17. Reduction potential of two metals M_1 and M_2 are $E^\circ_{M_1^{2+}|M_1} = -2.3V$ and $E^\circ_{M_1^{2+}|M_2} = 0.2V$ $E^\circ_{Fe^{2+}|Fe} = -0.44V$ Predict which one is better for coating the surface of iron.

Answer:

Oxidation potential of M1 is more +ve than the oxidation potential of Fe which indicates that it will prevent iron from rusting.

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.

Answer:

Cell reactions:

Oxidation at anode: $Cd\,(s) \rightarrow Cd^{2+}\,(aq) + 2e^-$ $\qquad (E^o_{ox})_{Cd|Cd^{2+}} = 0.4V$

Reduction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu\,(s)$ $\qquad (E^o_{red})_{Cu^{2+}|Cu} = 0.34V$

$$Cd(s) + 2e^- \rightarrow Cd^{2+}(aq) + Cu(s)$$

$$\begin{aligned} E^{\circ}_{cell} &= (E^{\circ}_{ox}) + (E^{o}_{red})_{cathode} \\ &= 0.4 + 0.34 \\ &= 0.74V. \end{aligned}$$

emf is +ve, so ΔG is (-)ve, the reaction is feasible.

19. In fuel cell H2 and O2 react to produce electricity. In the process, H2 gas is oxidized at the anode and 2 O at cathode. If 44.8 litre of H2 at 25°C and 1atm pressure reacts in 10 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu2+ , how many grams of deposited?

Answer:

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°C and 1 atm pressure, 1 mole of hydrogen gas occupies = 22.4 litres

$$\therefore \text{ no. of moles of hydrogen gas produced} = \frac{1\text{ mole}}{22.4\text{ litres}} \times 44.8\text{ litres}$$

$$= 2\text{ moles of hydrogen}$$

∴ 2 of moles of hydrogen produces 4 moles of electro 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 A

Electro deposition of copper

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

2F charge is required to deposit

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 2x 63.5 i.e., 127.0 g copper will be deposited at cathode.

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 52gm^{-1} respectively.

Answer:

$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni\ (s)$

$Cr^{2+}(aq)+3e^{-} \rightarrow Cr\ (s)$

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

$$\therefore \text{The amount of charge passed through the cell} = \frac{2F}{58.7g} \times 2.935g$$

$$= 0.1F$$

$\therefore$ if 0.1F charge is passed through chromium nitrate the amount of chromium deposited

$$= \frac{52g}{3F} \times 0.1F$$

$$= 1.733g$$

21. A copper electrode is dipped in 0.1M copper sulphate solution at $25^{\circ}C$. Calculate the electrode potential of copper. [Given: $E^{\circ}_{Cu^{2+}|Cu} = 0.34$].

Given that

$[Cu^{2+}] = 0.1M$

$E^{\circ}_{Cu^{2+}|Cu} = 0.34$

$E_{cell} = ?$

Cell reaction is

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

$$E_{cell} = E^{o} - \frac{0.0591}{n} \log \frac{[Cu]}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$= 0.34 - 0.0296$$

$$= 0.31V$$

22. For the cell $Mg\ (s)|Mg^{2+}(aq)\|Ag^{+}(aq)|Ag\ (s)$, calculate the equilibrium constant at $25^{\circ}C$ and maximum work that can be obtained during operation of cell. Given : $E^{\circ}_{Mg^{2+}|Mg} = -2.37V$ and $E^{\circ}_{Ag^{2+}|Ag} = 0.80V$.

Answer:

oxidation at anode

$$Mg \longrightarrow mg^{2+} + 2e^{-} \ldots\ldots\ldots\ldots(1) \quad \left(E^{\circ}_{ox}\right) = 2.37V$$

Reduction at cathode

$$Ag^{+} + e^{-} \rightarrow Ag \ldots\ldots\ldots\ (2) \qquad \left(E^{\circ}_{red}\right) = 0.80V$$

$$\therefore\ E^{\circ}_{cell} = \left(E^{\circ}_{ox}\right)_{anode} + \left(E^{\circ}_{red}\right)_{cathode}$$

$$= 2.37 + 0.80$$

$$= 3.17V$$

Overall reaction

$$\text{Equation } (1) + 2 \times \text{equation } (2) \Rightarrow$$

$$Mg + 2Ag^{2+} \longrightarrow Mg^{2+} + 2Ag$$

$$\Delta G^{\circ} = -nfE^{\circ}$$

$$= -2 \times 96500 \times 3.17$$

$$= 611.810\ J$$

$$\Delta G^{\circ} = -6.12 \times 10^{5}\ J$$

$$W = 6.12 \times 10^{5}\ J$$

$$\Delta G^{\circ} = -2.803\ RT \log^{K}C$$

$$\Rightarrow \log K_{c} = \frac{6.12 \times 10^{5}}{2.803 \times 8.314 \times 298}$$

$$K_{c} = \text{Antilog of } (107.2)$$

23. 8.2 x 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 x 10^{6} Cs^{-1} at an appropriate voltage. How many years would it like to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.

Hydrolysis of water

At anode:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \text{........}(1)$$

At cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Overall reaction $6H_2O \rightarrow 4H^+ + 4OH^- + 2H_2 + O_2$

(or)

Equation (1) +(2) ×2 $\Rightarrow$ $2H_2O \rightarrow 2H_2 + O_2$

$\therefore$ According to faradays Law of electrolysis, to electrolyse two mole of Water $(36g \simeq 36 \text{ mL of } H_2O)$, 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 $\dfrac{4 \times 96500 \text{ C}}{36 \text{ mL}} \times 9 \times 10^{12} \text{ L}$

$$= \frac{4 \times 96500 \times 9 \times 10^{12}}{36 \times 10^{-3}} \text{C}$$

$$= 96500 \times 10^{15} \text{ C}$$

$\therefore$ Given that in 1 second, 2×10^6 C is generated therefore, the time required to generate

$$96500 \times 10^{15} \text{ C is } = \frac{1 \text{ S}}{2 \times 10^6 \text{C}} \times 96500 \times 10^{15} \text{C}$$

$$= 48250 \times 10^9 \text{ S}$$

$\therefore$ 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 × 24 hours

= 365 × 24 × 60 min

= 365 × 24 × 60 × 60 sec.

24. Derive an expression for 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,

$$xA + yB \rightleftharpoons lC + mD$$

Reaction Quotient,

$$Q = \frac{[C]^l\ [D]^m}{[A]^x\ [B]^y} \quad \text{.....(1)}$$

We have already learnt that,

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{.....(2)}$$

$$\Delta G = -nFE_{cell} \quad ; \Delta G^\circ = -nFE^\circ_{cell} \quad \text{.....(3)}$$

Subsitute (1) and (3) in eqution (2)

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln\frac{[C]^l[D]^m}{[A]^x\ [B]^y} \quad \text{.....(4)}$$

Divide equation (4) by (-nF)

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^l[D]^m}{[A]^x\ [B]^y}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^l[D]^m}{[A]^x\ [B]^y} \quad \text{.....(5)}$$

Equation (5) is called Nernst equation

$$\left[\begin{array}{l} \therefore\ R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ T = 298 \text{ K.} \\ 1 \text{ F} = 96500 \text{ C mol}^{-1} \end{array}\right]$$ **Substitute these values in equation (5)**

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[C]^l[D]^m}{[A]^x\ [B]^y}$$

25. Write a note on sacrificial protection.

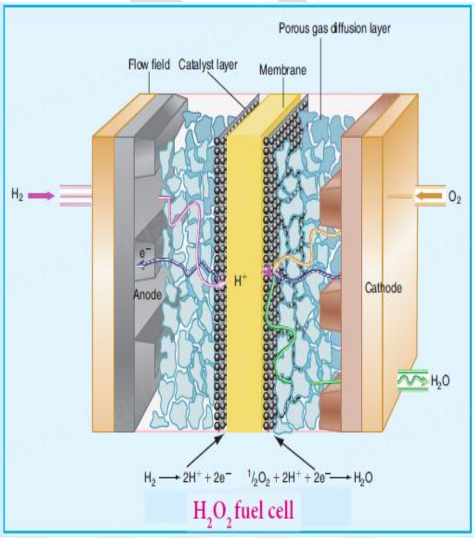
In this technique, unlike galvanising the entire surface of the metal to be protected need not be covered with a protecting metal. Instead, metals such as Mg or zinc which is corroded more easily than iron can be used as a sacrificial anode and the iron material acts as a cathode. So iron is protected,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

26. Explain the function of H_2–O_2 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 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 200oCand 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.



H_2O_2 fuel cell

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 - O 2 2 fuel cell. Other fuel cells like propane –O2 and methane O2 have also been developed.

27. Ionic conductance at infinite dilution of Al^{3+} and $SO4^{2-}$ 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.

Equivalent conductance

$$(\Lambda_{\propto})\ Al_2(SO_4)_3 = \frac{1}{3}(\lambda_\infty)\ Al^{3+} + \frac{1}{2}(\lambda_\infty)\ SO_4^{2-}$$
$$= \frac{189}{3} + \frac{160}{2}$$
$$= 63+80$$
$$= 143 \text{ mho } cm^2\ (g\ equiv)^{-1}$$

Molar conductance

$$(\Lambda^\circ_M)\ Al_2(SO_4)_3 = 2((\lambda^\circ_m)Al^{3+} + 3\ (\lambda^\circ_m)\ SO_4^{2-}$$
$$= (2 \times 189) + (3 \times 160)$$
$$= 378 + 480$$
$$= 858 \text{ mho } cm^2 \text{ mole}^{-1}$$

II. Evaluate yourself.

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

Given

$C = 0.01M$

$k = 14.114 \text{ X } 10^{-2} \text{ sm}^{-1}$

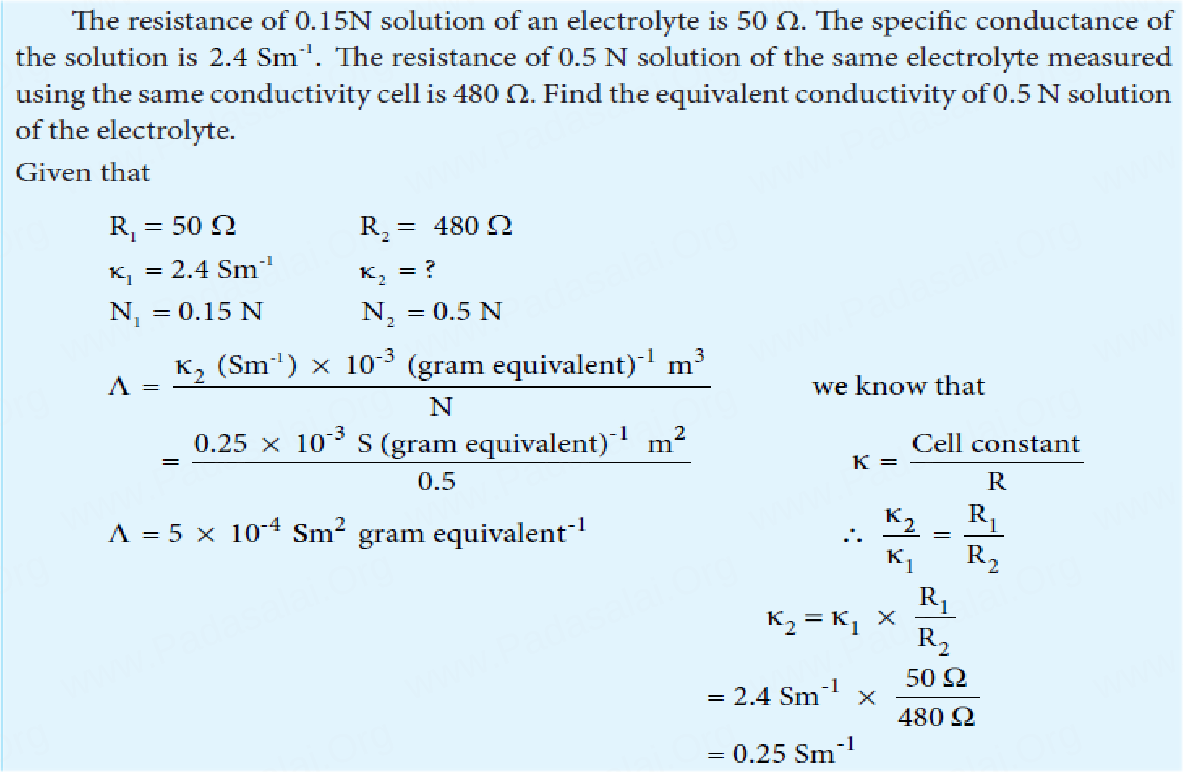
$\Lambda_m = ?$

$$\Lambda_m = \frac{K \, X \, 10^{-3}}{M} sm^{-1}mol^{-1}m^3$$

$$= \frac{14.11 \, X \, 10^{-2} X 10^{-3}}{0.01} sm^{-1}mol^{-1}m^3$$

$$= \frac{14.11 \, X \, 10^{-2} X 10^{-3}}{10^{-2}}$$

$$\Lambda_m = 14.114 \, X \, 10^{-3} sm^2 mol^{-1}$$

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

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

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

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

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

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

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

we know that

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

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

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

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

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

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

Pt (s) | H_2 (g, 1atm) | H^+(aq, 1M) || Cu^{2+} (aq1M) |Cu (s)

$$E^\circ_{cell} = 0.34V$$

$$E^\circ_{ox} H_2/H^+ = 0V$$

$$E^\circ_{red} Cu^{2+}/Cu = ?$$

$$E^\circ_{cell} = E^\circ_{ox} H_2/H^+ + E^\circ_{red} Cu^{2+}/Cu$$

$$0.34 = 0 + E^\circ_{red} Cu^{2+}/Cu$$

$$\therefore E^\circ_{red} Cu^{2+}/Cu = 0.34V$$

4. Using the calculated emf value of zinc and copper electrode, calculate the emf of the following cell at 25°C .
Zn (s) | Zn^{2+} (aq, 1M) || Cu^{2+}(aq, 1M) | Cu (s)

$$E^\circ_{cell} = ?$$

$$(E^\circ_{ox})Zn/Zn^{2+} = 0.26V$$

$$E^\circ_{red}Cu^{2+}/Cu = 0.34$$

$$E^\circ_{cell} = (E^\circ_{ox})Zn/Zn^{2+} + E^\circ_{red}Cu^{2+}/Cu$$

$$= 0.76 + 0.34$$

$$E^\circ_{cell} = 1.1V$$

5. Write the overall redox reaction which takes place in the galvanic cell,
Pt(s) | Fe^{2+}(aq) || Fe^{3+}(aq) MnO (aq), H (aq),Mn (aq) | Pt(s)

Oxidation half cell reaction:

$Fe^{2+} \rightarrow Fe^{-3} + e^-$ …..(1)

Reduction half cell reaction

$MnO_4^- \rightarrow Mn^{2+}$

Add 4H_2O to R.H.S

$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

Add 8H_2O L.H.S

$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

For balance charge add 5e^- to L.H.S

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ……(2)

Multiply equation (1) X 5

$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$ …….(3)

Add (2) + (3)

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

6. The electrochemical cell reaction of the Daniel cell:
Zn (s) + Cu^{2+}(aq) → Zn^{2+}(aq)+Cu (s)

At anode : $Zn_{(s)} \rightarrow Zn^{2+} + 2^{2e-} (oxdiation)$

At cathode : $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\ (reduction)$

n =2

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} log \frac{Zn^{2+}}{Cu^{2+}}$$

Activity of metals =1

So neglected.

$$[Zn^{2+}] = [Cu^{2+}] = 1M$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} log \frac{1}{1}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{2} X\ 0$$

$$E_{cell} = E^{\circ}$$

When anode compartment increased by a factor of 10.

$$E_{cell} = E^{\circ} - \frac{0.0591}{2} log \frac{10}{1}$$

$$E_{cell} = E^{\circ} - 0.02955\ X\ 1$$

∴ Cell voltage decrease by 0.02955V.

7. **A solution of salt of metal was electrolysed for 150 minutes with a current of 0.15 amperes. The mass of metal deposited at the cathode is 0.783g. calculate the equivalent mass of the metal.**

t = 150 min = 150 X 60 sec

I=0.15 amperes

m=0.783g

Faraday's First law,

m=Zit

m= $\frac{eq.mass}{F}\ X\ I\ X\ t$

equivalent mass = $\frac{m\ X\ F}{I\ X\ F}$

$$= \frac{0.783\ X\ 96500}{0.15\ X\ 150\ X\ 60}$$

$$= \frac{75559.5}{1350}$$

=55.97 g.equv^{-1}

Additional Questions:

1. **Check the feasibility of the following redox reaction with the help of electrochemical series.**

$$Ni_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Ni^{2+} + 2Ag_{(s)}$$

The E° value of Ni^{2+}/Ni is -0.25V while that of Ag^{+} / Ag is +0.80V. This means that nickel is placed below silver in the series and can easily reduce Ag^{+} ions to silver by releasing electrons. The redox reaction is therefore, feasible.

2. **Rusting of iron becomes quicker in saline medium. Explain.**

Saline medium has extra salts such as sodium chloride dissolved in water. This means that it has a greater concentration of electrolyte than ordinary medium. The ions present will favour the formation of more electrochemical cells and will thus promote rusting or corrosion.

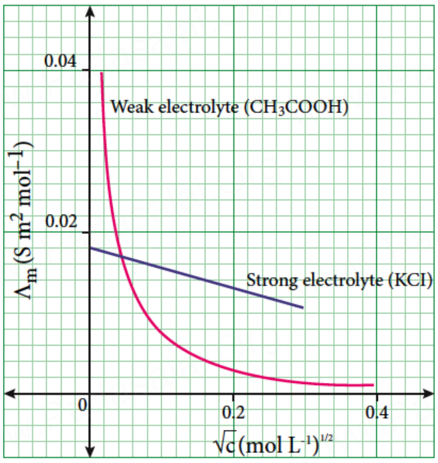
3. **Explain the factors affecting electrolytic conductance.**

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

- 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.

4. Explain the variation of molar conductivity with concentration.



- The molar reconductance of an electrolytic solution increases with dilution.
- The relationship between the molar conductance and the concentration is given by

$$\Lambda_m = \Lambda^\circ m \ - \ k\sqrt{C}$$

- The plot of Λ_m Vs C gives a straight line with a negative slope.
- The slope value is –k and the intercept is Λ° m
- For strong electrolytes it gives a straight line.
- For weak electrolytes it gives a non linear curve.

Variation of molar conductance of strong electrolytes with concentration

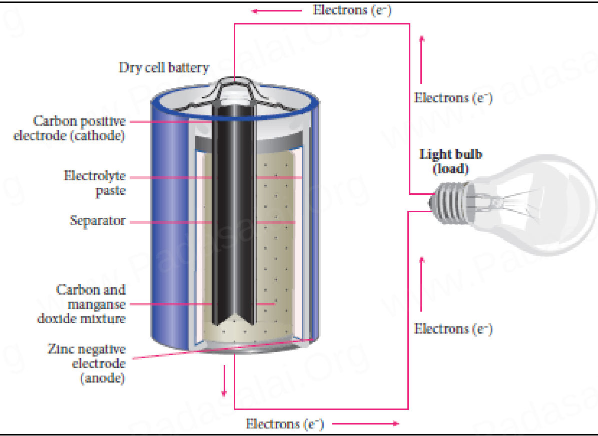
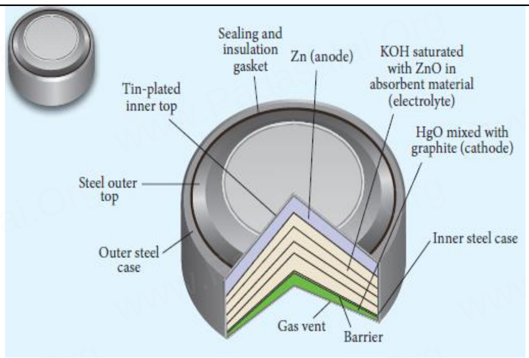
- For a strong electrolyte, at high concentration, the number of ions at a given volume is very high.
- The force of attraction between the ions is also very high.
- Viscous drag is very high.
- Hence molar conductance decrease at high concentration.
- But on dilution the molar conductance increase.
- On dilution the ions are far apart and the force of attraction between the ions decrease.

Various of molar conductance of weak electrolytes with concentration.

- For the weak electrolytes when the concentrations approaches zero, there is a sudden increase in the molar conductance and curve becomes parallel to the axis.
- On dilution the dissociation of the weak electrolyte increases.

5. Explain the construction of Leclanche cell and Mercury button cell.

	Leclanche Cell	**Mercury button Cell**
Anode	Zinc container	Zinc amalgamated with mercury.
Cathode	Graphite rod in contact with MnO_2	HgO mixed with graphite.
Electrolyte	Ammonium chloride and zinc chloride in water	Paste of KOH and ZnO
Emf of the cell	1.5 V	1.35 V
Cell reaction oxidation at anode.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Zn^\circ(s) + 2OH^-(aq) \rightarrow ZnO + H_2O(l) + 2^{e-}$
Reduction at cathode	$2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(aq) + H_{2(g)}$ H_2 gas is oxidized to H_2O by MnO_2. $H_2(g) + 2MnO_2(s) \rightarrow Mn_2O_3(s) + H_2O(l)$	$HgO(s) + H_2O(l) + 2^{e-} \rightarrow Hg(l) + 2OH^-(aq)$
Overall redox reaction	$Zn(s) + 2NH_4^+(aq) + 2MnO_2(S) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l) + 2NH_3$	$Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

6. **Explain the cell reactions of lead storage battery and Lithium –ion battery.**

	Lead storage battery	**Lithium – ion battery**
Anode	Spongy lead	Porous graphite.
Cathode	Lead plate bearing pbO_2	Transition metal oxide such as CoO_2
Electrolyte	38% by mass of H_2SO_4 with density 1.2g / mL.	Lithium salt in an organic solvent.
Oxidation occurs at anode	$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$.....(1) The Pb^{2+} ions combine with SO_4^{-2} from sulphuric acid to form $PbSO_4$ precipitate. $Pb^{2+}(aq) + SO_4^{2-}(aq) + \rightarrow PbSO_4(s)$.....(2)	$Li^+(s) \rightarrow Li^+(aq) + e^-$
Reduction at cathode	$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$ ......(3) The Pb^{2+} ions combine with SO_4^{-2} from sulphuric acid to form $PbSO_4$ precipitate. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4$.........(4)	$Li^+ + CoO_2(s) + e^- \rightarrow Li\,CoO_2(s)$
Overall reaction	Equation (1)+(2)+(3)+(4) $Pb_{(s)} + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-} \rightarrow 2PbSO_4(s) + 2H_2O(l)$	$Li(s) + CoO_2 \rightarrow Li\,CoO_2(s)$

7. **What is electro chemical series? Give its significance.**

The standard aqueous electrode potential at 298K for various metal - metal ion electrodes are arranged in the decreasing order of their standard reduction potential values. This series is called electrochemical series.

- The standard reduction potential (E)° is a measure of the oxidizing 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.

<u>Other Additional questions:</u>

1. The blue colour of copper sulphate solution is slowly discharged when a rode of zink is dipped in it. Explain.
2. Why is standard hydrogen electrode called reversible electrode?
3. Define molar conductance (Λ_m).

4. How will you measure the conductivity of ionic solution by using wheat stone bridge circuit?
5. Write Debye – Huckel and Onsagar equation.
6. How will you measure single electrode potential?
7. How will you relate emf with Gibb's free energy?
8. Give IUPAC definition for the following
   (i) Electrode potential (ii) Standard electrode potential
9. Explain the electrochemical mechanism of corrosion.
10. Name some process to protect metals from corrosion.
11. Define equivalent conductance.

UNIT 10 SURFACE CHEMISTRY

I. Text Book Questions:

1. Give two important characteristics of physisorption.

- ⇨ Physisorption decreases with increase in temperature.
- ⇨ In physisorption multilayer of the adsorbate is formed on the adsorbent.

2. Differentiate physisorption and chemisorption.

S.No	Chemical adsorption (Activated adsorption)	Physical adsorption (van der waals adsorption)
1	It is very slow.	It occurs immediately.
2	It is very specific depends on nature of adsorbent and adsorbate.	It is non-specific
3	Chemical adsorption is fast with increase pressure, it can not alter the amount.	In Physisorption, when pressure increases the extent of adsorption increases.
4	When temperature is raised chemisorption first increases and then decreases.	Physisorption decreases with increase in temperature.
5	Chemisorption involves transfer of electrons between the adsorbent and adsorbate.	No transfer of electrons
6	Heat of adsorption is high i.e., from 40-400KJ/mole.	Heat of adsorption is low in the order of 40kJ/mole.
7	Monolayer of the adsorbate is formed.	Multilayer of the adsorbate is formed on the adsorbent.
8	Adsorption occurs at fixed sites called active centres. It depends on surface area	It occurs on all sides.
9	Chemisorption involves the formation of activated complex with appreciable activation energy.	Activation energy is insignificant.

3. In case of chemisorption, why adsorption first increases and then decreases with temperature?

In chemisorption, adsorption first increases with rise in temperature due to the 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.

4. **Which will be adsorbed more readily on the surface of charcoal and why? NH_3 or CO_2?**

⇨ Gases with high critical temperature are adsorbed readily.

⇨ Critical temperature of ammonia (406K) is higher than the critical temperature of carbondioxide (304K). Hence ammonia (NH_3) will be adsorbed more readily on the surface of charcoal.

5. **Heat of adsorption is greater for chemisorptions than physisorption. Why?**

In chemical adsorption, gas molecules are held to the surface by formation of strong chemical bonds and hence heat of adsorption is high.

In physical adsorption, weak physical forces such as Vander Waals force of attraction, dipole-dipole interaction etc exist between adsorbent and adsorbate and hence heat of adsorption is low.

6. **In a coagulation experiment 10 mL of a colloid (X) is mixed with distilled water and 0.1M solution of an electrolyte AB so that the volume is 20 mL. It was found that all solutions containing more than 6.6 mL of AB coagulate within 5 minutes. What is the flocculation values of AB for sol (X)?**

Flocculation value is the minimum concentration of an electrolyte millimoles/lit required to cause precipitation of a sol in 2 hrs.

20 ml of sol (x) contains 0.1 mole of AB (electrolyte)

6.6ml of sol (x) contains $\frac{0.1 \times 6.6}{20}$ = 0.33 moles of AB

33 millimoles of AB(electrolyte)is required for coagulating 1litre of electrolyte sol(x)

Floculation value of AB for sol(x) = 33

[I mole = 1000 millimoles]

7. **Peptising agent is added to convert precipitate into colloidal solution. Explain with anexample.**

Due to common ion effect, when peptising or dispersing agent like HCl is added to AgCl precipitate, Cl^- ion is adsorbed on the precipitate and it is converted into colloidal solution.

$$\underset{\text{(Precipitate)}}{AgCl} \xrightarrow{HCl} \underset{\text{(Colloid)}}{AgCl}$$

8. What happens when a colloidal sol of Fe(OH)3 and As2O3 are mixed?

When colloidal sols with opposite charges are mixed mutual coagulation takes place. It is due to migration of ions form the surface of the particles.

When positively charged $Fe(OH)_3$ colloid is mixed with negativity charged As_2O_3 colloid mutual coagulation takes place.

9. What is the difference between a sol and a gel?

Sol is a colloidal solution of solid in liquid. Eg: Ink, Paint.

Gel is a colloidal solution of liquid in solid. Eg: Butter, Cheese.

10. Why are lyophillic colloidal sols are more stable than lyophobic colloidal sols?

- ⇨ In lyophillic colloidal sols , definite attractive force exists between dispersion medium and dispersed phase. E.g: sols of starch.
- ⇨ In lyophobic colloidal sols, no attractive force exists between the dispersed phase and dispersion medium. E.g: sols of gold , silver.
- ⇨ Hence, lyophillic colloidal sols are more stable than lyophobic colloidal sol.

11. Addition of Alum purifies water. Why?

Water containing suspended impurities are negatively charged. The Al^{3+} was present in alum coagulates the suspended impurities in water purifies water.

12. What are the factors which influence the adsorption of a gas on a solid?

The factors which influence the adsorption of a gas on a solid are

i) Nature of adsorbent ii) Nature of adsorbate

iii) Pressure iv) concentration at a given temperature. v) Temperature.

13. What are enzymes? Write a brief note on the mechanism of enzyme catalysis.

Enzymes are complex protein molecules with three dimensional structures. They catalyse the chemical reaction in living organisms. They are often present in colloidal state and extremely specific in catalytic action.

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.

14. What do you mean by activity and selectivity of catalyst?

Activity :

- ⇨ Ability of a catalyst to alter the rate of a reaction is called activity of catalyst
- ⇨ Ability of a catalyst depends on chemisorption.

Selectivity:

- ⇨ Ability of a catalyst to catalyse a specific reaction to form particular products is selectivity of a catalyst.

e.g: $CO_{(g)} + 3H_{2\,(g)} \xrightarrow{Ni} CH_4 + H_2O$

$CO_{(g)} + H_{2\,(g)} \xrightarrow{Cu} HCHO$

15. Describe some feature of catalysis by Zeolites.

i) Zeolites are microporous, crystalline, hydrated alumino silicates.
ii) They are made of silicon and aluminium tetrahedron.
iii) There are about 50 natural zeolites and 150 synthetic zeolites.
iv) As silicon is tetravalent and aluminum is trivalent, the zeolite matrix carries extra negative charge.
v) To balance the negative charge, there are extra framework cations for example, H^+ or Na^+ ions.
vi) Zeolites carrying protons are used as solid acids and in catalysis.
vii) They are extensively used in the petrochemical industry for cracking heavy hydrocarbon fractions into gasoline, diesel, etc.,
viii) Zeolites carrying Na^+ ions are used as basic catalysis.
ix) One of the most important applications of zeolite is their shape selectivity.
x) 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 with in 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.

16. Give three uses of emulsions.

Food:

Food stuffs like milk, cream, butter, etc are present in colloidal form.

In washing:

The cleansing action of soap is due to the formation of emulsion of soap molecules with dirt and grease.

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.

17. Why does bleeding stop by rubbing moist alum?

Ions present in moist alum (peptizing agent) neutralizes the colloidal protein present in blood and coagulate it. Due to coagulation of blood, bleeding stops by rubbing with moist alum.

18. Why is desorption important for a substance to act as good catalyst?

To create free surface on the catalyst for more reactants to adsorb and react, the products already formed on the surface of the catalyst should be desorbed.

Hence desorption is important for a substance to act as a good catalyst.

19. Comment on the statement: Colloid is not a substance but it is a state of substance.

- ⇨ Any substance can be converted into a colloid by reducing its particle size between 1nm and 200 nm.
- ⇨ Hence we can say that colloid is not a substance but it is a state of the substance, which is dependent on the size of the particle.
- ⇨ A colloidal state is intermediate between a true solution and suspension.

20. Explain any one method for coagulation

The flocculation and settling down of the sol particles is called coagulation.

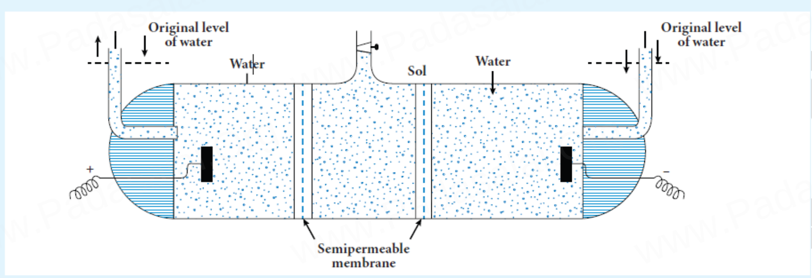
Electrophoresis is a method used for coagulation.

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.

21. Write a note on 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.



22. Write a note on catalytic poison.

Certain substances when added to a catalysed reaction either decreases or completely destroys the activity of a catalyst and they are often known as catalytic poisons.

$$2SO_{2(g)} + O_2 \xrightarrow[As_2O_3]{Pt} 2SO_{3(g)}$$

In this reaction,

Catalyst - Pt
Catalytic poison – As_2O_3.

23. Explain intermediate compound formation theory of catalysis with an example.

- 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 → AB ….. (1)
A+C → AC (intermediate) ……(2)
(where **C** is the catalyst)
AC+B → AB+ C (catalyst) …….(3)

Activation energies for the reactions (2) and (3) are lowered compared to that of (1). Hence the formation and decomposition of the intermediate accelerate the rate of the reaction.

Example:

$H_2 + \frac{1}{2}O_2 \xrightarrow{Cu} H_2O$ .....(1)

$2Cu + \frac{1}{2}O_2 \rightarrow Cu_2O$ (Intermediate) ......(2)

$Cu_2O + H_2 \rightarrow H_2O + 2Cu$ (Catalyst) ......(3)

This theory describes, (i) the specificity of a catalyst and (ii) the increase in the rate of the reaction with increase in concentration of a catalyst.

24. What is the difference between homogenous and heterogenous catalysis?

s.no	Homogenous catalysis	Heterogeneous catalysis
1	In a homogenous catalysed reaction, the reactants, products and catalyst are present in the same phase.	In a heterogeneous catalysis the catalyst is present in a different phase ie, it is not present in the same phase as that of reactants or products. It is also referred as contact catalysis.
2	$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$ In this reaction, all the reactants, catalyst and the products are in gaseous phase.	$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt_{(s)}} 2SO_{3(g)}$ In this reaction the catalyst (Pt) is in solid phase, where as the reactants and the product are in gaseous phase.

25. Describe adsorption theory of catalysis.

Adsorption theory explains the action of catalyst in heterogeneous catalysis. It 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 the bulk to the catalyst surface.
2. The reactant molecules are adsorbed on the surface of the catalyst.
3. The adsorbed reactant molecules are activated to form activated complex, which is decomposed to form the products.
4. The product molecules are desorbed.
5. The products diffuse away from the surface of the catalyst.

Additional questions:

1. Distinguish between adsorption and absorption.

S.no	Adsorption	Absorption
1	Adsorption is a surface phenomenon.	Absorption is a bulk phenomenon.
2	Adsorbate molecules are adsorbed on the surface of the adsorbent.	Adsorbate molecules are distributed throughout the adsorbent.
3	Adsorption is a quick process.	Absorption is a slow process.

2. What is called positive adsorption and negative adsorption.

- 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.

3. Give the characteristics of adsorption.

i) 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.

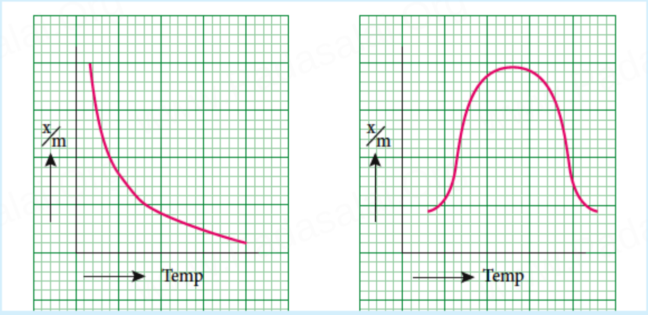
ii) Adsorption is a spontaneous process and it is always accompanied by decrease in free energy. When Δ G reaches zero, the equilibrium is attained.

iii) When molecules are adsorbed, there is always a decrease in randomness of the molecules.

4. What is called Adsorption isobar? Give an account on adsorption isobars of physisorption and chemisorption.

A plot of "amount of adsorption" versus temperature at constant pressure is called adsorption isobar.

Physical Adsorption Chemical Adsorption



x is the amount of adsorbate adsorbed on 'm' g of adsorbent.

- In physical adsorption, $\frac{x}{m}$ decreases with increase in Temperature.
- In chemical adsorption, $\frac{x}{m}$ increases with rise in temperature and then decreases.
- The increase of $\frac{x}{m}$ with rise in temperature is due to the 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.

5. What are called adsorption isotherms?

A plot between the amount of adsorbate adsorbed and pressure (or concentration of adsorbate) at constant temperature is called adsorption isotherms.

6. Write note on Freundlich adorption isotherm.

According to Freundlich,

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

For adsorption of gases in solutions, with 'C' as concentration.

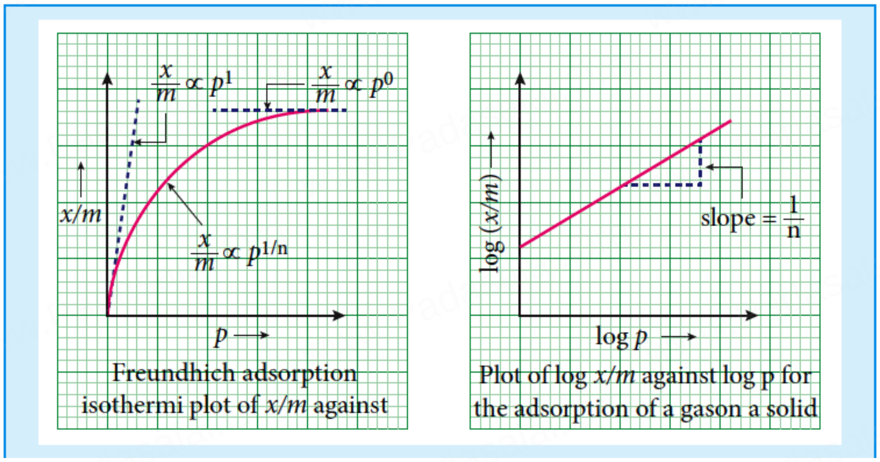
$$\frac{x}{m} = KC^{\frac{1}{n}}$$

where 'x' is the amount of adsorbate adsorbed on 'm' gm of adsorbent at a pressure of 'p'. K and n are constants.

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

Plot of log x/m against log p for the adsorption of a gason a solid

$\log\frac{x}{m}$ vs log p **graph**

7. Give the limitations of Freundlich adsorption isotherm.

- ⇨ Freundlich equation, $\frac{x}{m} = kp^{\frac{1}{n}}$ is purely empirical and valid over a limited pressure range.
- ⇨ The values of constants k and n are found vary with temperature.
- ⇨ No theoretical explanation were given.

8. How is principle of adsorption employed in the softening of hard water using permutit?

- ⇨ Permutit is employed in the process of softening of hard water.
- ⇨ Permutit adsorbs Ca^{2+} and Mg^{2+} ions present in hard water on its surface.
- ⇨ An ion exchange as shown below, occurs on the surface of Permutit
  $Na_2Al_2Si_4O_{12}+CaCl_2 \rightarrow CaAl_2Si_4O_{12} + 2NaCl$
- ⇨ Exhausted permutit is regenerated by adding a solution of common salt.
  $CaAl_2Si_4O_{12}+2NaCl \rightarrow Na_2Al_2Si_4O_{12}+CaCl_2$ (permutit)

9. Give an account on ion exchange resins.

(or)

Explain demineralization of water using ion exchange resins.

- ⇨ Ion exchange resins are working only based on the process of adsorption.
- ⇨ Ion exchange resins are used to demineralise water.
- ⇨ Water is passed through two columns of cation and anion exchange resins.

$$2RSO_3H + Ca^{2+} \rightarrow (RSO_3)_2Ca + 2H^+$$

Resin minerals in water Resin with mineral

$$R_4N^+OH^- + Cl^- \rightarrow R_4N^+Cl^- + OH^-$$

Resin mineral in water Resin with mineral

10. How is Vanaspathi obtained?

Hydrogenation of vegetable oil in presence of Nickel catalyst gives Vanaspathi.

$$vegetable\ oil + H_2 \xrightarrow[473K]{\text{Ni catalyst}} \text{Vanaspathi}$$

11. Define catalyst.

Catalyst is defined as a substance which alters the rate of chemical reaction without itself undergoing any chemical change.

12. What are positive and negative catalysis?

Positive catalysis is a process in which, the rate of a reaction is increased by the presence of catalyst.

$$H_2O_2 \overset{Pt}{\rightarrow} H_2O + \frac{1}{2}O_2$$

Negative catalysis is a process in which, the rate of reaction is decreased by the presence of a catalyst.

$$H_2O_2 \xrightarrow{glycerine} H_2O + \frac{1}{2}O_2$$

13. Give the characteristics of catalysts.

i) For a chemical reaction, catalyst is needed in very small quantity. Generally, a pinch of catalyst is enough for a reaction in bulk.

ii) There may be some physical changes, but the catalyst remains unchanged in mass and chemical composition in a chemical reaction.

iii) A catalyst itself cannot initiate a reaction. It means it cannot start a reaction which is not taking place. But, if the reaction is taking place in a slow rate it can increase its rate.

iv) A solid catalyst will be more effective if it is taken in a finely divided form.

v) A catalyst can catalyse a particular type of reaction, hence they are said to be specific in nature.

vi) 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.

vii) A catalyst is highly effective at a particular temperature called as optimum temperature.

viii) Presence of a catalyst generally does not change the nature of products

For example. $2SO_2 + O_2 \overset{Pt}{\rightarrow} 2SO_3$

This reaction is slow in the absence of a catalyst, but fast in the presence of Pt catalyst.

14. What are promoters?

In a catalysed reaction the presence of a certain substance increases the activity of a catalyst. Such a substance is called a promoter.

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

In Haber's process, the activity of the iron catalyst is increased by the presence of molybdenum. Hence molybdenum is called a promoter.

15. Illustrate auto catalysis(or) Ester hydrolysis reaction is slow in the beginning and becomes faster after sometime. Give reason.

In certain reactions one of the products formed acts as a catalyst to the reaction. Initially the rate of the reaction will be very slow but with the increase in time the rate of the reaction increases. Such reactions are called auto catalysis.

e.g: $CH_3\,COOC_2\,H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

In this reaction acetic acid acts as auto catalyst.

16. Give the limitations of intermediate compound formation theory.

i) The intermediate compound theory fails to explain the action of catalytic poison and promoters.

ii) This theory is unable to explain the mechanism of heterogeneous catalysed reactions.

17. Write notes on active centers.

- The surface of a catalyst is not smooth.
- It bears steps, cracks and corners.
- 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.
- The presence of such active centres increases the rate of reaction by adsorbing and activating the reactants.

18. Explain active centers on the basis of adsorption theory.

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.

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.

19. Give three examples for Enzyme catalysis.

i) The enzyme diastase, hydrolyses starch into maltose

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{diastase} nC_{12}H_{22}O_{11}$$

ii) The enzyme micoderma aceti oxidises alcohol into acetic acid.

$C_2H_5OH+O_2 \xrightarrow{micoderma\ aceti} CH_3COOH+H_2O$

iii) The enzyme urease, present in soya beans hydrolyses the urea.

$NH_2\text{-}CO\text{-}NH_2+H_2O \xrightarrow{urease} 2NH_3+CO_2$

20. Explain the general characteristics of enzyme catalysed reactions.

i) Effective and efficient conversion is the special characteristic of enzyme catalysed reactions.

An enzyme may transform a million molecules of reactant in a minute.

ii) Enzyme catalysis is highly specific in nature.

iii) Enzyme catalysed reaction has maximum rate at optimum temperature.

iv) The rate of enzyme catalysed reactions varies with the pH of the system. The rate is maximum at a pH called optimum pH.

v) Enzymes can be inhibited. Activity of an enzyme is decreased and destroyed by a poison.

Example: Penicillin inhibits the action of bacteria and used for curing diseases like pneumonia and other infectious diseases.

vi) Catalytic activity of enzymes is increased by coenzymes or activators.

A small non protein (vitamin) called a coenzyme promotes the catalytic activity of enzyme.

21. Describe phase transfer catalysis.

- ⇨ If the reactants of a reaction are present in two different solvents which are immiscible, then the reaction between them is very slow.
- ⇨ As the solvents form separate phases, the reactants have to migrate across the boundary to react. But it is not easy.
- ⇨ For such situations a third solvent is added which is miscible with both and hence phase boundary is eliminated, reactants freely mix and react fast.
- ⇨ For large scale production of any product, use of a third solvent is not convenient as it may be expensive.
- ⇨ Phase transfer catalysis provides a solution for it.
- ⇨ Phase transfer catalysis 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.

R – Cl	+	NaCN	→	R – CN	+	NaCl
Organic phase		Aquous phase		Organic phase		Aquous phase

Where, R – Cl is 1 – Chlorooctane
R – CN is 1- Cyanooctane

- By direct heating of organic 1-chlorooctane with aqueous sodium cyanide for several days, 1-cyanooctane is not obtained.
- If a small amount of quaternary ammonium salt like tetra alkyl ammonium chloride is added, a rapid transition
of 1-cyanooctane occurs in about 100% yield after 1 or 2 hours.
- In this reaction, the tetra alkyl ammonium cation, which has hydrophobic and hydrophilic ends, transports CN^- from the aqueous phase to the organic phase using its hydrophilic end facilitates the reaction with 1-chloro octane

$$NaCN + R_4N^+Cl^- \rightarrow R_4N^+CN^- + Cl^-$$

CN^- in aquous phase CN^- moved to organic phase

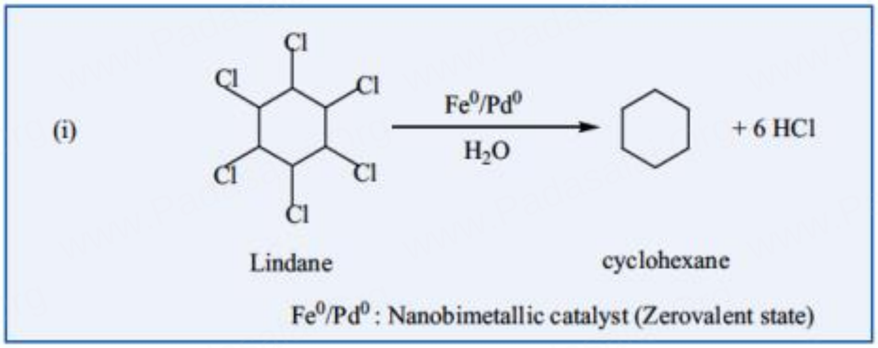
$$R_4N^+CN^- + R-Cl \rightarrow R-CN + R_4N^+Cl^-$$

Both in organic phase Organic phase

- So phase transfer catalyst, speeds up the reaction by transporting one reactant from one phase to another.

22. Give an account on Nano catalysis.

- Nano materials such a metallic nano particles, metal oxides, are used as catalyst in many chemical transformations.
- Nano catalysts carry the advantages of both homogeneous and heterogeneous catalyses.
- Like homogeneous catalysts, the nano catalysts give 100% selective transformations and excellent yield and show extremely high activity.
- Like the heterogenous catalysts nano catalysts can be recovered and recycled
- Nano catalysis are soluble heterogenous catalysts .



Fe^0/Pd^0 : Nanobimetallic catalyst (Zerovalent state)

23. Define colloids.

Colloid is a homogeneous mixture of two substances in which one substance is dispersed in another substance.

Size of the colloidal particle is 1-200 nm.

24. Explain dispersion methods of preparation of colloids in detail.

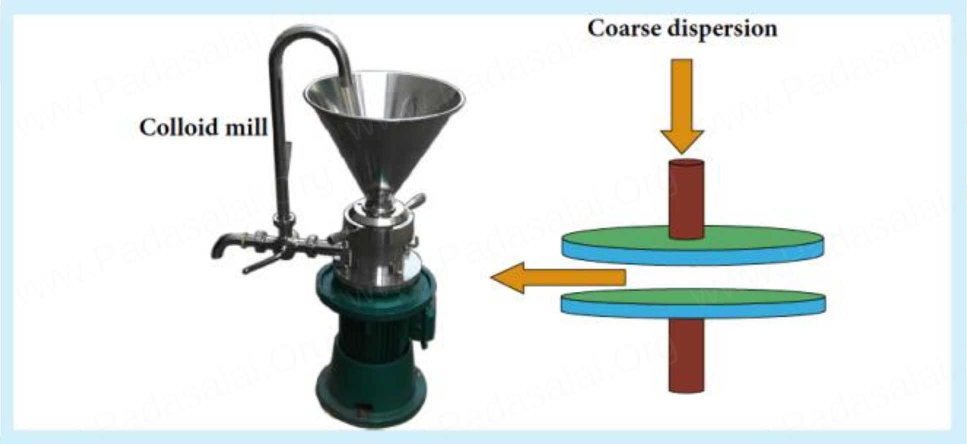
There are 4 methods of dispersion they are,

i) Mechanical dispersion
ii) Electro dispersion
iii) Ultrasonic dispersion
iv) Peptisation

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.

The colloidal particles of required colloidal size is obtained by adjusting the distance between two plates.

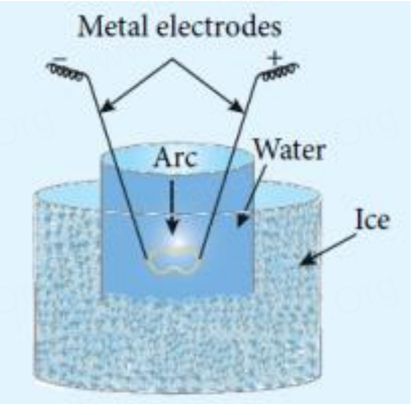


Colloidal Mill

By this method, colloidal solutions of ink and graphite are prepared.

Electro Dispersion:

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.



Bredig's arc method

Ultrasonic dispersion:

Sound waves of frequency more than 20kHz (audible limit) could cause transformation of coarse suspension to colloidal dimensions.

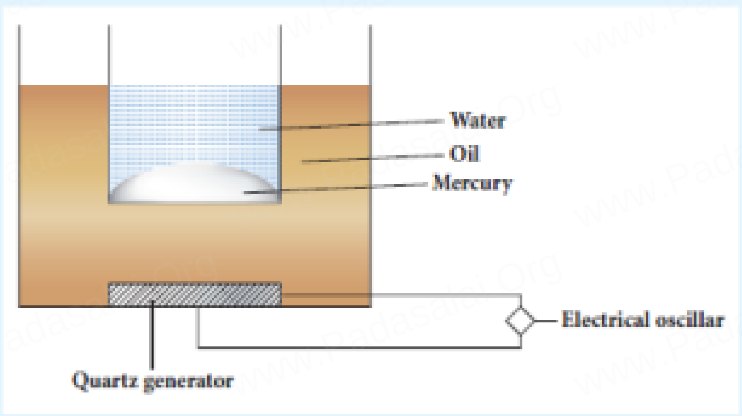


Figure : 10.10 Ultrasonic dispersion

Mercury sol can be obtained by subjecting mercury to sufficiently high frequency ultrasonic vibrations.

The Ultrasonic vibrations produces by generator spread the oil and transfer the vibration to the vessel with mercury in water

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.

$$\underset{\text{(precipitate)}}{AgCl} \xrightarrow{HCl} \underset{\text{(colloid)}}{AgCl}$$

25. Explain chemical methods of the preparation of colloids.

Oxidation:

Sols of some non metals are prepared by this method.

When hydroiodic acid is treated with iodic acid, I_2 sol is obtained.

$$HIO_3 + 5HI \rightarrow 3H_2O + I_2(sol)$$

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.

$$2AuCl_3+3HCHO+3H_2O \rightarrow 2Au(sol)+6HCl+3HCOOH$$

Hydrolysis:

Sols of hydroxides of metals like chromium and aluminium can be produced by this method.

$$FeCl_3+3H_2O \rightarrow Fe(OH)_3+3HCl$$

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.

$$As_2O_3+3H_2S \rightarrow As_2S_3(sol)+3H_2O$$

Decomposition:

When few drops of an acid is added to a dilute solution of sodium thiosulphate, the Colloidal sulphur is prepared

$$S_2O_3^{2-} + 2H^+ \rightarrow S+H_2O+SO_2$$

26. What is tyndall effect.

When light passes through colloidal solution, it is scattered in all directions. This effect is called as Tyndall effect.

27. What is Brownian movement?

When a colloidal solution is viewed through ultra microscope, continuous bombardment of colloidal sol particles with the molecules of the dispersion medium can be seen and they show a random, zigzag, ceaseless motion. This is called Brownian movement.

28. Mention and brief the property of colloid, which explains its stability (or) What is 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.

As the particles nearby are having similar charges they cannot come close and condense. Hence this helps to explain the stability of colloid

29. What is coagulation? Mention the various methods of coagulation.

The flocculation and settling down of the sol particles is called coagulation.

Various methods of coagulation are:

(i) Addition of electrolytes
(ii) Electrophoresis
(iii) Mixing oppositively charged sols.
(iv) Boiling

30. What is flocculation value?

The precipitation power of electrolyte is determined by finding the minimum concentration (millimoles/lit) required to cause precipitation of a sol in 2 hours. This value is called flocculation value. The smaller the flocculation value greater will be precipitation.

31. Define Gold number.

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.

32. What are Emulsions? What are the two types of Emulsions?

Emulsions are colloidal solution in which a liquid is dispersed in another liquid. Generally there are two types of emulsions.

(i) Oil in water (O/W) (ii) Water in oil (W/O)

33. What is inversion of phases? Give example.

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 $AlCl_3$.

34. Give an account on dispersion medium and dispersed phase.

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.

35. Mention the dispersion medium of the colloids.

i) Hydrosols or aquasols ii) alcosols iii) benzosol

S.no	Colloid	Dispersion medium
1	Hydrosols (aquasols)	Water
2	Alcosols	Alcohol
3	Benzosol	Benzene

36. Why gas in gas colloid is not following formed?

- ⇨ Gases are completely miscible with each other and form a homogeneous mixture.
- ⇨ A gas in gas is a true solution and not a colloidal solution.

37. Give the principle involved in the dispersion and condensation methods of preparation of colloids.

Dispersion methods: In this larger particles are broken into colloidal dimensions.

Condensation methods: In this small sized particles or molecules or ions are converted into larger colloidal sized particles.

38. How is colloid of phosphorous or sulphur prepared?

- ⇨ Colloid of phosphorous or sulphur is prepared by the method of exchange of solvent.
- ⇨ Solution of phosphorus or sulphur is prepared in alcohol and then it is poured into water. As they are insoluble in water, they form colloidal solution.

Other important questions:

1. Explain the methods of purification of colloids by

i) Dialysis ii) Electrodialysis iii) ultrafiltration

2. Give the advantages of Brownian movement.
3. Illustrate the method of detection of charge on colloidal particles.

Or

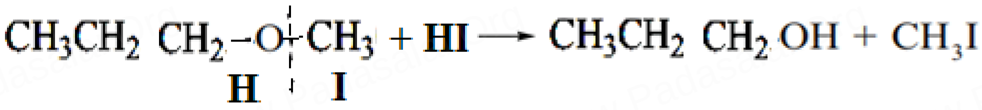
Write a note on Electrophoresis.

4. Give an account on protective action of gold sol.
5. What is called emulsification? Mention three types of emulsifications.
6. Discuss the different tests to indentify two types of emulsions, oil in water (O/W) and water in oil (W/O).
7. What is de-emulsification? Give various de-emulsification techniques.
8. Give the application of cortrell's precipitator?
9. Write short note on Delta?
10. Distinguish between lyophilic and lyophobic colloids.
11. Give the uses of colloids in medicine.
12. What is tanning of leather?

UNIT - 11 HYDROXY DERIVATIVES

I TEXT BOOK QUESTIONS AND ANSWERS

1. **Identify the product (s) is / or formed when 1 – methoxy propane is heated with excess of HI . Name the mechanism involved in the reaction.**



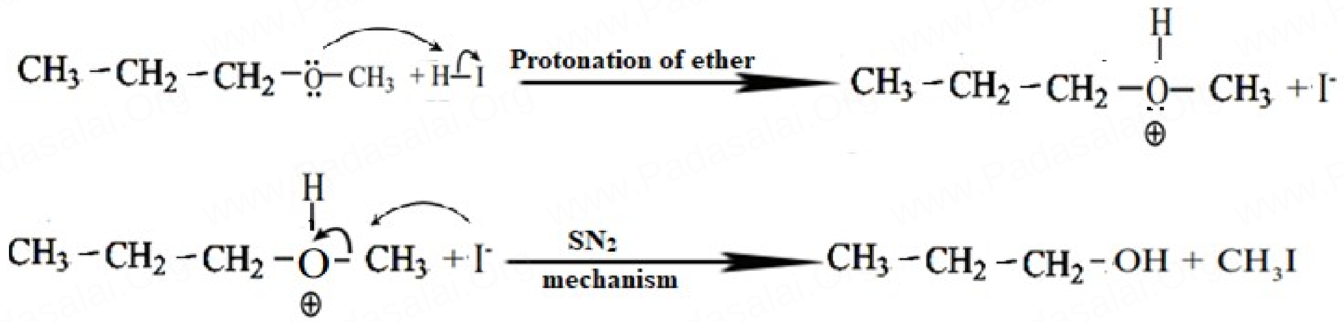
$$CH_3CH_2\,CH_2-O-CH_3 + HI \longrightarrow CH_3CH_2\,CH_2\,OH + CH_3I$$

$$CH_3CH_2CH_2OH + HI \rightleftharpoons CH_3CH_2CH_2\,I + H_2$$

The final products are methyl iodide (CH_3I) and n- propyl iodidie ($CH_3CH_2CH_2\,I$)

Mechanism:

Nucleophilic substitution (SN_2 mechanism)

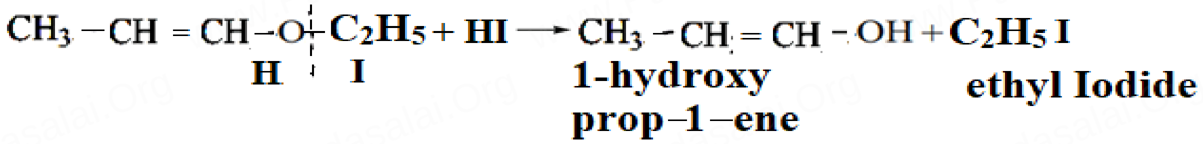


$$CH_3-CH_2-CH_2-\ddot{O}-CH_3 + H-I \xrightarrow{\text{Protonation of ether}} CH_3-CH_2-CH_2-\overset{H}{\underset{\oplus}{O}}-CH_3 + I^-$$

$$CH_3-CH_2-CH_2-\overset{H}{\underset{\oplus}{O}}-CH_3 + I^- \xrightarrow[\text{mechanism}]{SN_2} CH_3-CH_2-CH_2-OH + CH_3I$$

Halide ion attack the alkyl group contain less number of carbon atom (Because it is less crowded) by SN_2 mechanism.

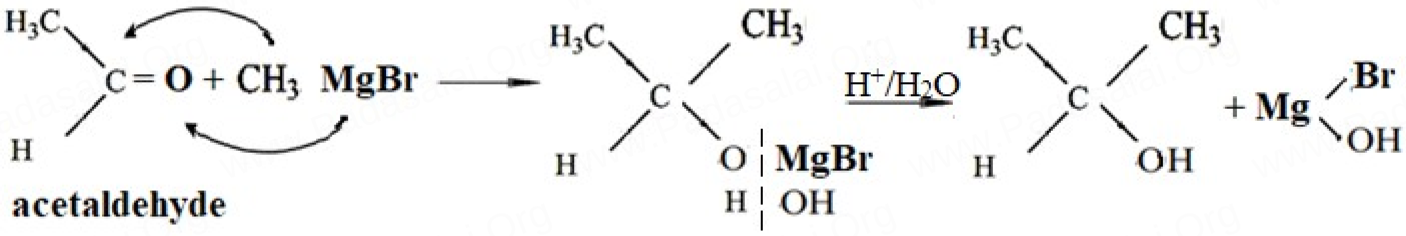
2. **Draw the major product formed when 1 – ethoxy prop 1 ene is heated with one equivalent of HI**



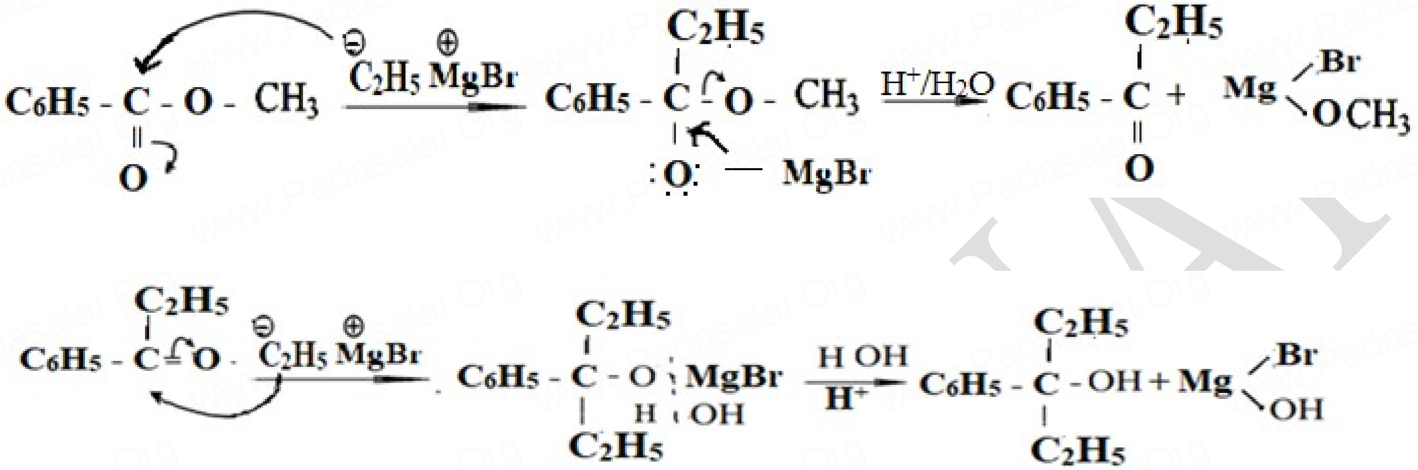
$$CH_3-CH=CH-O-C_2H_5 + HI \longrightarrow CH_3-CH=CH-OH + C_2H_5I$$

3. **Suggest a suitable reagent to prepare sec – alcohol with identical group using Grignard reagent.**

When Grignard reagent reacts with aldehydes gives secondary alcohol. If aldehyde contains same alkyl or aryl group as Grignard reagent, it gives secondary alcohol with identical groups.



4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.



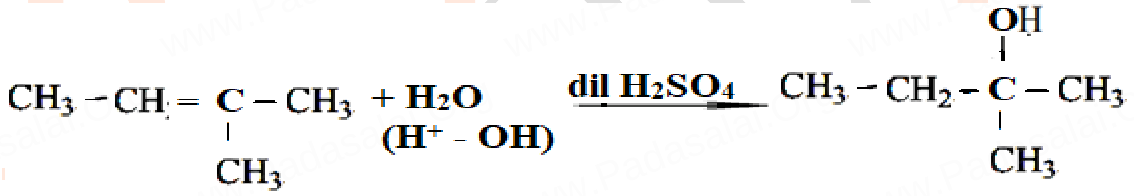
$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-CH_3 \xrightarrow{\overset{\ominus}{C_2H_5}\overset{\oplus}{MgBr}} C_6H_5-\overset{C_2H_5}{\underset{:\ddot{O}:-MgBr}{C}}-O-CH_3 \xrightarrow{H^+/H_2O} C_6H_5-\overset{C_2H_5}{\underset{\underset{O}{\|}}{C}} + Mg\begin{smallmatrix}Br\\OCH_3\end{smallmatrix}$$

$$C_6H_5-\overset{C_2H_5}{C}=O \;\; \overset{\ominus}{C_2H_5}\overset{\oplus}{MgBr} \longrightarrow C_6H_5-\overset{C_2H_5}{\underset{C_2H_5}{C}}-O\,\underset{H\;\;OH}{MgBr} \xrightarrow[H^+]{H\,OH} C_6H_5-\overset{C_2H_5}{\underset{C_2H_5}{C}}-OH + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

3 - phenyl pentane - 3 - ol

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

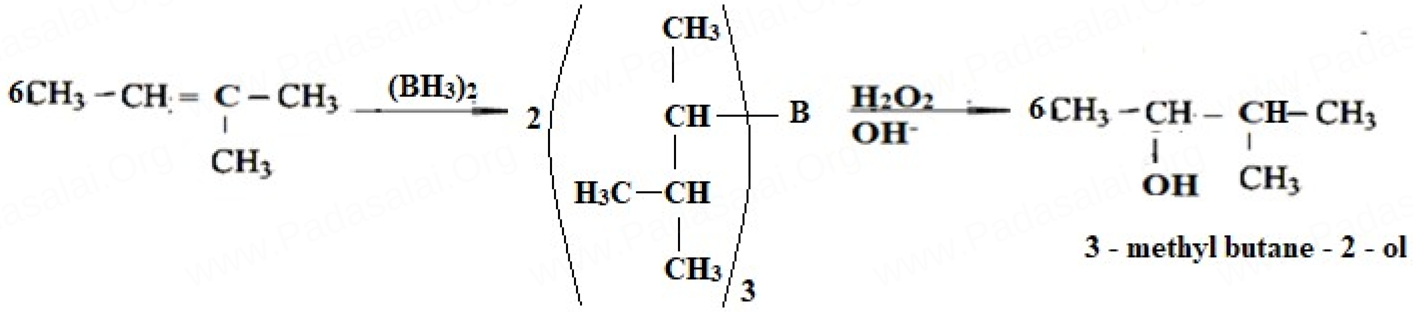


$$CH_3-CH=\underset{CH_3}{C}-CH_3 + H_2O\,(H^+ - OH) \xrightarrow{\text{dil } H_2SO_4} CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

ethyl dimethyl carbinol
(2 methylbutan2ol)

(Addition takes place according to Markownikoff's rule)

(ii) Hydroboration



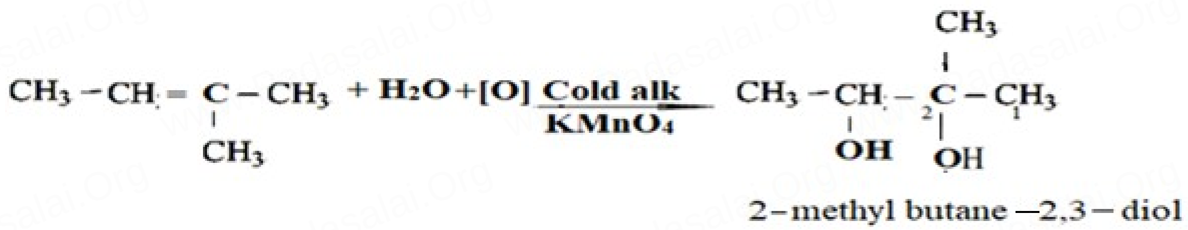
$$6CH_3-CH=\underset{CH_3}{C}-CH_3 \xrightarrow{(BH_3)_2} 2\left(\begin{matrix}CH_3\\|\\CH\\|\\H_3C-CH\\|\\CH_3\end{matrix}\right)_3 B \xrightarrow[OH^-]{H_2O_2} 6CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3$$

3 - methyl butane - 2 - ol

(Addition takes place according to Anti Markownikoff's rule)

(No carbocation intermediate is formed)

(iii)Hydroxylation using Baeyer's reagent



$$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CH_3 + H_2O+[O] \xrightarrow[KMnO_4]{Cold\ alk} CH_3-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$$

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

<u>2 –methylpropan -2-ol</u>

Tert- butyl alcohol is having more branches, so it has less surface area and less vanderwaals force So boiling point is very low.

<u>Butan – 2- ol</u>

Butan –2– ol is having one branch, so it has less surface area and less vanderwaals force. So it has low boiling point than Butan –1–ol.

<u>Butan -1-ol</u>

Butan -1-ol is having no branching more surface area. So it has high boiling point

2 –methylpropan -2-ol < Butan – 2- ol < Butan -1-ol

(ii) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol

<u>propan -1,2,3-triol</u> (glycerol)

Contains 3 OH groups, so hydrogen bond is strong, it has high boiling point

<u>propan -1,3 – diol</u>

Contains 2 OH groups, so hydrogen bond is strong but less compared to glycerol.

<u>propan -2-ol</u>

Its having one branch so it has less surface area and less vanderwaals force less boiling point than propan – 1- ol.

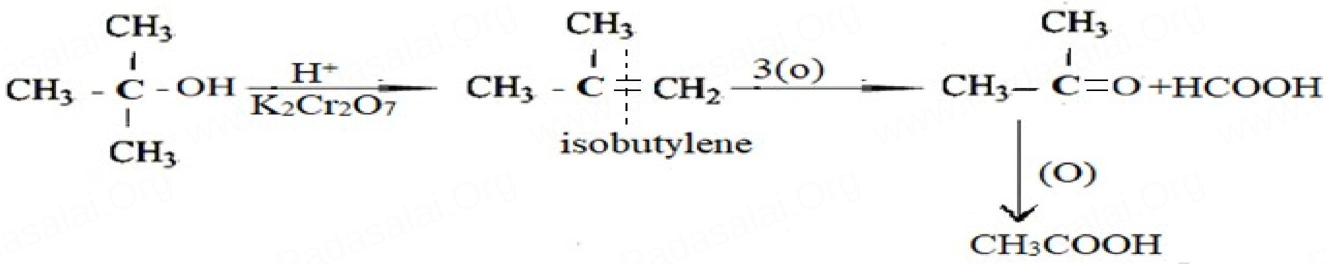
propan -2-ol < propan – 1ol < propan -1,3 – diol < propan -1,2,3-triol

7. **Can we use nucelophiles such as NH_3, CH_3O^- for the Nucleophilic substitution of alcohols**

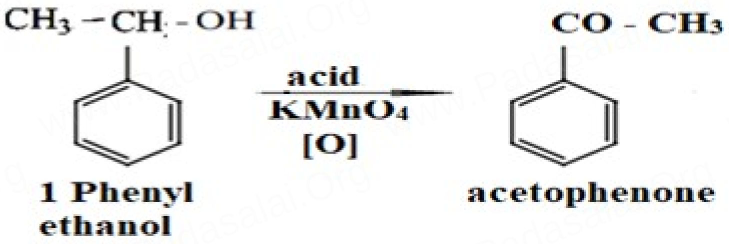
Both NH_3, CH_3O^- pickup a proton from the alcohol and thus gives NH_4^+ ion and CH_3OH. This considerably reduces the nucleophilic tendency of NH_3, CH_3O^- towards alcohol.

8. **Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound.**

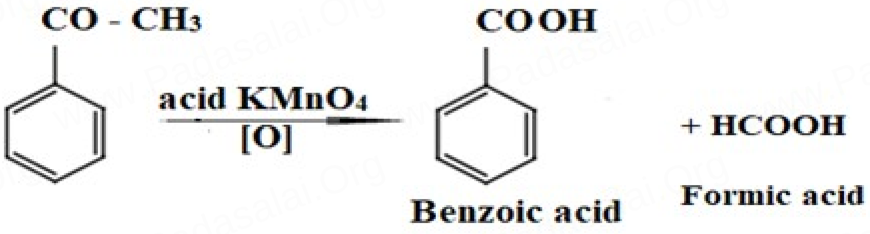
No, Tertiary alcohols are stable to oxidation under normal conditions. But at elevated temperature, cleavage of C = C bond takes place to give a mixture of carboxylic acid with lesser number of carbon atoms.



9. **What happens when 1-phenyl ethanol is treated with acidified KMnO₄.**



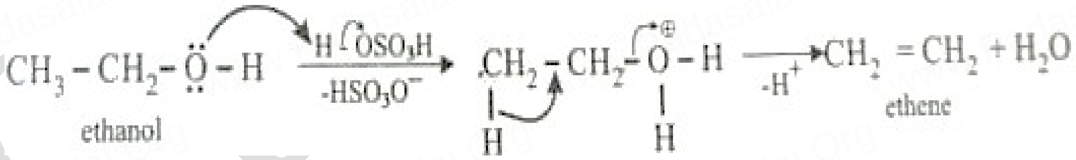
(sec – alcohol on oxidation gives ketone)



10. **Write the mechanism of acid catalysed dehydration of ethanol to give ethene.**

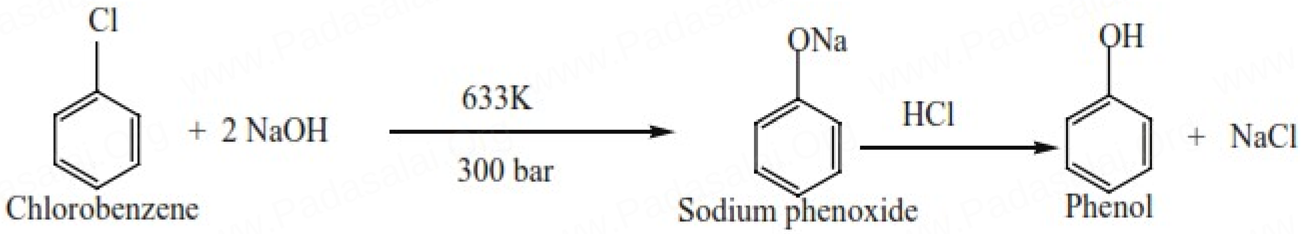
$$CH_3CH_2OH \xrightarrow[443K]{Con\ H_2SO_4} CH_2 = CH_2 + H_2O$$

Mechanism: Primary alcohols undergo dehydration by E_2 mechanism.

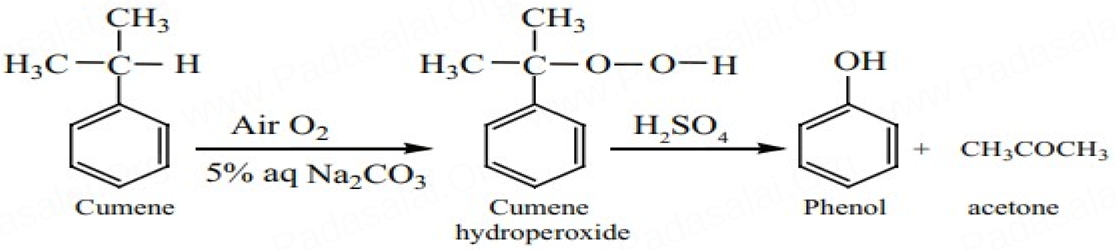


11. **How is phenol prepared from a. chloro benzene b. isopropyl benzene**

Dow 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.

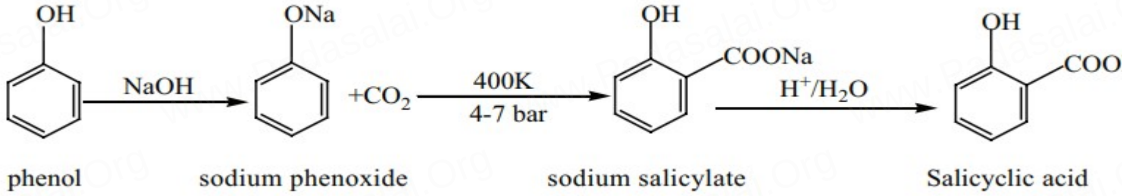


Isopropyl benzene: On passing air to a mixture of cumene (or) isopropyl benzene and 5% aqueous sodium carbonate solution, cumene hydro peroxide is formed by oxidation. It is treated with dilute acid to get phenol and acetone.



12. **Explain kolbe's reaction.**

Kolbe's reaction: Sodium phenoxide prepared from phenol by adding NaOH and it is heated with CO_2 at 400 K and 4 -7 bar pressure sodium salicylate is formed then it reacts with dil.HCl, salicylic acid is formed.

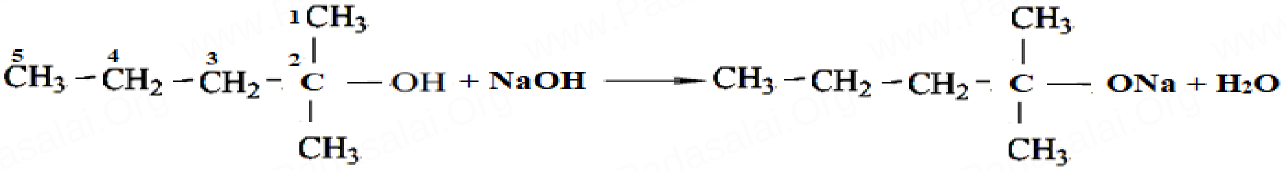


13. **Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol**

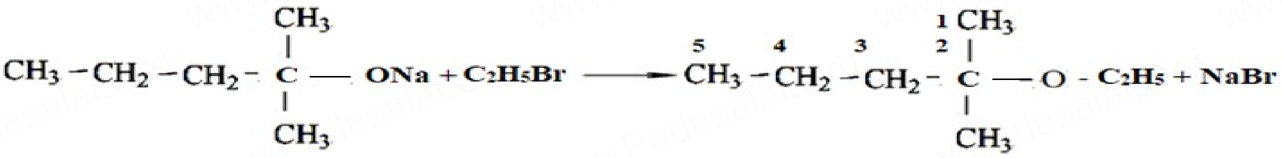
In Williamson synthesis, an alkyl halide reacts with an alkoxide ion, Also it is an SN^2 reaction. In this reaction, alkyl halides should be primary having the less steric hindrance.

If you prepare ether form alkyl halide and tert - alcohol, it undergoes SN^1 mechanism.

$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$



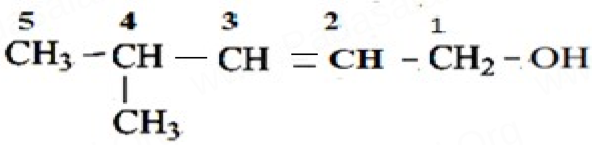
$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{C}(\overset{1}{CH_3})(CH_3)-OH + NaOH \longrightarrow CH_3-CH_2-CH_2-C(CH_3)(CH_3)-ONa + H_2O$$



$$CH_3-CH_2-CH_2-C(CH_3)(CH_3)-ONa + C_2H_5Br \longrightarrow \overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{C}(\overset{1}{CH_3})(CH_3)-O-C_2H_5 + NaBr$$

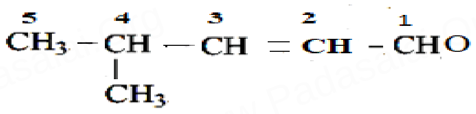
2 ethoxy 2 methyl pentane

14. **Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent -2-en-1-ol.**



$$\overset{5}{CH_3}-\overset{4}{CH}(CH_3)-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_2}-OH$$

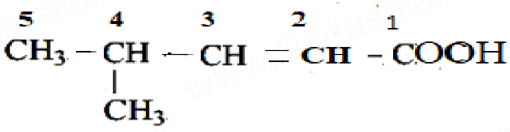
1. **Aldehyde**



$$\overset{5}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{4}{CH}} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{CHO}$$

4 methyl pent 2 en 1 al

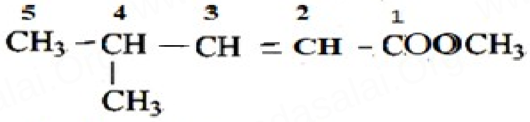
2. Acid



$$\overset{5}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{4}{CH}} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{COOH}$$

4 methyl pent 2 en 1 oic acid

3. Ester



$$\overset{5}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{4}{CH}} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{COOCH_3}$$

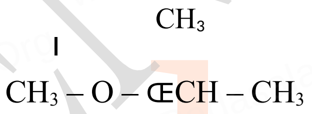
methyl 4 methyl pent 2 enoate

15. What is Metamerism? Give the structure and IUPAC name of metamers of 2 – methoxy propane.

It is isomerism in which molecules with same molecular formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

$CH_3 - O - CH_2\,CH_2\,CH_3$
1 – methoxy propane

$CH_3\,CH_2 - O - CH_2CH_3$
ethoxy ethane



$$CH_3 - O - \overset{\overset{CH_3}{|}}{CH} - CH_3$$

2 – methoxy propane

ŒI

16. How are the following conversions effected.

a. Benzyl chloride to benzylalcohol b. Benzylalcohol to benzoic acid.

a. Benzyl chloride to benzylalcohol:

Benzyl chloride is treated with aqueous NaOH form benzyl alcohol.

$$C_6H_5CH_2Cl \xrightarrow{NaOH} C_6H_5CH_2OH + NaCl$$

b. Benzylalcohol to benzoic acid.

Oxidation with acidic $K_2Cr_2O_7$ (or) alkaline $KMnO_4$, benzylalcohol is first oxidized to benzaldehyde which undergoes further oxidation to benzoic acid.

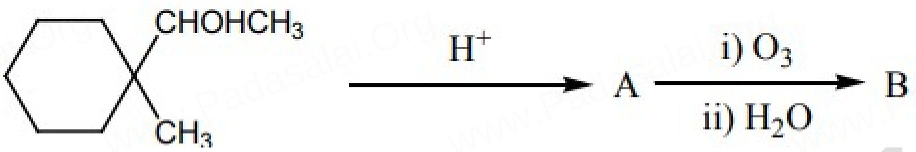
$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[\text{Alk } KMnO_4]{K_2Cr_2O_7\ /\ H^+} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{(O)} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

17. Complete the following reactions

i) $CH_3-CH_2-OH \xrightarrow{PBr_3} A \xrightarrow{aq.NaOH} B \xrightarrow{Na} C$

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) 

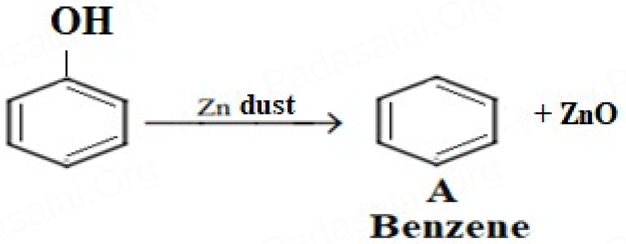
i) $CH_3-CH_2-OH \xrightarrow{PBr_3} A \xrightarrow{aq.NaOH} B \xrightarrow{Na} C$

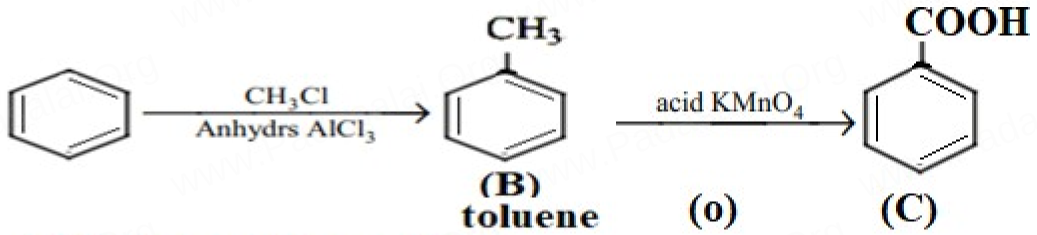
$$3CH_3CH_2OH + \xrightarrow{PBr_3} \underset{\textbf{A}}{3CH_3CH_2Br} + H_3PO_3$$

$$\underset{\textbf{A}}{CH_3CH_2Br} \xrightarrow{aq.NaOH} \underset{\substack{\textbf{ethanol}\\ \textbf{(B)}}}{CH_3CH_2OH} + NaBr$$

$$2CH_3CH_2OH \xrightarrow{Na} \underset{\substack{\textbf{(C)}\\ \textbf{Sodium ethoxide}}}{2CH_3CH_2ONa} + H_2$$

ii) $C_6H_5-OH \xrightarrow{Zn\ dust} A \xrightarrow[Anhydrs\ AlCl_3]{CH_3Cl} B \xrightarrow{acid\ KMnO_4} C$

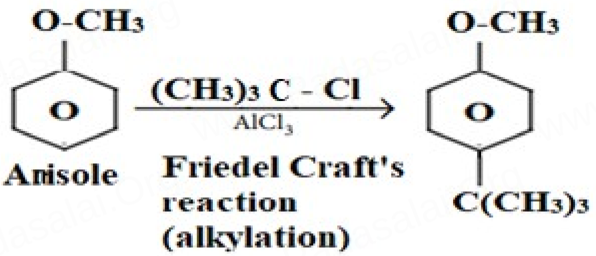




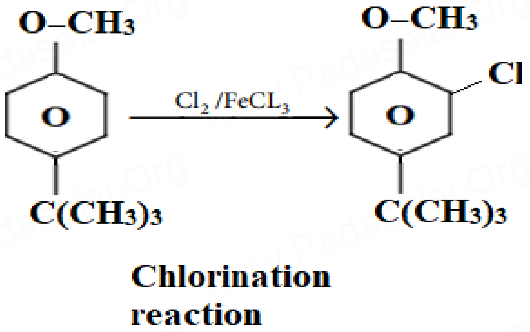
(Friedel-craft's reaction)

- CH_3, - C_2H_5, - CH_2OH, groups are oxidised to – COOH

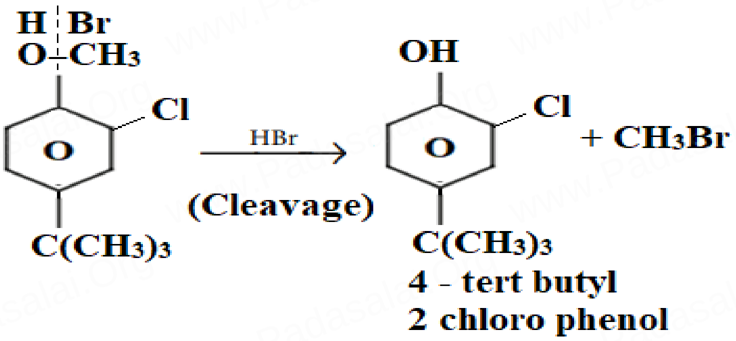
iii) Anisole $\xrightarrow[AlCl_3]{t\text{-}butylchloride} A \xrightarrow{Cl_2/FeCL_3} B \xrightarrow{HBr} C$



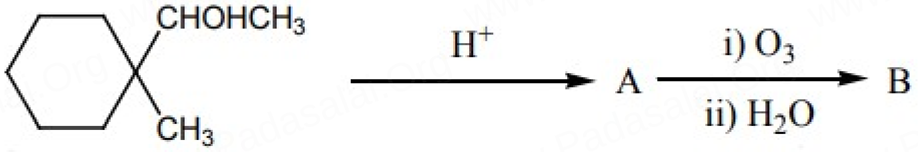
O – CH_3 is O, P directing group due to steric reason P – isomer is formed

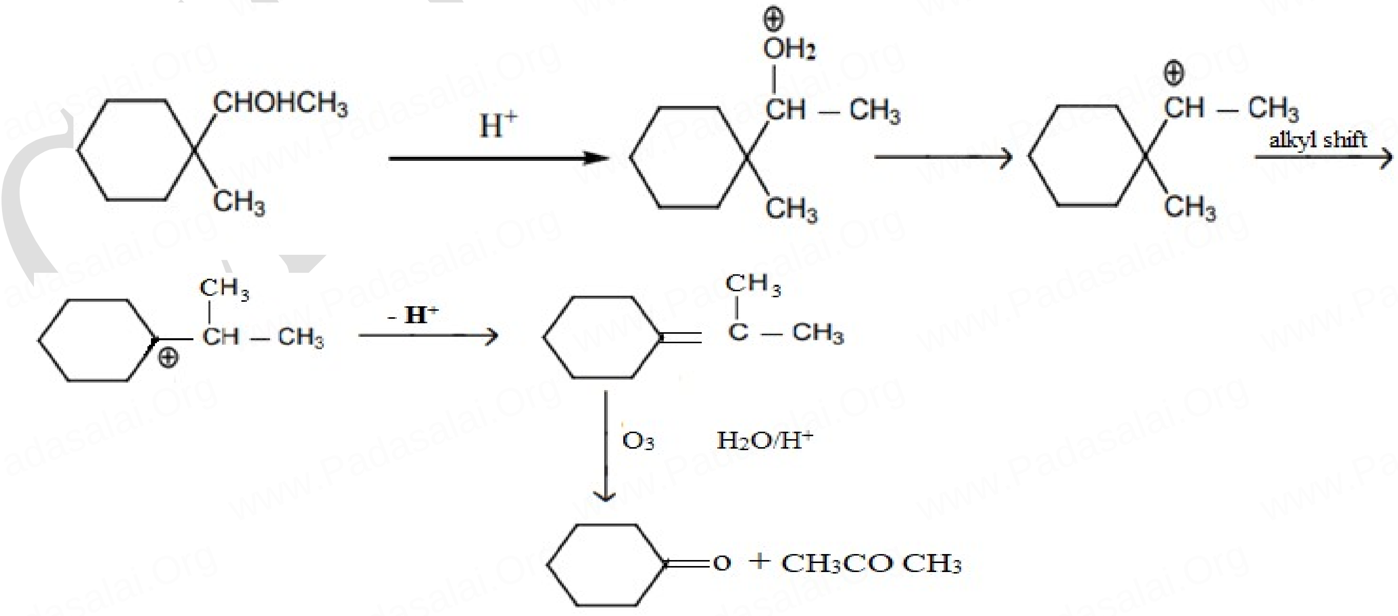


Since – O – CH_3 is O, P directing group Cl^+ enters into O position.



iv)





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.

$ROH + CH_3MgI \rightarrow R - O - MgI + CH_4$

At STP , 22400 cm^3 (1 mole) of methane is liberated by 1 mole of monohydric alcohol

At STP 112 cm^3 of methane is liberated by $\frac{1 \times 112}{22400} = 0.005\, mole\, of\, alcohol$

Given mass of 0.005 mole of alcohol = 0.44 g

Mass of 1 mole of alcohol = $\frac{0.44 \times 1}{0.005} = 88\, g$ mol^{-1}

Molar Mass of alcohol is = 88 g mol^{-1}

With PCC (Pyridinium chloro chromate) Alcohol form a compound that answers silver mirror test. So the compound formed is aldehyde and the alcohol is primary alcohol.

We know general formula of alcohol $C_nH_{2n+2}O$

Molar mass = 88

$12n + (2n + 2) \times 1 + 16 = 88$

$12n + 2n + 2 + 16 = 88$

$14n = 88 - 18$

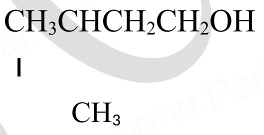
$14n = 70$

$n = 5$

Formula $C_5H_{12}O$

n pentyl alcohol and isopentyl alcohol are the possible primary alcohols with five carbon atoms.

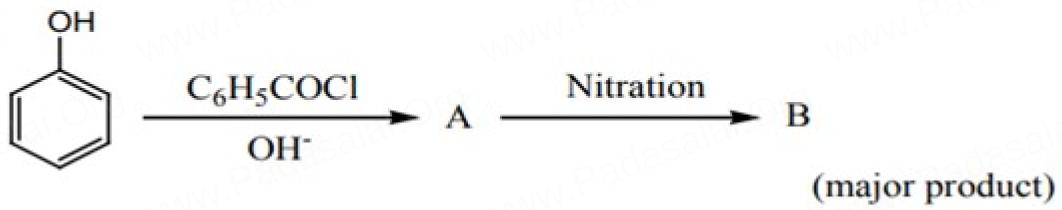
$CH_3CH_2CH_2CH_2CH_2OH$ (OR)

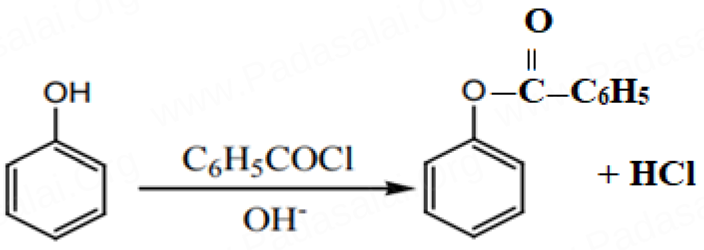


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2CH_2OH$

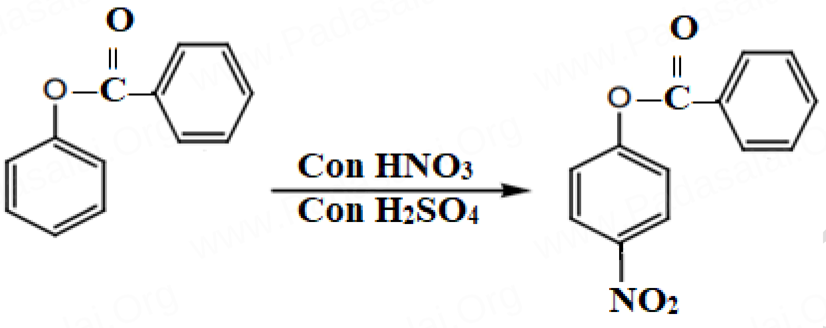
19.

i)

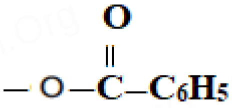


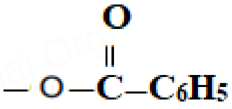


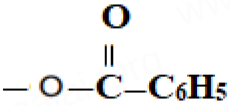
Schotten Baumann reaction **phenyl benzoate**



4 - nitrophenyl benzoate

NO_2 group will enter the ring that is attached to O – atom as  $-O-\overset{\overset{\large O}{\|}}{C}-C_6H_5$ is activating group.

It will not enter the ring attached to the carbonyl group as  $-O-\overset{\overset{\large O}{\|}}{C}-C_6H_5$ is deactivating group.

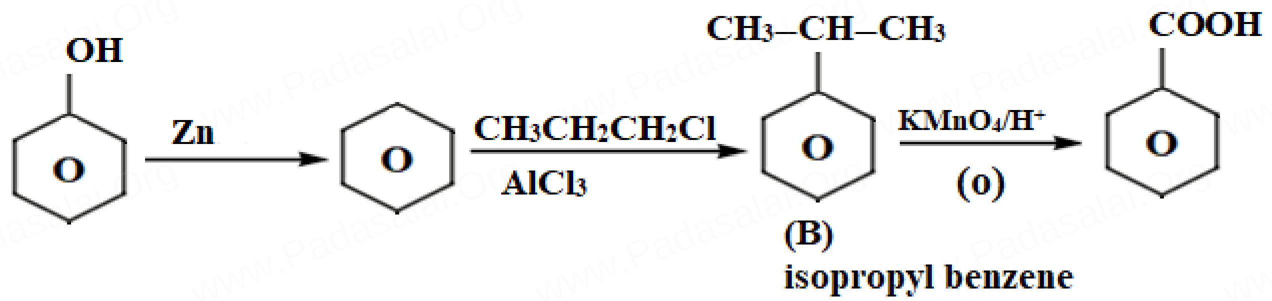
 $-O-\overset{\overset{\large O}{\|}}{C}-C_6H_5$ is O, P directing group. Due to steric hinderence, P isomer is only formed.

ii) $C_6H_5 - CH_2 - CH(OH)\,CH\,(CH_3) \xrightarrow{Conc.H_2SO_4}$

Product is based on Saytzeff's rule during intra molecular 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 ie stable alkene .

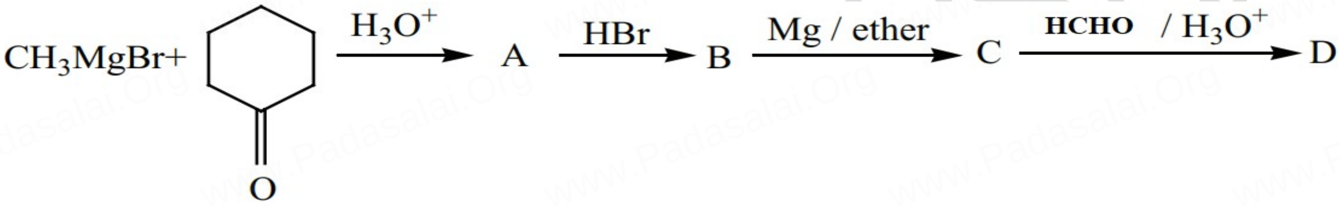
$$C_6H_5 - CH_2 - CH(OH)\,\underset{\underset{CH_3}{|}}{CH} - CH_3 \xrightarrow{Conc.H_2SO_4} C_6H_5 - CH_2 - CH = \underset{\underset{CH_3}{|}}{C} - CH_3$$

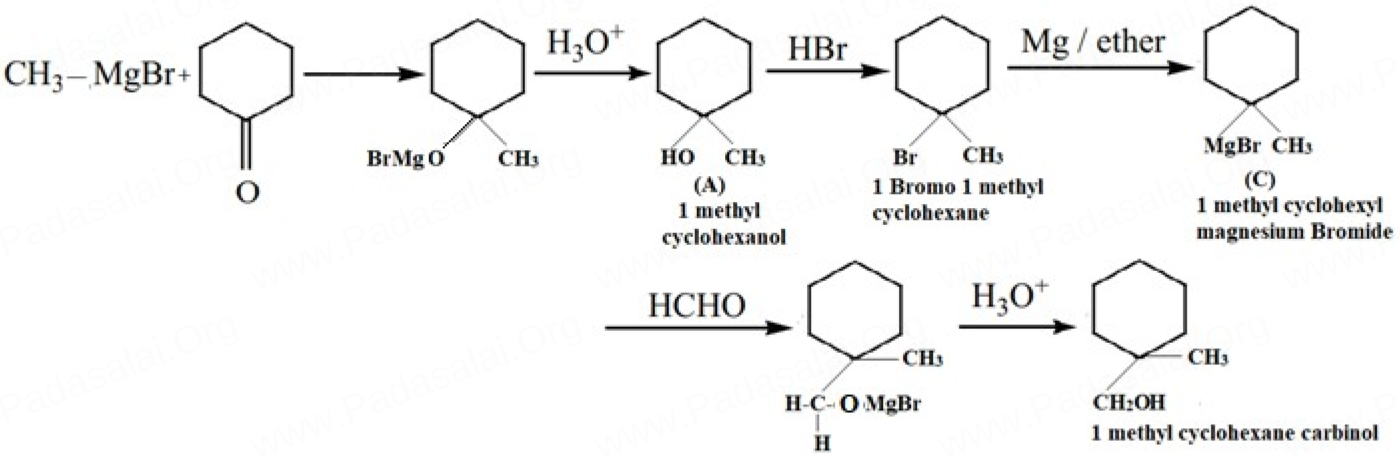
20. Phenol is distilled with Zn dust gives A followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A, B and C.



n propyl carbonium ion formed rearranges to give isopropyl carbonium ion. Since it is more stable. The electrophile is $CH_3-\overset{+}{C}H-CH_3$ Iso propyl carbonium ion (More stable)

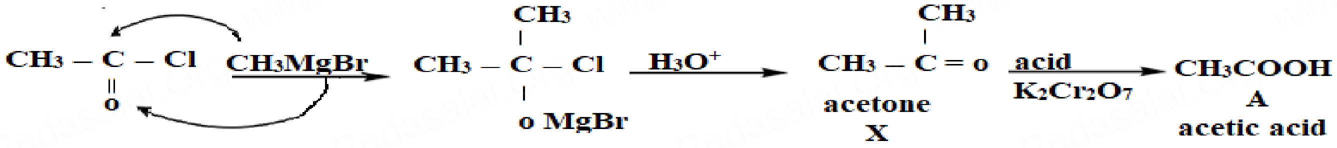
21.





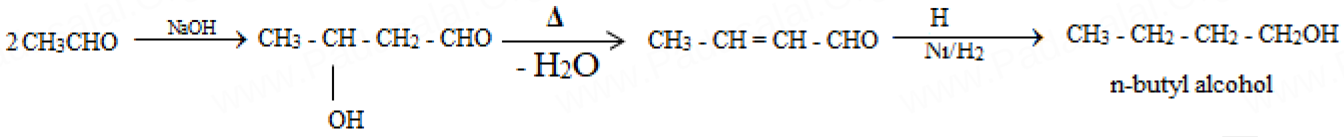
22. What will be the product (X and A) for the following reaction

$$\text{acetylchloride} \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}CH_3MgBr} X \xrightarrow[K_2Cr_2O_7]{\text{acid}} A$$



23. How will you convert acetylene into n-butyl alcohol.

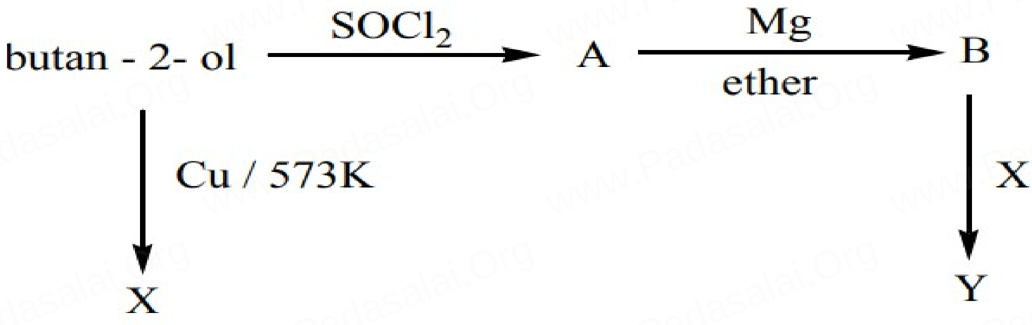
$$CH \equiv CH \xrightarrow[HgSO_4]{H_2SO_4} [CH_2 = CH - OH] \longrightarrow CH_3CHO$$

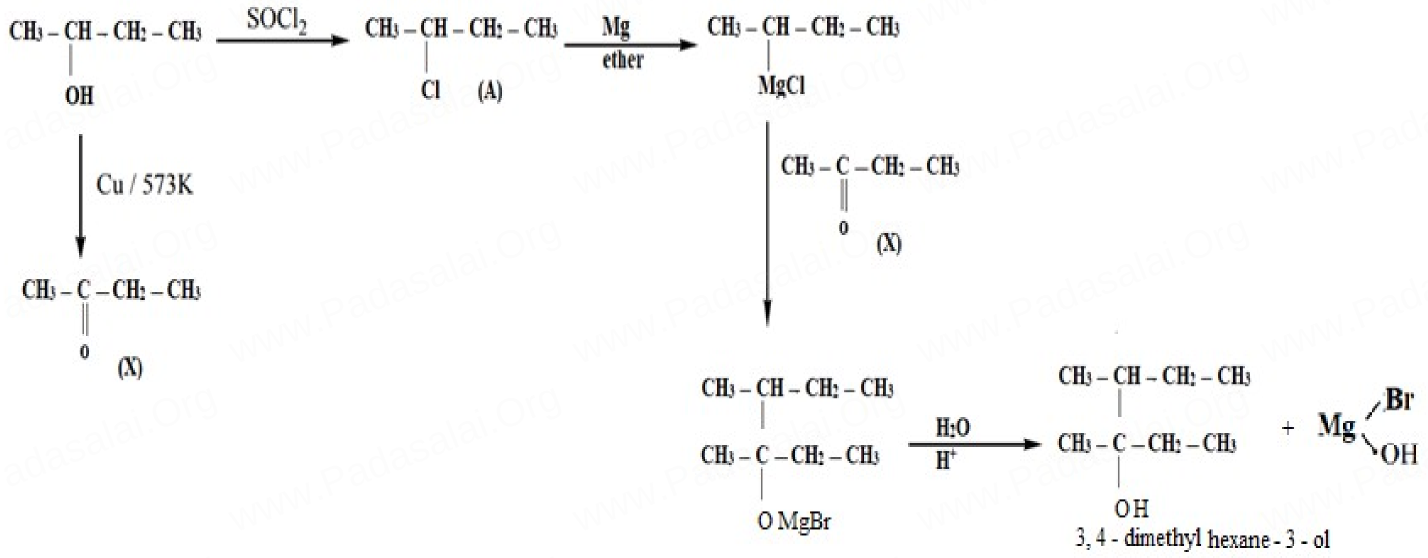


$$2\,CH_3CHO \xrightarrow{NaOH} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO \xrightarrow[Ni/H_2]{H} CH_3-CH_2-CH_2-CH_2OH$$

n-butyl alcohol

24. Predict the product A, B, X and Y in the following sequence of reaction





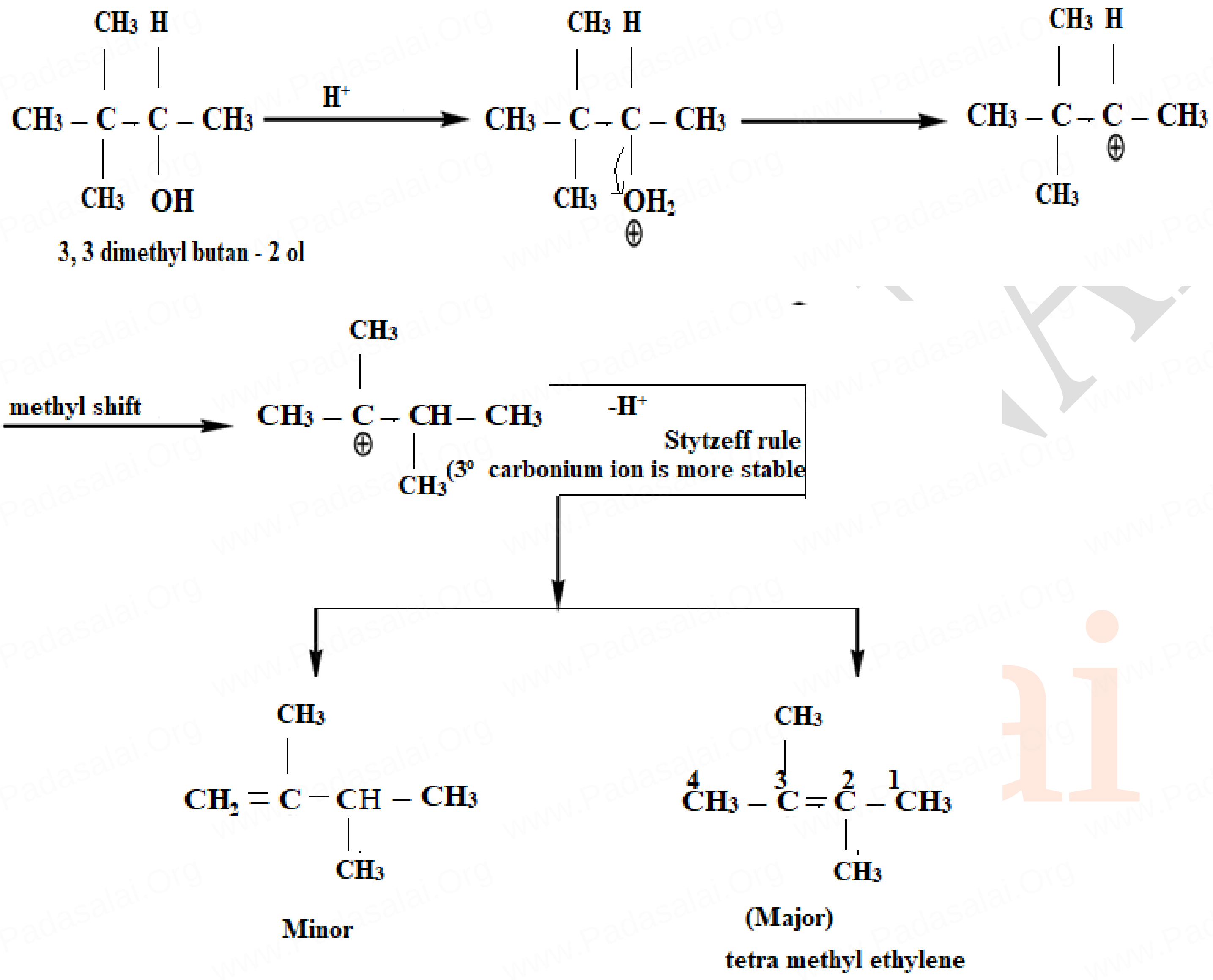
A = 2 – chlorobutane

X = 2 – butanone

B = Sec butyl magnesium chloride

Y = 3,4 dimethyl -3- hexanol

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.

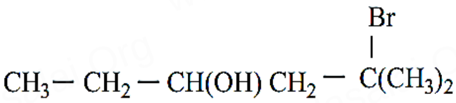


Stytzeff rule:

According to stytzeff rule in dehydrohalogenation reactions the preferred product is alkene which has the greater number of alkyl groups attached to the double bonded carbon atoms.

II SELF EVALUATION QUESTIONS AND ANSWERS

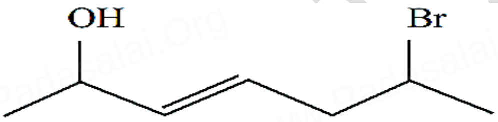
1. Classify the following alcohols as 1º, 2º, and 3º and give their IUPAC Names.

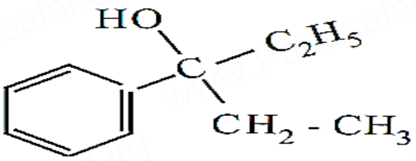
a. 

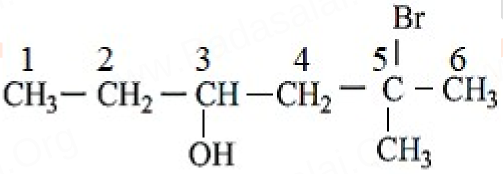
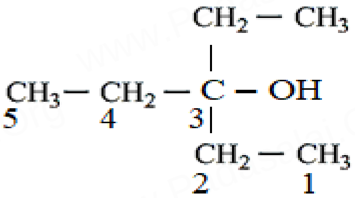
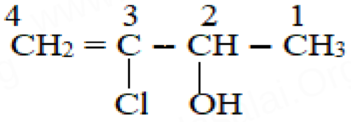
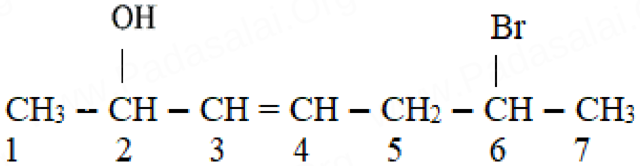
$CH_3-CH_2-CH(OH)CH_2-\overset{Br}{C}(CH_3)_2$

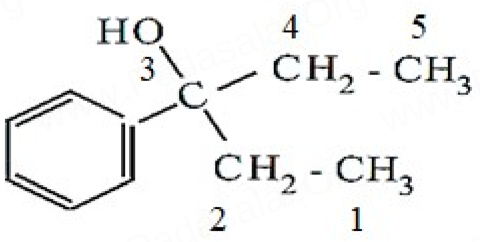
b. $(C_2H_5)_3COH$

c. $CH_2=C(Cl)-CH(OH)CH_3$

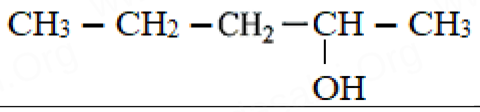
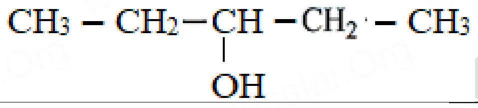
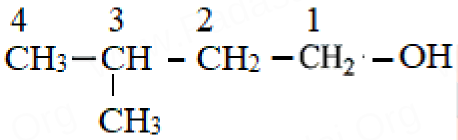
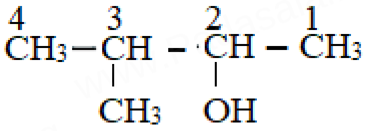
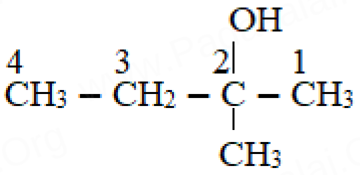
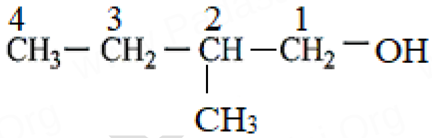
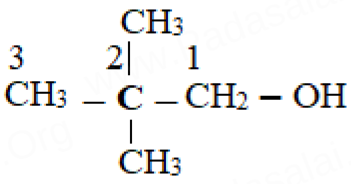
d. 

e. 

SNo.	Structure	Nature	IUPAC Name
a	 $\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{OH}{\overset{3}{CH}}-\overset{4}{CH_2}-\underset{CH_3}{\overset{Br}{\overset{5}{C}}}-\overset{6}{CH_3}$	2º alcohol	5 Bromo 5 methyl hexan 3 ol
b	 $\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{\underset{2\quad 1}{CH_2-CH_3}}{\overset{CH_2-CH_3}{\underset{3}{C}}}-OH$	3º alcohol	3 ethyl pentan 3 ol
c	 $\overset{4}{CH_2}=\underset{Cl}{\overset{3}{C}}-\underset{OH}{\overset{2}{CH}}-\overset{1}{CH_3}$	2º alcohol	3 chloro but 3 en 2 ol
d	 $\underset{1}{CH_3}-\underset{2}{\overset{OH}{CH}}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_2}-\underset{6}{\overset{Br}{CH}}-\underset{7}{CH_3}$	2º alcohol	6 Bromo hept 3 en 2 ol

e		3° alcohol	3 phenyl pentan 3 ol

2. **Write all the possible isomers of an alcohol having the molecular formula $C_5H_{12}O$ and give their IUPAC names.**

SNo	**Structure**	**IUPAC NAMES**
1	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	pentan 1 ol
2	 $CH_3-CH_2-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_3$	pentan 2 ol
3	 $CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	pentan 3 ol
4	 $\overset{4}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$	3 methyl butan 1 ol
5	 $\overset{4}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{3}{CH}}-\underset{\underset{OH}{\vert}}{\overset{2}{CH}}-\overset{1}{CH_3}$	3 methyl butan 2 ol
6	 $\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{\vert}}{\overset{\overset{OH}{2\vert}}{C}}-\overset{1}{CH_3}$	2 methyl butan 2 ol
7	 $\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{\vert}}{\overset{2}{CH}}-\overset{1}{CH_2}-OH$	2 methyl butan 1 ol
8	 $\overset{3}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{2\vert}}{C}}-\overset{1}{CH_2}-OH$	2, 2 dimethyl propan 1 ol

EVALUATE YOURSELF – 2

1. **Suggest a suitable carbonyl compound for the preparation of pent-2-en-1-ol using LiAlH$_4$?**

Pent 2 en 1ol structure

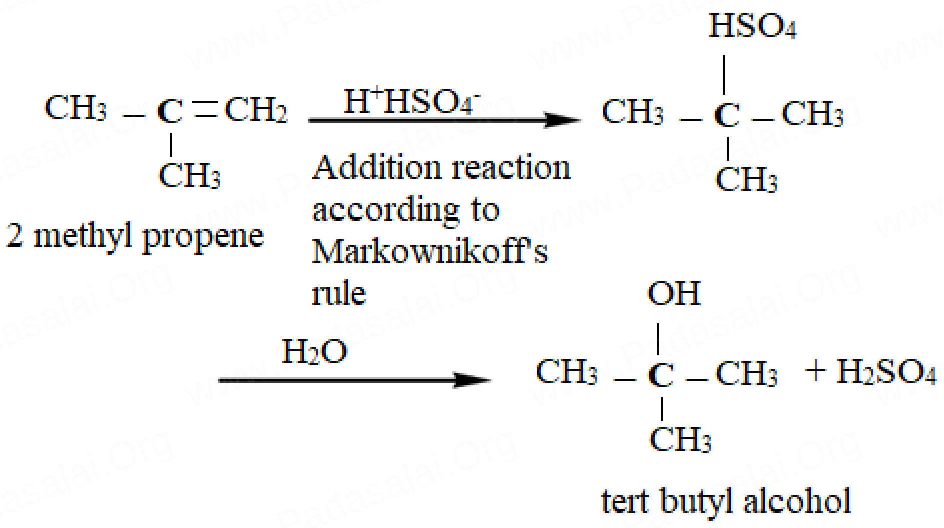
$$\overset{5}{CH_3} - \overset{4}{CH_2} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{CH_2} - OH$$

It is obtained by reducing

Pent 2 en 1 al

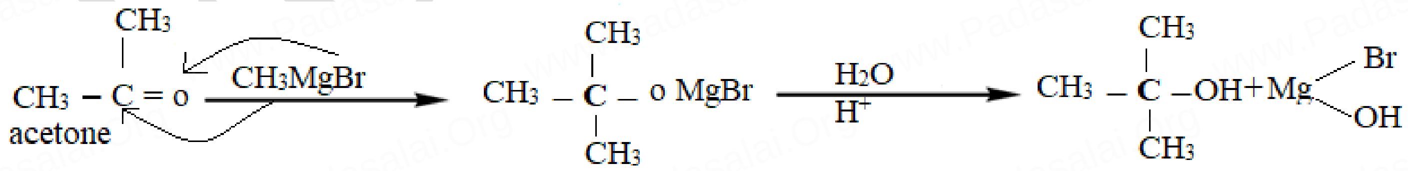
$$CH_3 - CH_2 - CH = CH - CHO \xrightarrow{LiAlH_4} CH_3 - CH_2 - CH = CH - CH_2OH$$

2. **2-methylpropan-1-ene** $\xrightarrow{H_2SO_4/H_2O}$?



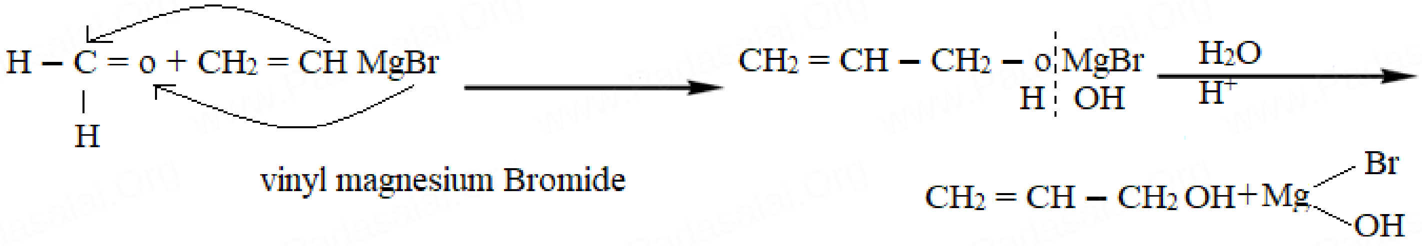
3. **How will you prepare the following using Grignard reagent.**

i) t-butyl alcohol



ii) allyl alcohol

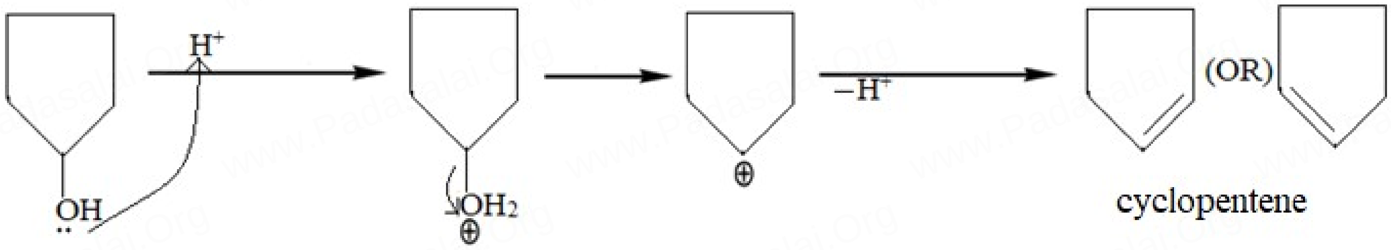
Allyl alcohol is 1° alcohol. Grignard reagent reacts with HCHO gives 1° alcohol. For the preparation of allyl alcohol we use vinyl magnesium bromide.



EVALUATE YOURSELF – 3

Identify the products in the following reactions. Write their IUPAC names and mention the mechanism involved in the reactions.

i) $\text{cyclopentanol} \xrightarrow[\Delta]{H_2SO_4} ?$



Mechanism: Dehydration

ii) $\text{butan-1-ol} \xrightarrow[H_2SO_4]{NaBr} ?$

$NaBr \rightarrow Na^+ + Br^-$

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$CH_3 - CH_2 - CH_2 - CH_2 - \ddot{O}H \xrightarrow{H^+}$

$CH_3 - CH_2 - CH_2 - CH_2 - \overset{\oplus}{O}H_2$

$Br^- + CH_3 - CH_2 - CH_2 - CH_2 - \overset{\oplus}{O}H_2 \xrightarrow{SN_2\ \text{mechanism}}$

$[Br^- \ldots\ldots CH_2(-CH_2 - CH_2 - CH_3) \ldots\ldots \overset{\oplus}{O}H_2]$

Transition state

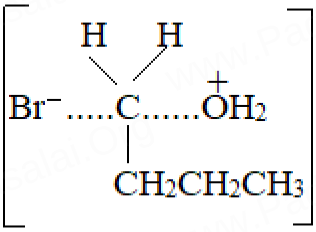
$\longrightarrow CH_3CH_2CH_2-CH_2-Br + H_2O$

1 Bromo butane

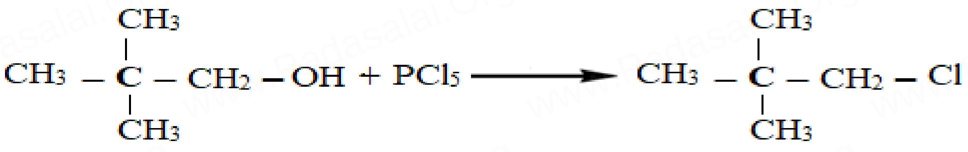
Br^- acts as nucleophile

SN^2 mechanism

Structure of T.T

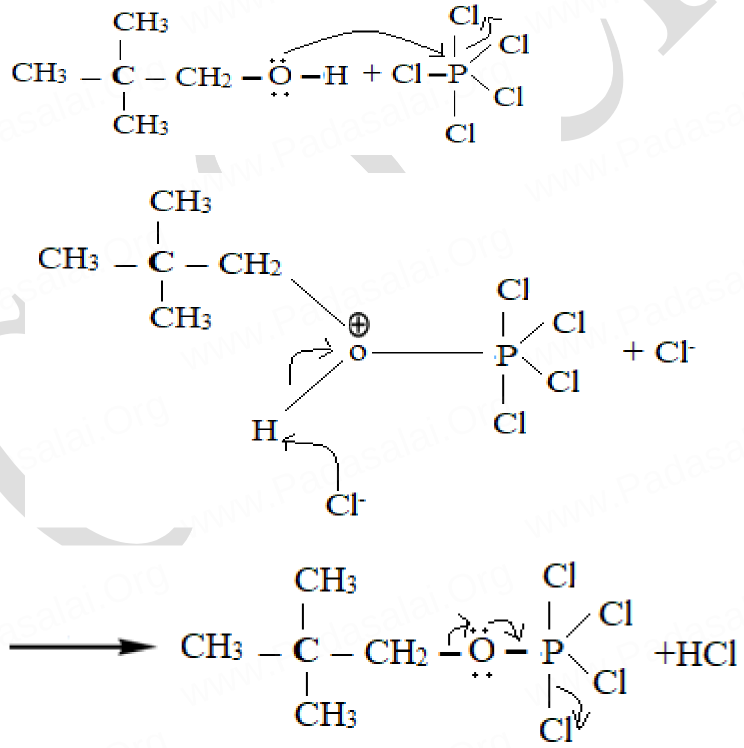


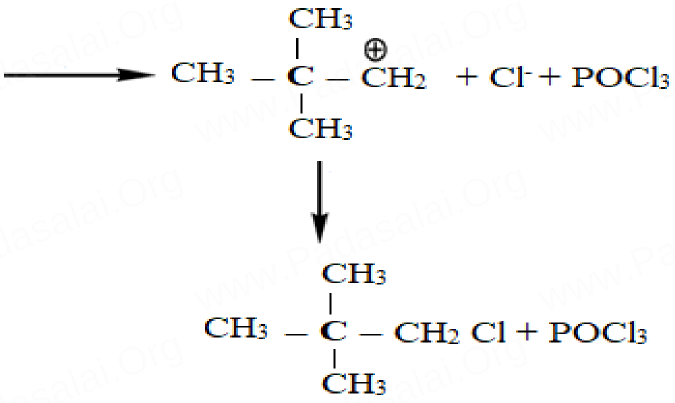
iii) neopentyl alcohol $\xrightarrow{PCl_5}$?



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH + PCl_5 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl$$

1 chloro 2, 2
dimethyl propane

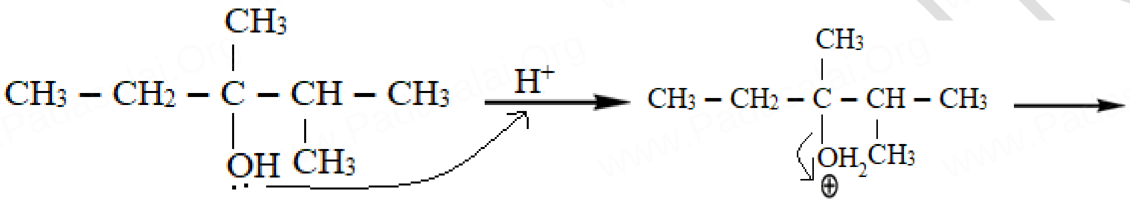




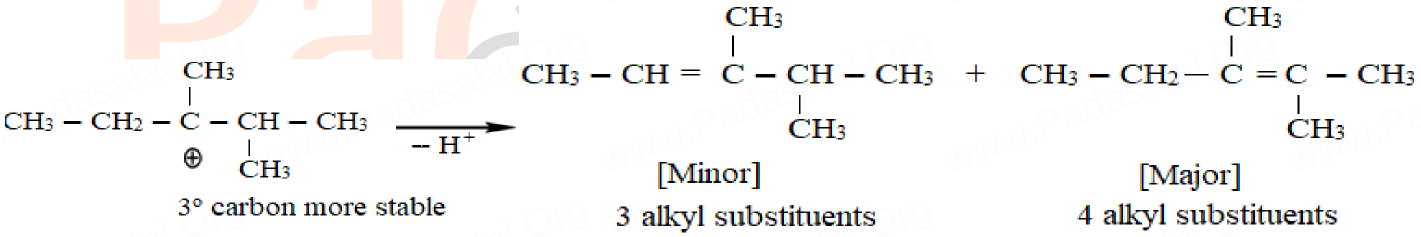
SN^2 mechanism

EVALUATE YOURSELF –4

What is the major product obtained when 2, 3 – dimethyl pentan -3 – ol is heated in the presence of H_2SO_4.



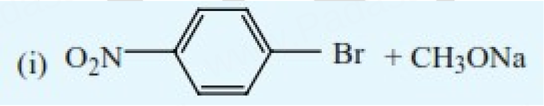
2, 3 dimethyl pentan 3 ol

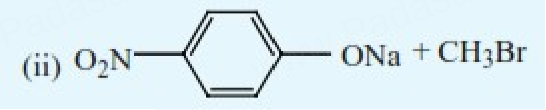


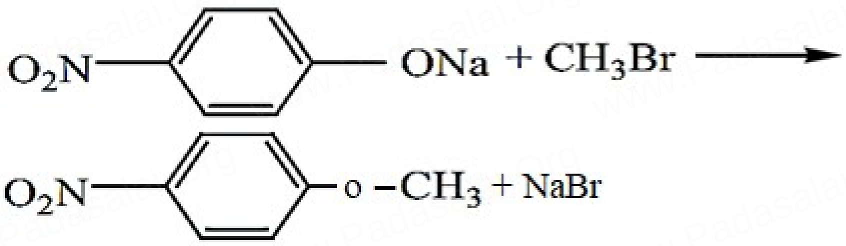
Saytzeff's rule

EVALUATE YOURSELF – 5

Which of the following set of reactants will give 1-methoxy-4-nitrobenzene.



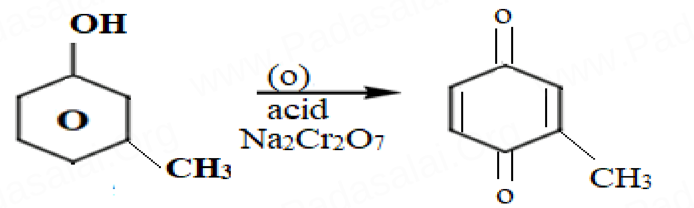




2^{nd} option

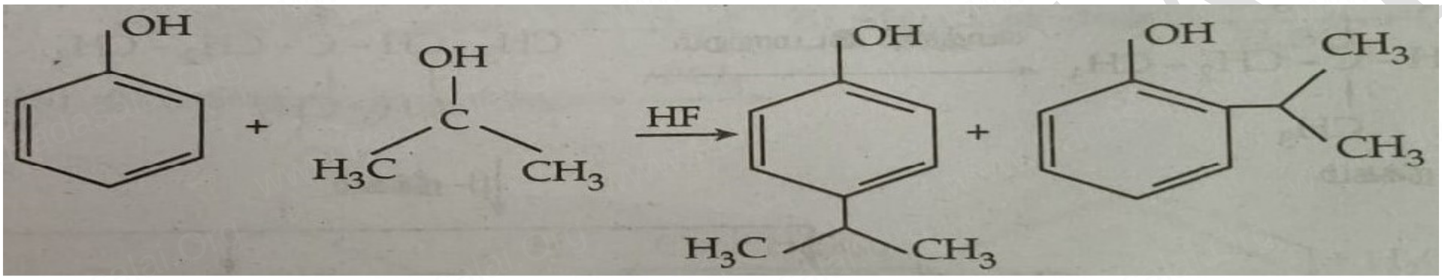
In P – nitrobromo benzene, Bromine is strongly bonded to Benzene ring. So C – Br Bond is not easily cleaved. We donot take P – nitro bromo benzene and sodium methoxide.

2. What happens when m-cresol is treated with acidic solution of sodium dichromate?



2, methyl 1, 4P benzo quinone

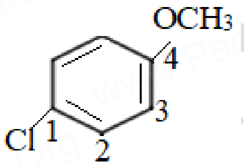
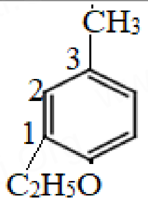
3. When phenol is treated with propan – 2 – ol in the presence of HF , Friedel –Craft reaction takes place. Identify the products.

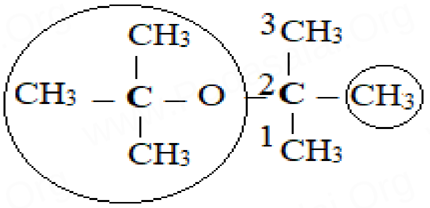
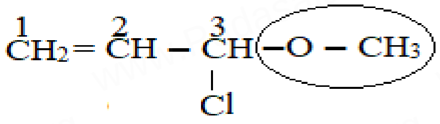
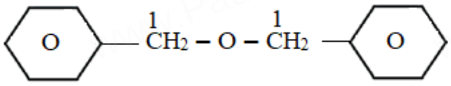


4 - **isopropyl phenol** 2 **- isopropyl phenol**

EVALUATE YOURSELF –6

Give the IUPAC name for the following ethers and classify them as simple or mixed.

SN o	Structure	IUPAC NAME
1	$CH_3 – CH_2 – O – CH_2\ CH_2\ CH_2 – CH_3$	1 ethoxy butane (Mixed ether)
2		1 chloro 4 methoxy benzene (Mixed ether)
3		1 ethoxy 3 methyl benzene (Mixed ether)
4.	$(CH_3)_3 – C – O – C\ (CH_3)_3$	2 (tert but oxy) 2 methyl propane (Simple ether)

	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-\overset{3\,CH_3}{\underset{1\,CH_3}{^{2}C}}-CH_3$	
5.	 $\overset{1}{C}H_2=\overset{2}{C}H-\underset{Cl}{\overset{3}{C}H}-O-CH_3$	3 chloro 3 methoxy prop 1 ene (Mixed ether)
6.	Dibenzyl ether $(C_6H_5CH_2)_2O$ 	1, 1 (oxy di methylene) dibenzene (Simple ether)
7.	Vinyl allyl ether $CH_2 = CH - O - \overset{3}{C}H_2 - \overset{2}{C}H = \overset{1}{C}H_2$	3 (ethenoxy) prop -1-ene (Mixed ether)

EVALUATE YOURSELF – 7

1. **Which of the following reaction will give 1-methoxy-4-nitrobenzene.**
   a. **4-nitro -1- bromobenzene + sodium methoxide**
   b. **b. 4-nitro sodium phenoxide + bromomethane**

Option b

4 – Nitro sodium phenoxide + Bromo methane

2. **Arrange the following compounds in the increasing order of their acid strength. propan1-ol, 2, 4, 6-trinitrophenol, 3-nitrophenol, 3, 5-dinitrophenol, phenol, 4-methylphenol.**

In 2, 4, 6 trinitrophenol, due to strong electron with drawal effect of the three nitrogroups, which stabilize the phenoxide ion formed.

In 3, 5 dinitrophenol, due to – I effect of 2 nitrogroups. It is more acidic than phenol.

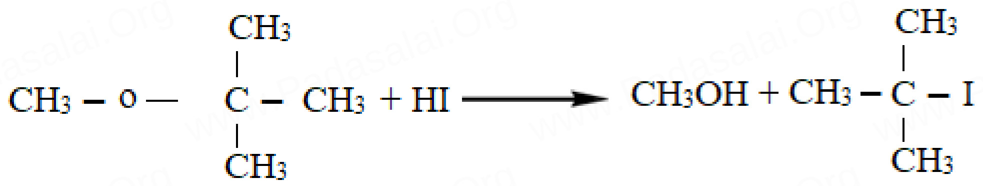
Phenol is acidic due to resonance stabilization of phenoxide ion.

4 methyl phenol is less acidic than phenol due to + I effect.

Propan – 1 ol is less acidic than 4 methyl phenol.

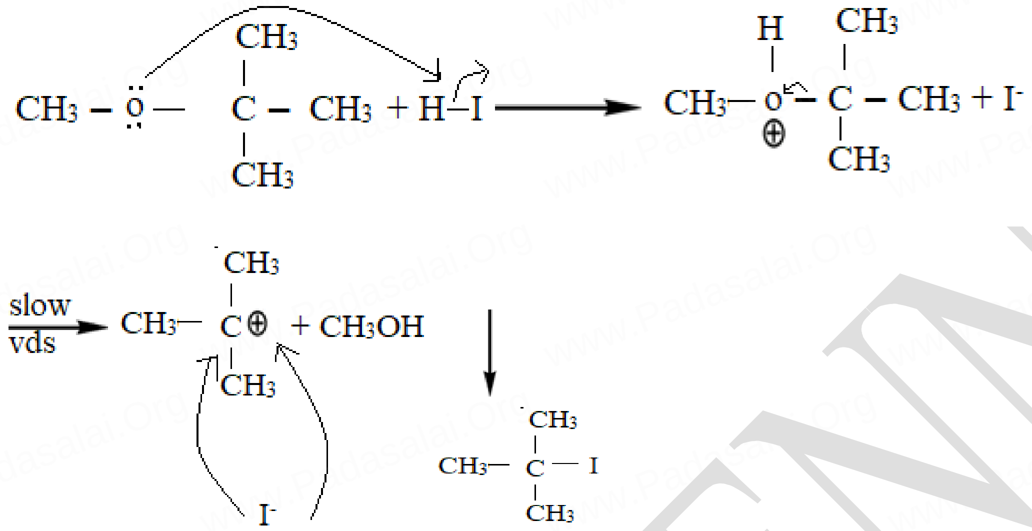
Propan 1 ol < 4 methyl phenol < phenol < 3-nitrophenol < 3, 5- dinitrophenol < 2, 4, 6 trinitrophenol

9. **1mole of HI is allowed to react with t-butyl methylether. Identify the product and write down the mechanism of the reaction.**



$$CH_3-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + HI \longrightarrow CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

The reaction involves protonation of oxygen which is followed by SN^1 mechanism



III. ADDITONAL QUESTIONS AND ANSWERS

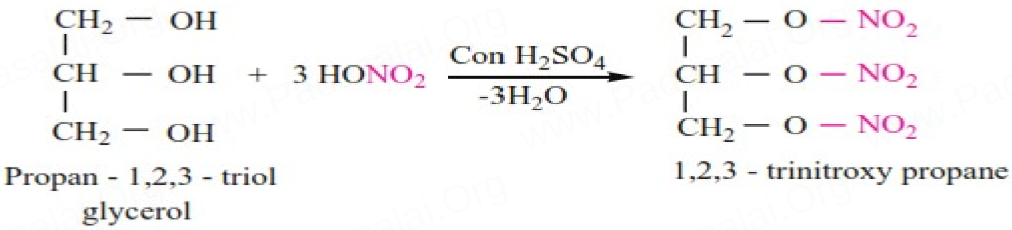
1. **Write the uses of ethylene glycol.**

i. It is used as an antifreeze in automobile radiator.

ii. Its dinitrate is used as an explosive in the name of DNG.

2. **How will you prepare nitroglycerine (TNG)?**

Glycerol is treated with mixture of con.HNO_3 and con. H_2SO_4 nitroglycerine is formed.Use: an explosive.



3. **Give the uses of glycerol.**

i. It is used as a sweetening agent in confectionary and beverages.

ii. It is used in the manufacture of cosmetics and transparent soaps.

iii. It is used in making printing inks and stamp pad ink and lubricant for watches and clocks.

iv. It is used in the manufacture of explosive like dynamite and cordite by mixing it with china clay.

4. **Write the uses of methanol.**

i. It is used as a solvent for paints, varnishes shellac, gums and cement.

ii. In the manufacture of dyes, drugs, perfumes and formaldehyde.

5. **Write the uses of ethanol.**

i. It is used as an important beverage.

ii. It is also used in the preparation of

a. Paints and varnishes.

b. Organic compounds like ether, $CHCl_3$, CHI_3**.**

c. Dyes, transparent soaps.

iii. As a substitute for petrol under the name power alcohol used as fuel for aeroplane

iv. It is used as a preservative for biological specimens.

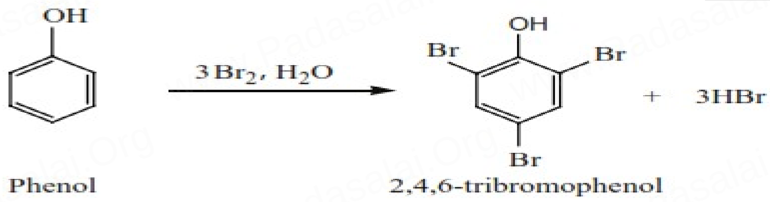
6. **What happens when phenol is heated with Zinc dust?**

Phenol is converted to benzene on heating with zinc dust.

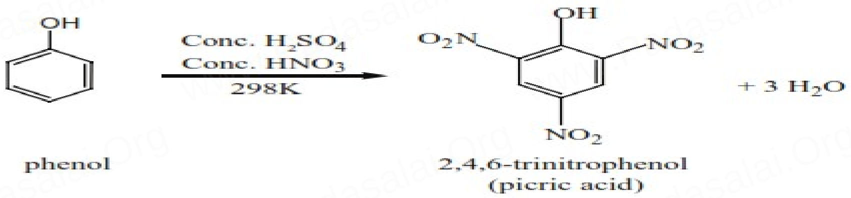
$$C_6H_5OH \xrightarrow[\Delta]{Zn} \underset{\text{Benzene}}{C_6H_6} + ZnO$$

7. **How to prepare the following from phenol?**

a. 2, 4, 6 – tri bromo phenol: When phenol is treated with bromine water, it gives white precipitate which is 2, 4, 6 – tri bromophenol.

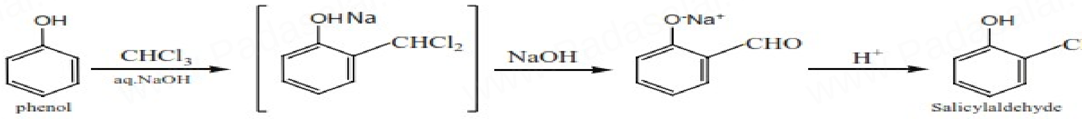


b. Picric acid: When phenol reacts with nitrating mixture con. H_2SO_4 and con. HNO_3 the product formed is picric acid.



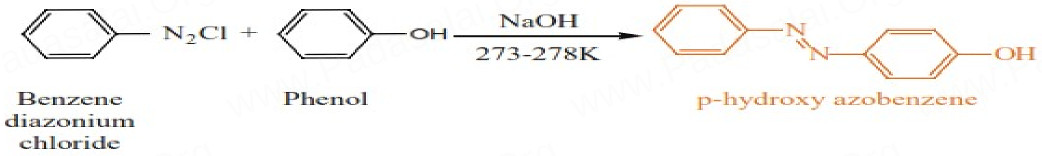
8. **Write note on Riemer – Tiemann reaction.**

When phenol is heated with $CHCl_3$/NaOH the product formed is salicylaldehyde.



9. **Write note on coupling reaction.**

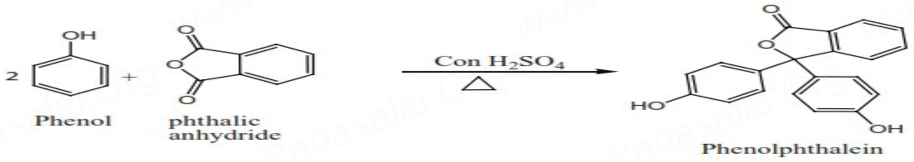
P – hydroxy azobenzene: When phenol, benzene diazonium chloride and NaOH solution are mixed coupling reaction take place to give p - hydroxy azobenzene.



This is called dye test.

10. **Explain Phthalein reaction.**

Phthalein fusion reaction: Phenols are heated with phthalic anhydride and con. H_2SO_4 to give phenolphthalein.



11. **Write any three tests to differentiate alcohols and phenols.**

a. Phenols + neutral $FeCl_3$ → Purple colour

b. Phenol + C6H5$N_2^+Cl^-$ → Red orange colour.

c. Phenol + NaOH → Sodium phenoxide

Alcohols do not answer all the above tests.

12. **Write the uses of phenol.**

i. It is used for making phenol formaldehyde resin (Bakelite).

ii. Starting material for the preparation of

- **a.** Drugs such as phenacetin, Salol, aspirin.
- **b.** Phenolphthalein indicator.
- **c.** explosive like picric acid.

iii. It is used as an antiseptic – carbolic lotion and carbolic soaps.

13. **Give the uses of diethyl ether and anisole.**

a. Diethylether:

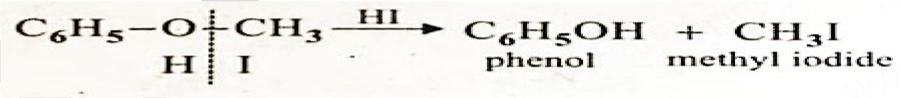
- **i.** It is used as a surgical anaesthetic agent.
- **ii.** Good solvent for organic reactions and extraction.
- **iii.** A volatile starting fluid for diesel and gasoline engine.
- **iv.** As a refrigerant.

b. Anisole:

- **i.** It is a precursor to the synthesis of perfumes and insecticide pheromones.
- **ii.** As a pharmaceutical agent.

14. **What happens when Anisole reacts with HI?**

Anisole reacts with HI to give phenol and methyl iodide.



$$\underset{H}{C_6H_5-O} \vdots \underset{I}{CH_3} \xrightarrow{HI} \underset{\text{phenol}}{C_6H_5OH} + \underset{\text{methyl iodide}}{CH_3I}$$

UNIT: 12

CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS

I. TEXT BOOK QUESTIONS AND ANSWERS.

1. How is propanoic acid prepared starting from (a) an alcohol (b) an alkyl halide (c) an alkene

a) From an alcohol:- primary alcohols can be oxidised to carboxylic acids with oxidising agents such as potassium permanganate (in acidic or alkaline medium), potassium dichromate (in acid medium).

$$\underset{\text{Propane-l-ol}}{CH_3-CH_2-CH_2-OH} \xrightarrow[(O)]{H^+/K_2Cr_2O_7} \underset{\text{propanoic acid}}{CH_3CH_2COOH}$$

b) From an alkyl halide:-

$$\underset{\text{Bromo propane}}{CH_3-CH_2-CH_2Br} \xrightarrow{\text{aquous KOH}} \underset{\text{propan-1-ol}}{CH_3-CH_2-CH_2-OH} \xrightarrow[(O)]{H^+/K_2Cr_2O_7} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

c) From an alkene:-

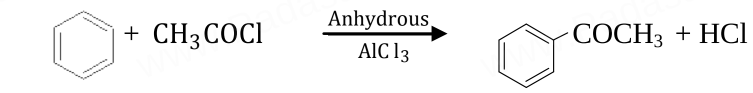
$$\underset{\text{Propene}}{6CH_3 - CH = CH_2} \xrightarrow[\text{(ii)}H_2O_2/OH]{\text{(I) }B_2H_6} \underset{\text{Propan-l-ol}}{CH_3CH_2CH_2OH} \xrightarrow[H^+/K_2Cr_2O_7]{(O)} \underset{\text{Propanoic acid.}}{CH_3CH_2COOH}$$

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 ofanhydrous $AlCl_3$ to give copound (D). Compound (D) on reduction with Zn-Hg Con HCl gives (E). Identity (A), (B), (C), (D) and (E) Write the equations.

Compound (A) with molecular formula C_2H_3N is methyl cyanide (CH_3CN)

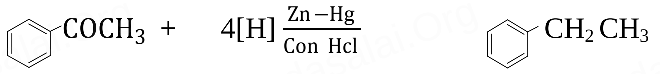
$$\underset{\substack{\text{(A)}\\ \text{Methyl cyanide}}}{CH_3CN} \xrightarrow{H^+/H_2O} \underset{\substack{\text{(B)}\\ \text{Acetic acid}}}{CH_3COOH}$$

$$\underset{\substack{\text{(B)}\\ \text{Acetic acid}}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\substack{\text{(C)}\\ \text{Acetyl chloride}}}{CH_3COCl} + SO_2 + HCl$$

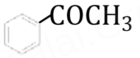
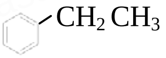


Benzene (C) (D)

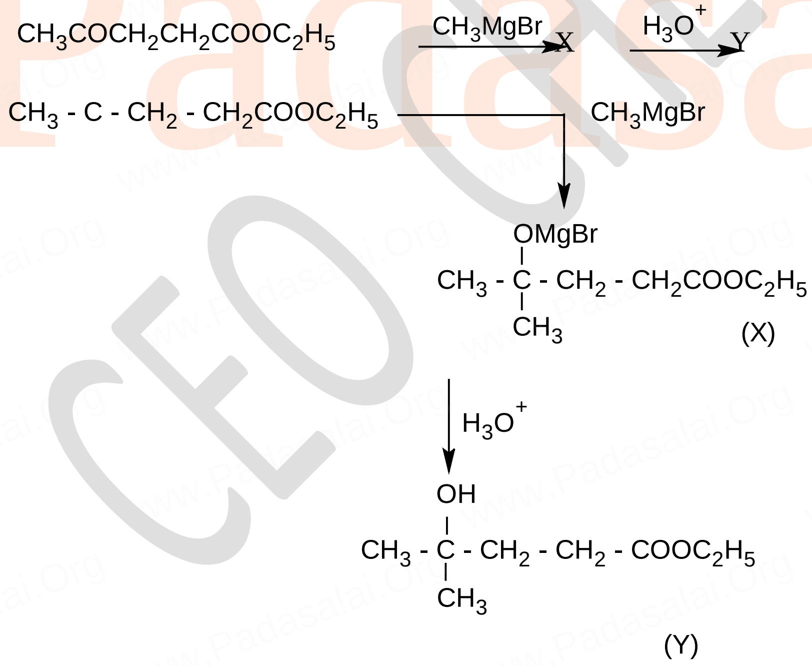
Acetophenone



Acetophenone Ethyl benzene

A	CH_3CN	Methyl cyanide
B	CH_3COOH	Acetic Acid
C	CH_3COCl	Acetyl chloride
D		Acetophenone
E		Ethyl benzene

3. Identify x and y.



$CH_3COCH_2CH_2COOC_2H_5 \xrightarrow{CH_3MgBr} X \xrightarrow{H_3O^+} Y$

$CH_3 - C - CH_2 - CH_2COOC_2H_5$ CH_3MgBr

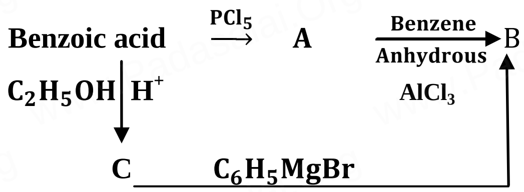
$CH_3 - \overset{OMgBr}{\underset{CH_3}{C}} - CH_2 - CH_2COOC_2H_5$ (X)

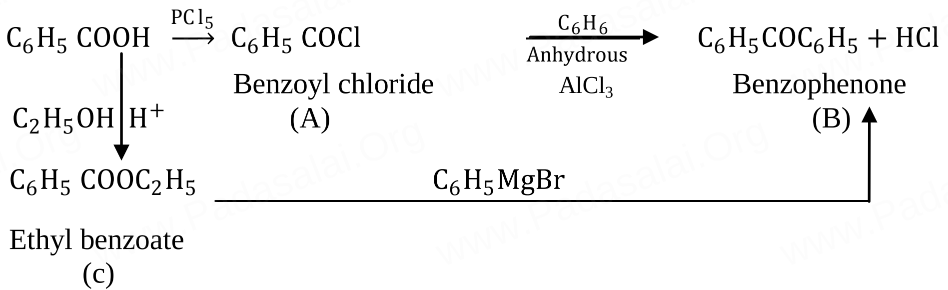
$\downarrow H_3O^+$

$CH_3 - \overset{OH}{\underset{CH_3}{C}} - CH_2 - CH_2 - COOC_2H_5$

(Y)

4. Identify A, B, and C.





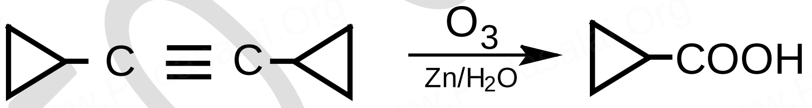
A	C_6H_5COCl	Benzoyl chloride
B	$C_6H_5COC_6H_5$	Benzophenone
C	$C_6H_5COOC_2H_5$	Ethyl benzoate

5. A hydrocarbon (A) (molecular formula C_8H_{10}) on ozonolysis gives (B) ($C_4H_6O_2$) only. compound (C_3H_5Br) on treatment with Magnesium in dry ether gives (D) which on treatment with CO_2 followed by acidification gives (C). identify A,B,C&D

compound (A) molecular formula C_8H_{10} is 1,2 - dicyclopropylethyne.

(A)

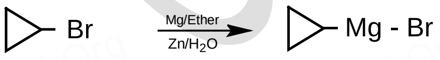
1,2 - dicyclopropylethyne (A) on ozonolysis gives cyclopropylcarboxylic acid (B)



(A) (B)

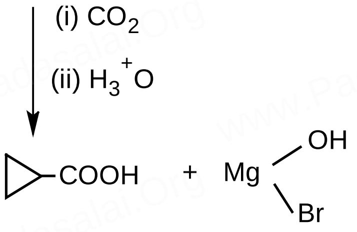
Cyclopropyl carboxdylic acid

compound C_3H_5Br is Bromo cyclo propane.



(C) (D)

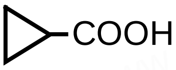
Bromo Cyclo propane Cyclo propyl magnesium bromide



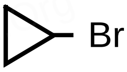
(B)

A) 

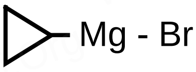
1,2 - dicyclo propyl ethyne

B) 

cyclopropyl carboxylic acid

C) 

Bromo cyclo propane

D) 

Cyclo propyl magnesium bromide

6. Identity A, B, C and D.

Ethanoic acid $\xrightarrow{SOCl_2}$ A $\xrightarrow{Pd/Bas\,o_4}$ B $\xrightarrow{NaOH}$ C $\xrightarrow[\Delta]{}$ D

$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl \xrightarrow[H_2]{Pd/\ Bas\,o_4} CH_3CHO + HCl$

Acetyl chloride (A) Acetaldehyde (B)

$\downarrow$ NaOH

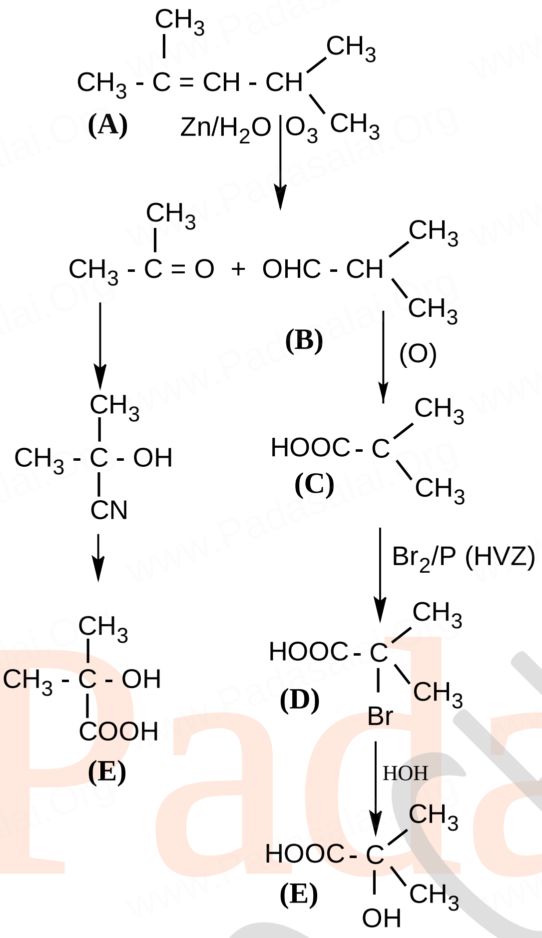
$CH_3-CH=CH-CHO \xleftarrow[\Delta]{-H_2O} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO$

Crotonaldehyde 3- hydroxyl butanal (Aldol)

(D) (c)

A	CH_3COCl	Acetyl chloride
B	CH_3CHO	Acetaldehyde
C	$CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2-CHO$	3-hydroxyl butanal
D	$CH_3-CH=CH-CHO$	Crotonaldehyde

7. An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidized (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.



A	2,4 - dimethyl pent - 2 - ene
B	2 - methyl propanal
C	2 - methyl propanoic acid
D	2- bromo - 2 - methyl propanoic acid
E	2 - hydroxyl - 2 - methyl propanoic acid

8. How will you convert benzaldehyde into the following compounds?

i. **Benzophenone** ii. **Benzoic acid**

iii. **∝- hydroxy phenylacetic acid.**

i. Benzaldehyde into Benzophenone.

$$C_6H_5CHO + Cl_2 \longrightarrow C_6H_5COCl \xrightarrow[\text{anhy } AlCl_3]{C_6H_6} C_6H_5COC_6H_5$$

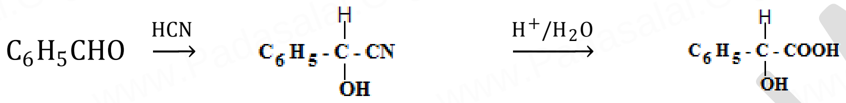
Benzaldehyde Benzoylchloride Benzophenone.

ii. Benzaldehyde into benzoic acid.

$$C_6H_5CHO \xrightarrow[(O)]{H^+/K_2Cr_2O_7} C_6H_5COOH$$

Benzaldehyde Benzoic acid

iii. Benzaldehyde into ∝- hydroxy phenyl acetic acid.



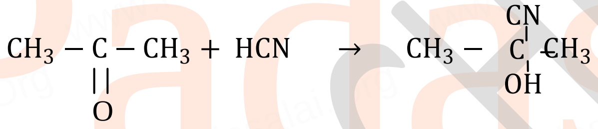
$$C_6H_5CHO \xrightarrow{HCN} C_6H_5-\underset{OH}{\overset{H}{C}}-CN \xrightarrow{H^+/H_2O} C_6H_5-\underset{OH}{\overset{H}{C}}-COOH$$

Benzaldehyde Phenyl Cyanohydrin ∝- hydroxy phenyl acetic acid
Mandelic acid

9. What is the action of HCN on

(i) Propanone (ii) 2,4 dichloro benzaldehyde

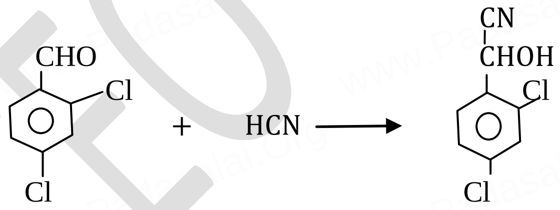
(iii) ethanal



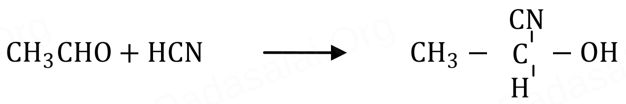
i. $$CH_3-\underset{O}{\underset{||}{C}}-CH_3 + HCN \rightarrow CH_3-\underset{OH}{\overset{CN}{C}}-CH_3$$

Propanone Acetone Cyanohydrin

ii.



2,4- dichloro benzaldehyde 2,4-dichloro benzaldehyde cyano-hydrin



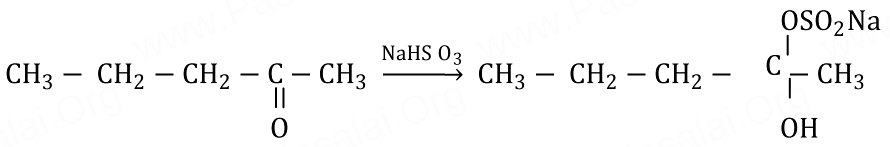
iii $$CH_3CHO + HCN \longrightarrow CH_3-\underset{H}{\overset{CN}{C}}-OH$$

ethanal Acetaldehyde cyano-hydrin

10. 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'.

Compound (A) having molecular formula $C_5H_{10}O$ is pentan -2-one

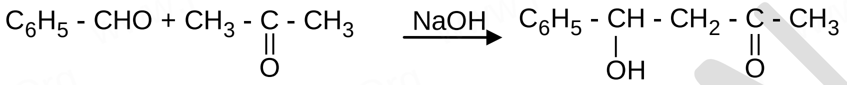
It gives positive iodoform test, but does not reduce fehling solution.



$$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaHSO_3} CH_3-CH_2-CH_2-\overset{OSO_2Na}{\underset{OH}{C}}-CH_3$$

Pentan-2-one

11. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.



$$C_6H_5-CHO+CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} C_6H_5-\underset{OH}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

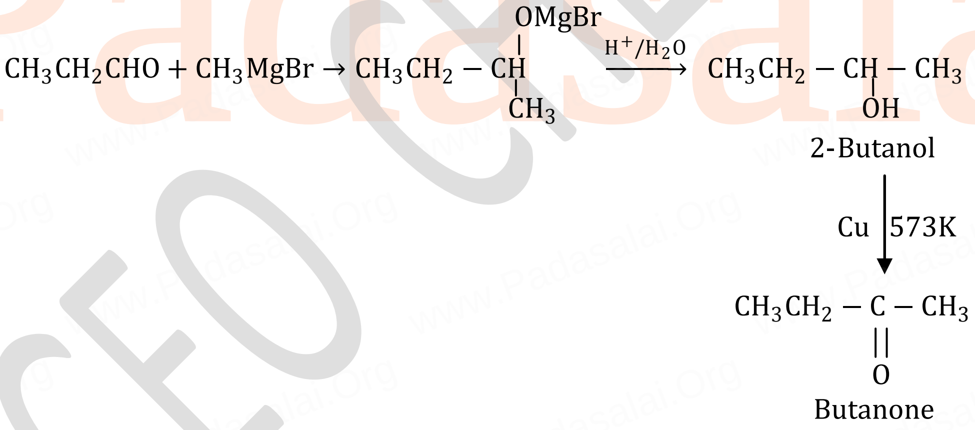
12. How are the following conversions effected.

a) Propanal into butanone

b) Hex-3-yne into hexan-3-one

c) Phenyl methanal into benzoic acid

d) Phenyl methanal into benzion



$$CH_3CH_2CHO+CH_3MgBr \rightarrow CH_3CH_2-\overset{OMgBr}{\underset{CH_3}{CH}} \xrightarrow{H^+/H_2O} CH_3CH_2-\underset{OH}{CH}-CH_3$$

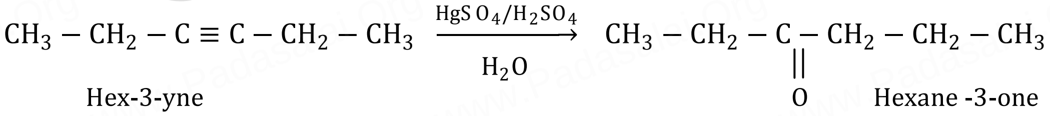
2-Butanol

$$\downarrow \text{Cu } 573K$$

$$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Butanone

b) Hex-3-yne into hexan-3-one



$$CH_3-CH_2-C\equiv C-CH_2-CH_3 \xrightarrow[H_2O]{HgSO_4/H_2SO_4} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

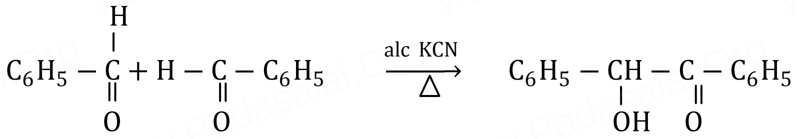
Hex-3-yne Hexane -3-one

c) Phenyl methanal into benzoic acid

$$C_6H_5CHO \xrightarrow[(O)]{H^+/K_2Cr_2O_7} C_6H_5COOH$$

Phenyl methanal (Benzaldehyde) Benzoic acid

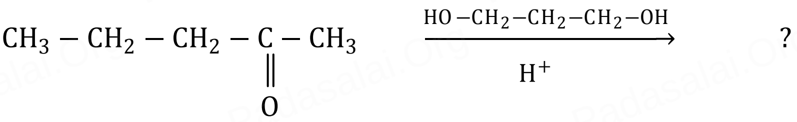
d) Phenyl methanal into benzoin (Benzoin Condensation)



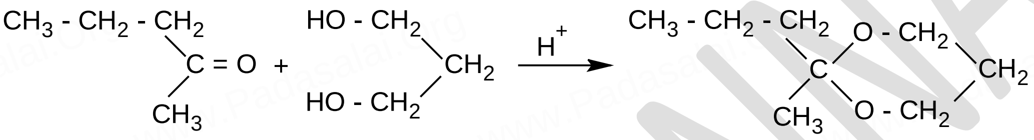
$$C_6H_5-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}}+H-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[\Delta]{alc\ KCN} C_6H_5-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-C_6H_5$$

Phenyl methanol benzoin

13. Complete the following reaction.

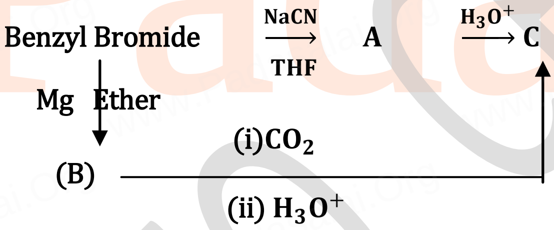


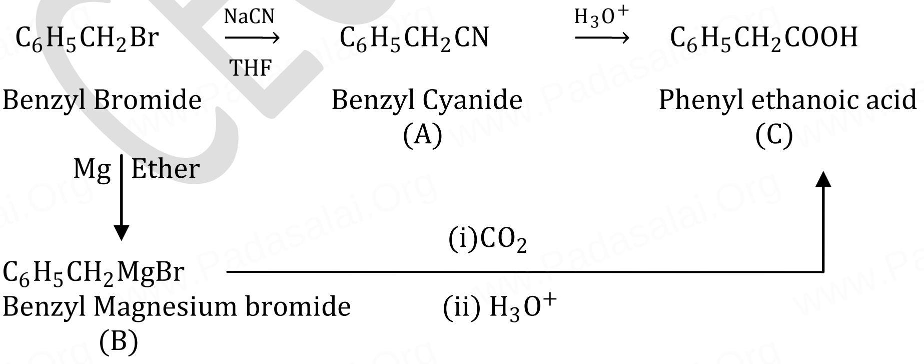
$$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[H^+]{HO-CH_2-CH_2-CH_2-OH} ?$$



Cyxlicketal

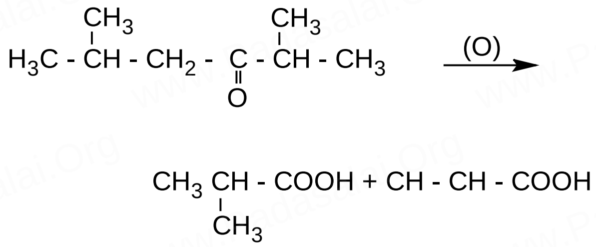
14. Identify A, B and C





A	$C_6H_5CH_2CN$	Benzyl Cyanide
B	$C_6H_5CH_2MgBr$	Benzyl Magnesium Bromide
C	$C_6H_5CH_2COOH$	Phenyl ethanoic acid

15. oxidation of ketones involves carbon - carbon bond cleavage. Name the product(s) is / are formed on oxidizing 2,5 - dimethyl hexan - 3 - one sing strong oxidizing agent.



$$H_3C-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_3 \xrightarrow{(O)}$$

$$CH_3\,\underset{CH_3}{\underset{|}{CH}}-COOH+CH-CH-COOH$$

16. How will you prepare

(i) Acetic anhydride from acetic acid

(ii) Ethyl acetate from methyl acetate

(iii) Acetamide from methyl cyanide

(iv) Lactic acid from ethanol

(v) Acetephenone from acetyl chloride

(vi) Ethane from sodium acetate

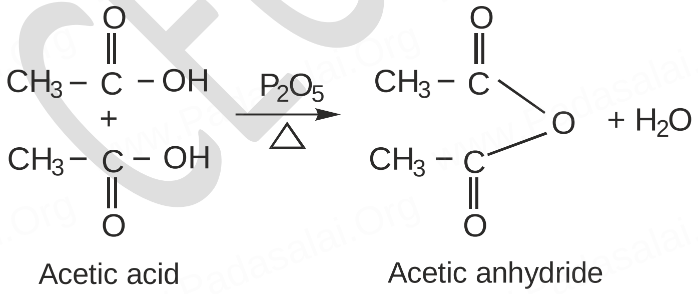
(vii) Benzoic acid from tolueue

(viii) Malachite green from benzaldehyde

(ix) Cinnamic acid from benzaldehyde

(x) Acetaldehyde from ethyne

(i) Acetic antydride from acetic acid



(ii) Ethyl acetate from methyl acetate (trans esterifcation)

$CH_3COOCH_3 + C_2H_5OH \xrightarrow{H+} CH_3COOC_2H_5 + CH_3OH$

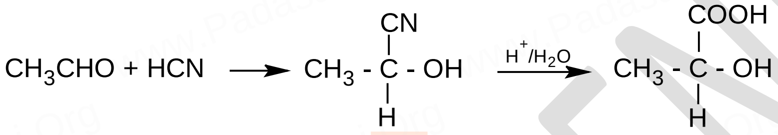
methyl acetate Ethanol ethyl acetate Methanol

(iii) Acetamide from methyl cyanide

$CH_3CN \xrightarrow[H_2O]{\text{Conc HCl}} CH_3CONH_2$

methyl cyanide Acetamide

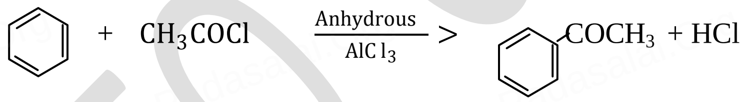
(iv) Lactic acid from ethanal



$$CH_3CHO + HCN \longrightarrow CH_3-\overset{\overset{\Large CN}{|}}{\underset{\underset{\Large H}{|}}{C}}-OH \xrightarrow{H^+/H_2O} CH_3-\overset{\overset{\Large COOH}{|}}{\underset{\underset{\Large H}{|}}{C}}-OH$$

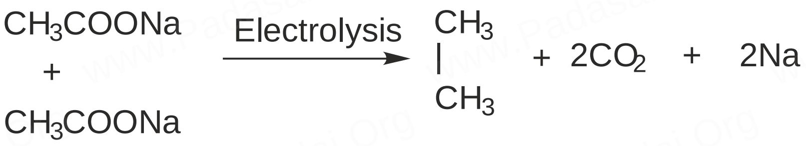
ethanal Acetaldehyde cyanohydrin Lactic acid

(v) Acetephenone from acetyl chloride



Benzene Acetyl chloride Acetophenone

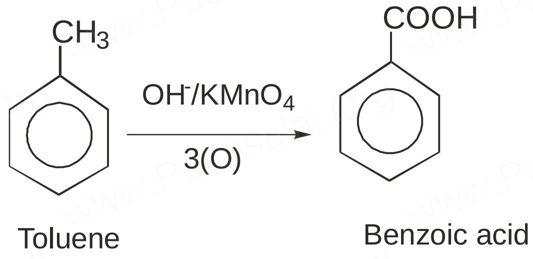
(vi) Ethane from sodium acetate (Kolbe 's Electrolysis)



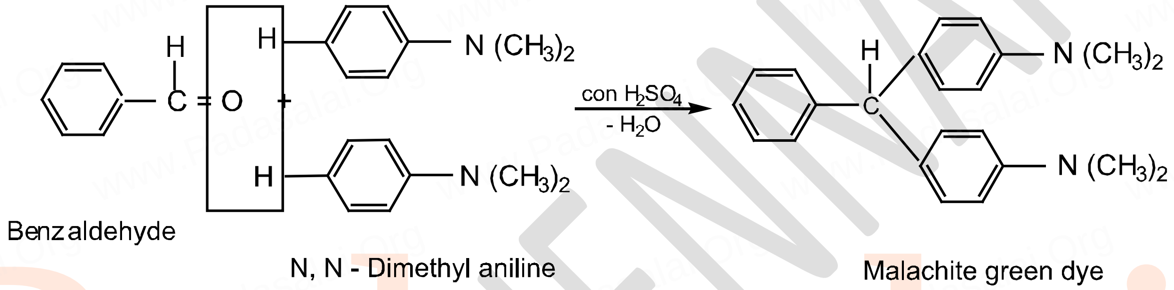
$$\begin{array}{c} CH_3COONa \\ + \\ CH_3COONa \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2CO_2 + 2Na$$

sodium acetate ethane

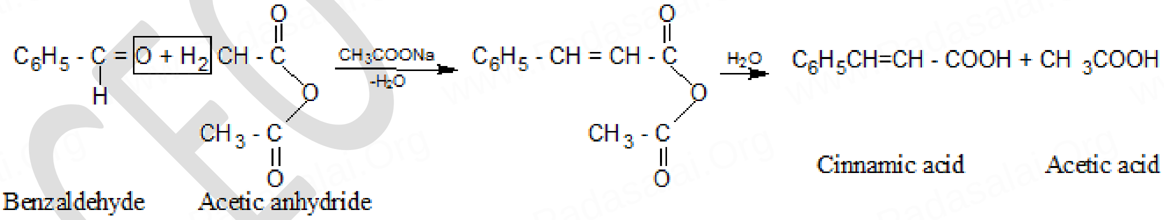
(vii) Benzoic acid from toluene



(viii) Malachitegreen from benzaldehyde



(ix) Cinnamic acid from benzaldehyde (Perkin's Reaction)



(x) Acetaldehyde from ethyne

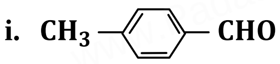
$$HC\equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} CH_3-CHO$$

ethyne acetaldehyde

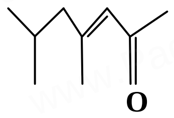
II. Evaluate yourself.

Evaluate yourself – 1 (page 148)

1. Write the IUPAC name for the following compound.

i. 

ii. $(CH_3)_2\ C = CH\ COCH_3$

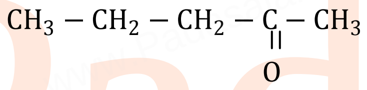
iii. 

iv. $(CH_3)_2C(OH)CH_2CHO$

Answer:

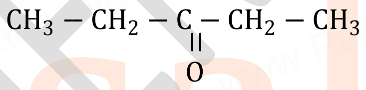
i. 4- Methyl benzaladehyde
ii. 4- Methyl pent-3-en-2-one
iii. 4,6-dimethyl hept -3-en-2-one
iv. 3 hydroxy -3-methyl butanal

2. Write all possible structural isomers and position isomers for the ketone represented by the molecular formula $C_5\ H_{10}O$

i. 

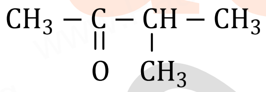
$CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_3$

Pentan-2-one

ii. 

$CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3$

Pentan-3-one

iii. 

$CH_3 - \underset{\underset{O}{\|}}{C} - \underset{\underset{CH_3}{|}}{CH} - CH_3$

3-Methyl butan-2-one

Evaluate yourself – II (page 149)

1. What happens when the following alkenes are subjected to reductive ozonolysis ?

i. propene ii. 1-Butene iii. Isobutylene

i. propene

$$CH_3CH = CH_2 \xrightarrow[Zn/H_2O]{O_3} CH_3CHO + H\ CHO$$

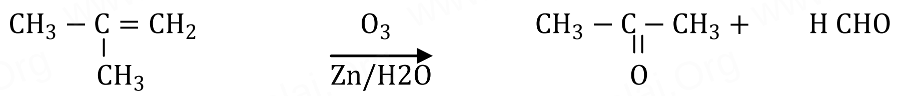
Propene acetaldehyde formaldehyde

ii. 1-Butene

$$CH_3CH_2CH = CH_2 \xrightarrow[Zn/H_2O]{O_3} CH_3CH_2CHO + H\ CHO$$

1-Butene Propanaldehyde formaldehyde

iii. Isobutylene

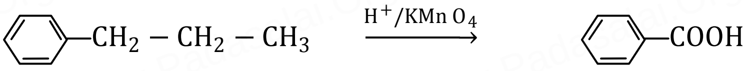


$$CH_3 - \underset{\substack{| \\ CH_3}}{C} = CH_2 \xrightarrow[Zn/H2O]{O_3} CH_3 - \underset{\substack{|| \\ O}}{C} - CH_3 + HCHO$$

Isobutylene Acetone formaldehyde

Evaluate yourself III (Page 171)

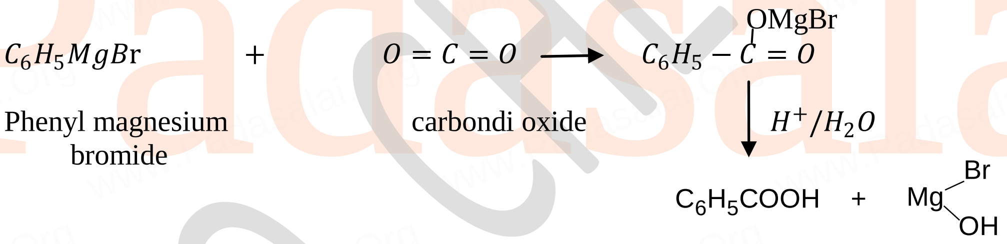
1. **What happens when n-propyl benzene is oxidized using $H^+/KMnO_4$?**



n-propyl benzene Benzoic acid

The entire side chain is oxidised to – COOH group irrespective of the length of the side chain.

2. **How will you prepare benzoic acid using grinard reagent?**



C_6H_5MgBr + $O = C = O$ → $C_6H_5 - \overset{\substack{OMgBr \\ |}}{C} = O$ $\xrightarrow{H^+/H_2O}$ C_6H_5COOH + Mg(Br)(OH)

Phenyl magnesium bromide carbondi oxide

Benzoic acid

Evaluate yourself IV (page-186)

Why is acid anhydride preferred to acyl chloride for carrying out acylation reactions ?

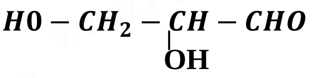
When acylation is carried out with acetyl chloride, the by product is HCl which is a strong acid that leads to side reaction. Whereas acid anhydride is used for acylation, acetic acid is formed. Acetic acid is a weak acid and there is no side reaction.

III. Additional Questions and Answers

1. **Give the IUPAC name of the following**

(i) $CH_2 = CH - CHO$ **(ii)** $CH_3CH = CH - CHO$

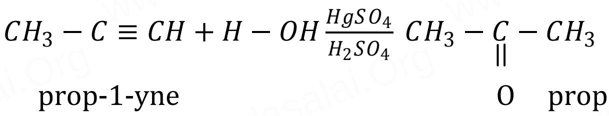
(iii)



$HO - CH_2 - \underset{\substack{| \\ OH}}{CH} - CHO$

(i) prop-2-enal
(ii) but-2-enal
(iii) 2,3 dihydroxy propanal

2. How will you prepare propanone from prop-1-yne?

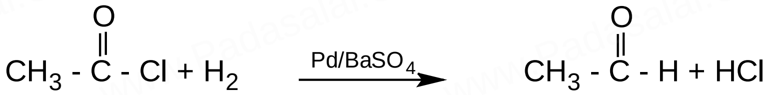


$$CH_3 - C \equiv CH + H - OH \xrightarrow[H_2SO_4]{HgSO_4} CH_3 - \underset{\underset{O}{\parallel}}{C} - CH_3$$

prop-1-yne propanone

3. Wite about Rosenmund reduction:

Aldehydes can be prepared by hydrogenation of acid chloride, in the presence of Pd / $BaSO_4$

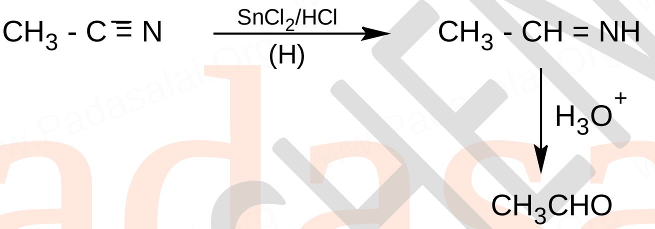


$$CH_3 - \overset{\overset{O}{\parallel}}{C} - Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3 - \overset{\overset{O}{\parallel}}{C} - H + HCl$$

Acetyl chloride Acetaldehyde

4. Explain Stephen's reaction:

When alkylcyanides are reduces using $Sncl_2$/HCl, imines are formed, which on hydrolysis gives corresponding aldehyde

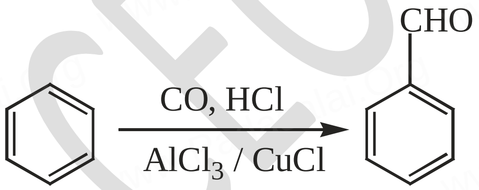


$$CH_3 - C \equiv N \xrightarrow[(H)]{SnCl_2/HCl} CH_3 - CH = NH \xrightarrow{H_3O^+} CH_3CHO$$

Acetaldehyde

5. Write about 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.



6. How is urotropine prepared? Write its use?

Formaldehyde reacts with ammonia to form hexa methylene tetramine which is also known as urotropine.

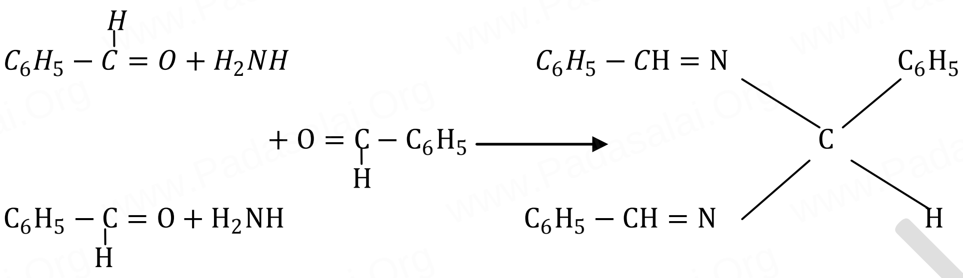
$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$

Formaldehyde urotropine

Use : Medicine to treat urinary infection

7. How is hydro benzamide prepared?

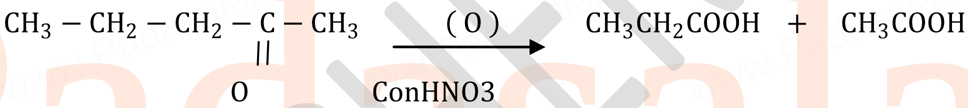
Benzaldehyde form a complex condensation product with ammonia.



Benzaldehyde ammonia. hydro benzamide

8. What is popoff's rule? Give example (or) The oxidization of unsymmetrical ketone is governed by which rule? State the rule with suitable example

popoff's rule 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.

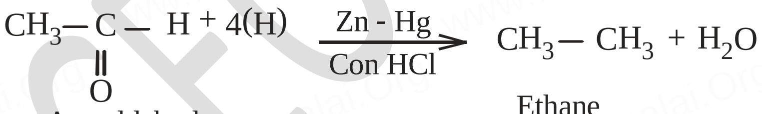


$$CH_3-CH_2-CH_2-\underset{\underset{O}{||}}{C}-CH_3 \xrightarrow[\text{ConHNO3}]{(O)} CH_3CH_2COOH + CH_3COOH$$

Pentan-2-one propanoic acid ethanoic acid

9. Explain Clemmensen reduction:

Aldehydes and ketones when heated with Zinc amalgam and concentrates hydrochloric and gives hydrocarbons.

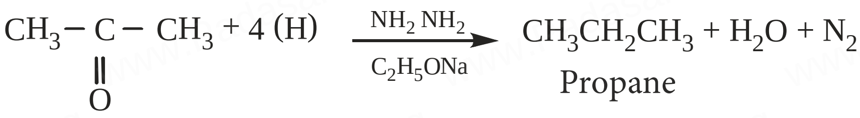


$$CH_3-\underset{\underset{O}{\|}}{C}-H + 4(H) \xrightarrow[\text{Con HCl}]{\text{Zn - Hg}} CH_3-CH_3 + H_2O$$

Acetaldehyde Ethane

10. What is Wolf Kishner reduction? Give example.

Aldehydes and ketones when heated hydrazine (NH_2NH_2) and Sodium ethoxide, hydrocarbons are formed.

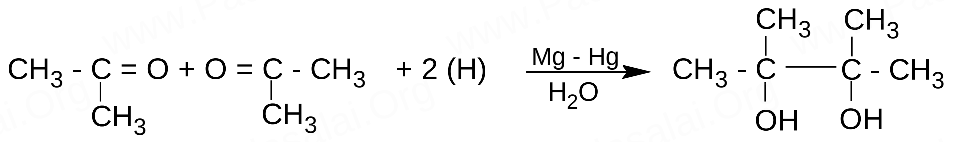


$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 4\,(H) \xrightarrow[C_2H_5ONa]{NH_2\,NH_2} CH_3CH_2CH_3 + H_2O + N_2$$

Acetone Propane

11. How are pinacols obtained?

Ketones, on reduction with magnesium, amalgam and water are reduced to symmetrical diols known as pinacol.



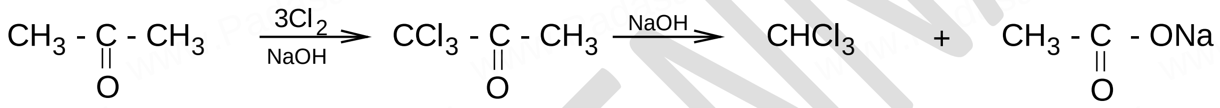
$$CH_3-\underset{CH_3}{\underset{|}{C}}=O + O=\underset{CH_3}{\underset{|}{C}}-CH_3 + 2(H) \xrightarrow[H_2O]{Mg-Hg} CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$$

Acetone Acetone 2,3 – dimethyl butane – 2,3 – diol

(pinacol)

12. Explain Haloform reaction:

Acetaldehyde and methyl ketones, containing $CH_3-\underset{O}{\underset{\|}{C}}-$ group, when treated with halogen and alkali give the corresponding haloform



$$CH_3-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow[NaOH]{3Cl_2} CCl_3-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{NaOH} CHCl_3 + CH_3-\underset{O}{\underset{\|}{C}}-ONa$$

chloroform

13. Give Claisen-Schmidt Condensation:

Benzadehyde condenses with aliphatic aldehyde or methyl ketone in the presence of dil alkali at room temperature to form unsaturated aldehyde or ketone.

$$C_6H_5CH\boxed{O+H_2}CH\ CHO \xrightarrow{dil\,NaOH} C_6H_5CH=CH-CHO + H_2O$$

Benzaldehyde Acetaldehyde Cinnamaldehyde

14. How is Schiff's base obtained?

Aromatic aldehyes react with primary amines (aliphatic or aromatic) in the presence of an acid to form schiff's base

$$C_6H_5CHO + H_2N-C_6H_5 \xrightarrow[\Delta]{H^+} C_6H_5CH=N-C_6H_5 + H_2O$$

Benzal aniline
(Schiff's base)

15. Give the tests for Aldehydes:

(i) Tollen's Reagent test : When an aldehyde is warmed with Tollen's reagent a bright silver mirror is produced

(ii) Fehlings solution test: When aldehyde is warmed with Fehlings solution deep blue colour solution is changed to red precipitate

(iii) Benedict's solution test: Benedicts solution is reduced by aldehyde to give red precipitate

(iv) Schiff's reagent test: Dilute solution of aldehydes when added to Schiff's reagent yields its red colour

16. Mention the Tests for Carboxylic acid:

(i) Turns blue litmus red

(ii) Gives brisk effervescence with sodium bicarbonate

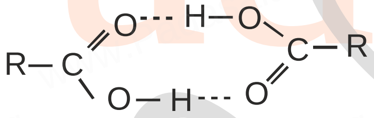
(iii) Warmed with alcohol and conc H_2SO_4 it forms an ester, which is detected by its fruity odour

17. Why acetic acid is less acidic than Formic acid?

In acetic acid, the electron releasing group (+I group) increases the negative charge on the carboxylate ion and destabilize it and hence the loss of proton becomes difficult.

18. Why Carboxylic acids have higher boiling point than aldehyeds, ketones and alcohols of comparable molecular masses?

This is due to more association of carboxylic acid molecules through intermolecular hydrogen bonding. They exist as dimer in its vapour state.

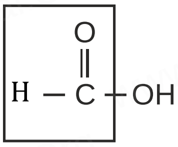


19. What is glacial acetic acid? How is it obtained?

Pure acetic acid is called glacial acetic acid. Because it forms ice like crystal when cooled. When aqueous acetic acid is cooled at 289.5K, acetic acid solidifies and forms ice like crystals, where as water remains in liquid state and removed by filtration.

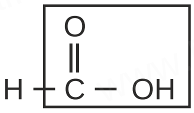
20. Why formic acid reduces Tollens reagent and Fehlings solution? (or) Account for reducing property of formic acid?

Formic acid contains both an aldehyde as well as an acid group.
Like other aldehydes, formic acid can easily be oxidised and thereore acts as a strong reducing agent.



$H-\overset{\overset{O}{\|}}{C}-OH$

Aldehyde group



$H-\overset{\overset{O}{\|}}{C}-OH$

Carboxylic acid group

Hence it reduces Tollens reagent and Fehlings solution

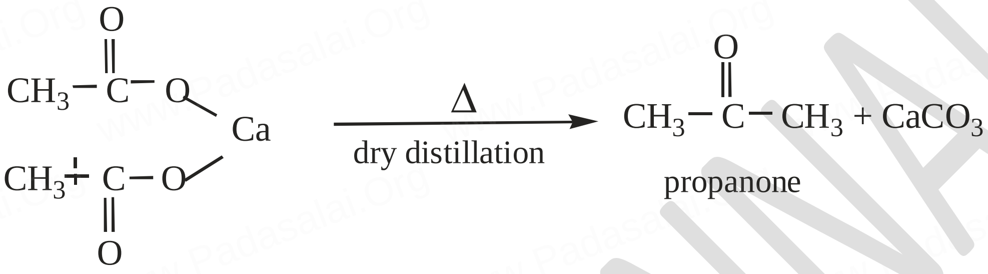
example: $HCOO^- + 2Ag^+ + 3OH^- \longrightarrow 2Ag + CO_3^{2-} + 2H_2O$

21. Formic acid does not undergo HVZ reactive (Hell-Volhard Zelinsky reaction) but CH_3COOH give HVZ reaction? Why?

Formic acid does not contain ∝-hydrogen atom, but acetic acid contains ∝-hydrogen ato

22. Explain dry distillation of Calcium ethanoate.

Dry distillation of calcium ethanoate gives propanone



Calcium ethanoate

23. Give the uses of the following

a) formaldehyde
b) Acetaldehyde
c) Aetone
d) Benzaldehyde
e) Acetophenone
f) Benzophenone
g) Formic acid
h) Acetic acid
i) benzoic acid:
k) Acetic anhydride
l) Ethyl acetate:

a) Uses of formaldehyde

1. 40% aqueous solution of formaldehyde is called formalin. It is used for preserving biological specimens
2. It has hardening effect, hence it is used for tanning
3. Used in the production of thermo setting plastic-bakelite

b) Uses of Acetaldehyde

(i) Used for silvering of mirrors
(ii) Paraldehyde is used in medicine as a hypnotic
(iii) Commercial preparation of acetic acid, ethyl acetate etc.,

c) Uses of Aetone

(i) Used as solvent in the manufacture of smokeless powder(cordite)
(ii) Used as a nail polish remover
(iii) Used in the preparation of sulphonal, a hypnotic
(iv) Used in the manufacture of thermosoftening plastic Perspex

d) Uses of Benzaldehyde

(i) As a flavoring agent
(ii) Used in perfumes
(iii) Used in dye intermediates
(iv) As starting materials for the synthesis of cinnamaldehyde, Cinnamic acid, benzoyl chloride etc.,

e) Uses of Acetophenone

(i) Used in perfumary
(ii) As a hypnotic under the name hypnone

f) Uses of Benzophenone

(i) Used in perfumary
(ii) In the preparation of benzhydrol drop

g) Uses of 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 anticeptic in the preservation of fruit juice

h) Uses of Acetic acid

(i) As table vinegar
(ii) For coagulating rubber latex
(iii) For manufacture of cellulose acetate and poly vinyl acetate

i) Uses of benzoic acid:

(i) As food preservative either in pure form or in the form of Sodium benzoate
(ii) In medicine as an urinary antiseptic
(iii) Manaufacture of dyes

j) Uses of acetyl chloride:

(i) Acylating agent in organic analysis
(ii) In detection and estimation of –OH, -NH_2 groups in organic compounds

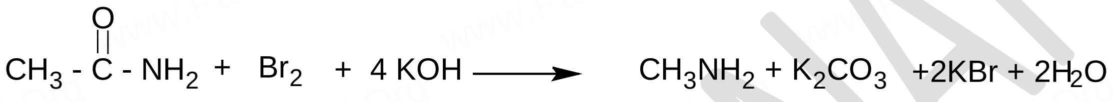
k) Uses of Acetic anhydride

(iii) Acylating agent
(iv) Preparation of medicine lite asprin and phenacetin
(v) Manufacture of plastics like, Cellulose acetate and poly vinyl acetate

l) Uses of Ethyl acetate:

(i) Preparation of artificial fruit essences
(ii) Solvent for lacquers
(iii) Preparation of ethyl acetoacetate

24. How will you convert acetamide into methyl amine? (or) Explain Hoffmann's degradation reaction.

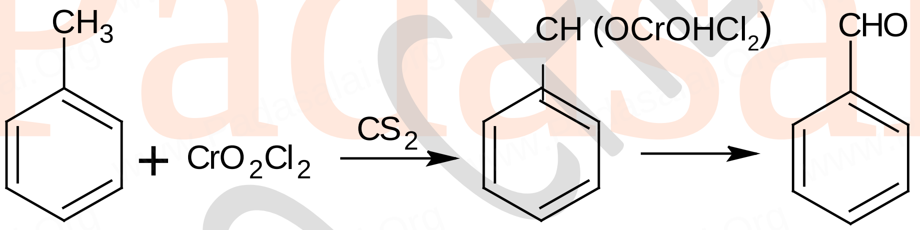


$$CH_3-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4\,KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Acetamide methyl amine

25. Write a note on Etard reaction:

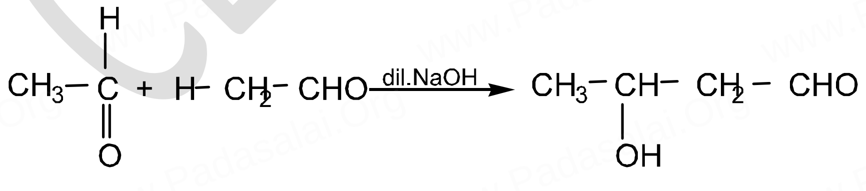
When Chromyl Chloride is used as an oxidizing agent, toluene gives benzaldehyde Acetic anhydride and CrO_3 can also be used.



Methyl benzene Benzaldehyde

26. Write the mechanism of aldol condensation

Acetaldehyde when warmed with dil NaOH gives β – hydroxyl butraldehyde (acetaldol)



$$CH_3-\underset{\underset{O}{||}}{\overset{\overset{H}{|}}{C}} + H-CH_2-CHO \xrightarrow{dil.NaOH} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

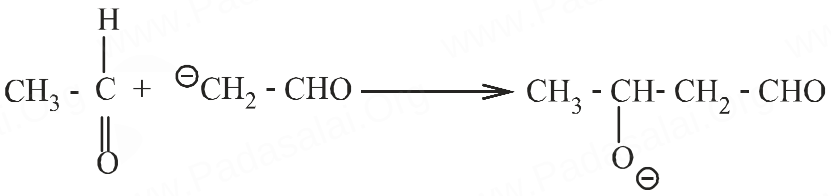
Acetaldehyde

Acetaldol
(3 - Hydroxy butanal)

Mechanism :
Step 1 :

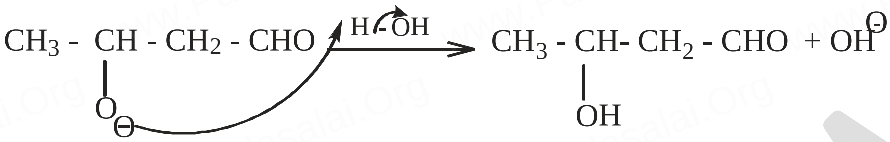
$$HO^{\ominus} + H-CH_2-CHO \longrightarrow {}^{\ominus}CH_2-CHO + H_2O$$

Step 2 :



$CH_3-\overset{H}{\underset{O}{C}} + {}^{\ominus}CH_2-CHO \longrightarrow CH_3-\underset{O^{\ominus}}{CH}-CH_2-CHO$

Step 3 :

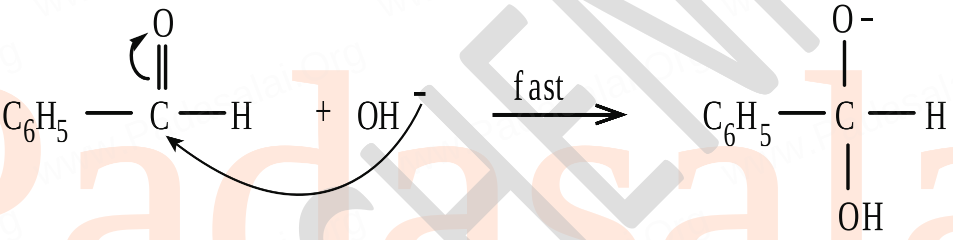


$CH_3-\underset{O^{\ominus}}{CH}-CH_2-CHO \xrightarrow{H-OH} CH_3-\underset{OH}{CH}-CH_2-CHO + OH^{\ominus}$

3-Hydroxy butanal

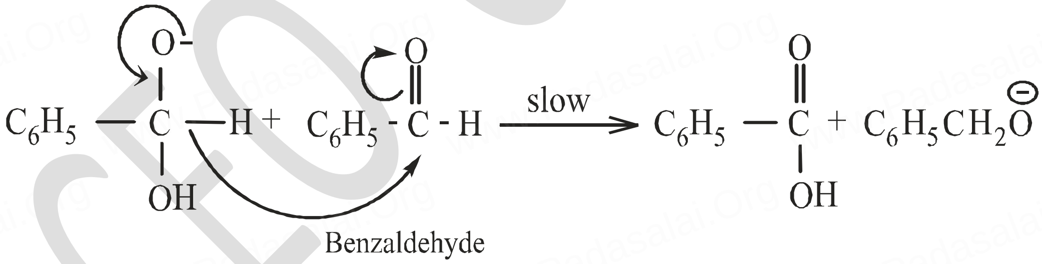
27. Give the mechanism of cannizaro reaction :

Step 1 : Attack of OH $^-$ on the carbonyl carbons



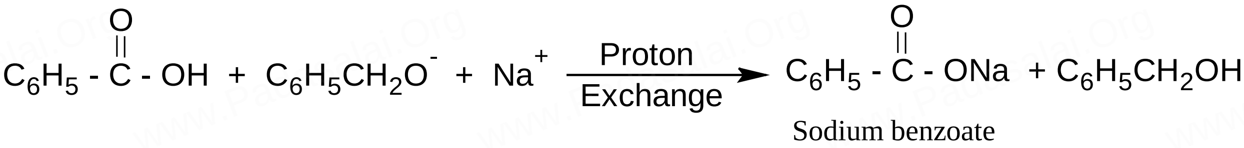
$C_6H_5-\overset{O}{\overset{\|}{C}}-H + OH^- \xrightarrow{fast} C_6H_5-\overset{O^-}{\underset{OH}{C}}-H$

Step 2 : Hydride ion transfer



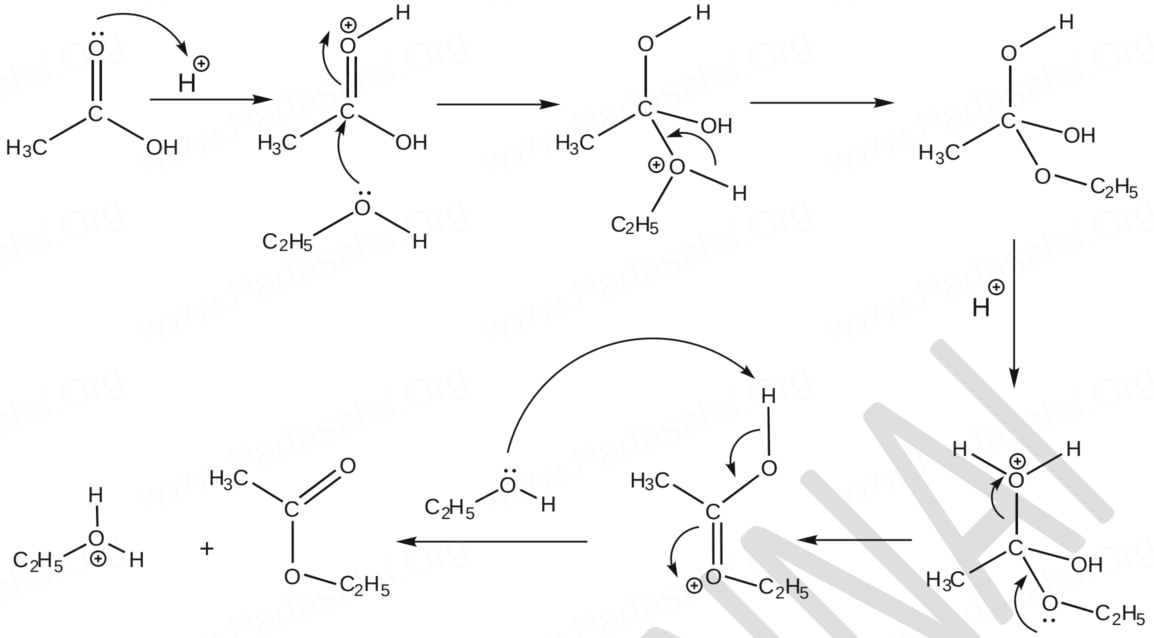
$C_6H_5-\overset{O^-}{\underset{OH}{C}}-H + C_6H_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow{slow} C_6H_5-\overset{O}{\underset{OH}{C}} + C_6H_5CH_2O^{\ominus}$

Step 3 : Acid-base reaction



$C_6H_5-\overset{O}{\overset{\|}{C}}-OH + C_6H_5CH_2O^- + Na^+ \xrightarrow[Exchange]{Proton} C_6H_5-\overset{O}{\overset{\|}{C}}-ONa + C_6H_5CH_2OH$

42. Give the mechanism of esterification :



28. Differentiate the following?

(i) Formaldehyde and acetaldehyde

(ii) acetaldehyde and Benzaldehyde

(iii) Acetaldehyde and Acetone

(iv) Formic acid and Acetic acid

(v) Acetophenone and Benzophenone

(vi) Phenol and Benzoic acid

(vii) Pent - 2 - one and Pent - 3 -one

(i) Formaldehyde and acetaldehyde

	Formaldehyde	Acetaldehyde
1.	Does not undergo iodoform test	Undergoes iodoform test
2.	With caustic soda undergoes Cannizzaro reaction	Undergoes aldol condensation

(ii) Acetaldehyde and benzaldehyde

	Acetaldehyde	Benzaldehyde
1.	Heating with Fehling's solution gives a red precipitate	No Reaction with Fehling's solution
2.	With primary amines does not form Schiff's base	Forms Schiff's base
3.	Undergoes aldol condensation with caustic soda	Undergoes Cannizzaro reaction with caustic soda

(iii) Acetaldehyde and Acetone

	Acetaldehyde	Acetone
1.	on oxidation gives acetic acid	on oxidation gives acetic acid with loss of one carbon atom
2.	Reduces Tollen's reagent	Does not reduce Tollen's reagent
3.	Reduces Fehling's solution	Does not reduce Fehling's solution
4.	on reduction with $NaBH_4$ gives ethanol (primary Alcohol)	on reduction with $NaBH_4$ gives Iso propyl Alcohol (secondry Alcohol)

(iv) Formic acid and Acetic acid

	Formic acid	Acetic acid
1.	Reduces Tollen's reagent	Does not reduce Tollen's reagent
2.	Calcium salt of formic acid on dry distillation gives formaldehyde	Calcium salt of acetic acid on dry distillation gives acetone
3.	It contains both aldehyde and carboxylic acid group	It contains only carboxylic acid group

(v) Acetophenone and benzophenone

Acetophenone gives idoform test but benzophenone does not gives idoform test

(vi) Phenol and Benzoic acid

	Phenol	Benzoic acid
1.	Phenol does not react with $NaHCO_3$	Benzoic acid reacts with $NaHCO_3$ gives CO_2 effervescence
2.	Phenol gives violet colour with neutral $FeCl_3$	Benzoic acid does not give violet colour with neutral $FeCl_3$

(vii) Pent - 2 - one and Pent - 3 - one

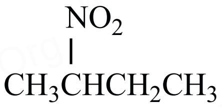
Pent - 2 - one undergoes idoform reaction, but Pent - 3 -one does not undergo idoform reaction.

LESSON -13 ORGANIC NITROGEN COMPOUNDS

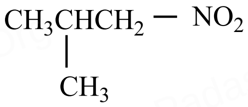
BOOK BACK QUESTIONS AND ANSWERS

1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC Names.

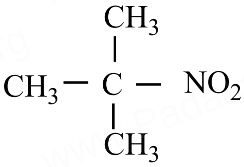
1. $CH_3CH_2CH_2CH_2 - NO_2$ 1 - nitrobutane

2. 

$CH_3\overset{NO_2}{\overset{|}{C}}HCH_2CH_3$ 2-nitro butane

3. 

$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2 - NO_2$ 2 - methyl - 1-nitropropane

4. 

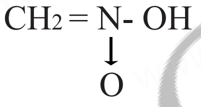
$CH_3 - \underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}} - NO_2$ 2 - methyl - 2-nitropropane

5. $CH_3CH_2CH_2CH_2 - O - N = O$ butyl nitrite

2. There are two isomers with the formula CH_3NO_2. How will you distinguish between them?

Isomers of CH_3NO_2

i) CH_3NO_2 Nitro methane

ii) 

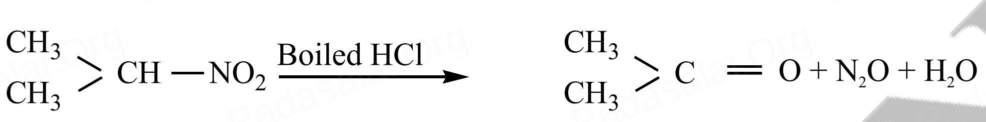
$CH_2 = \underset{O}{\underset{\downarrow}{N}}- OH$ Methyl nitrite

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic and also called pseudoacids (or) nitronic acids
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

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.**

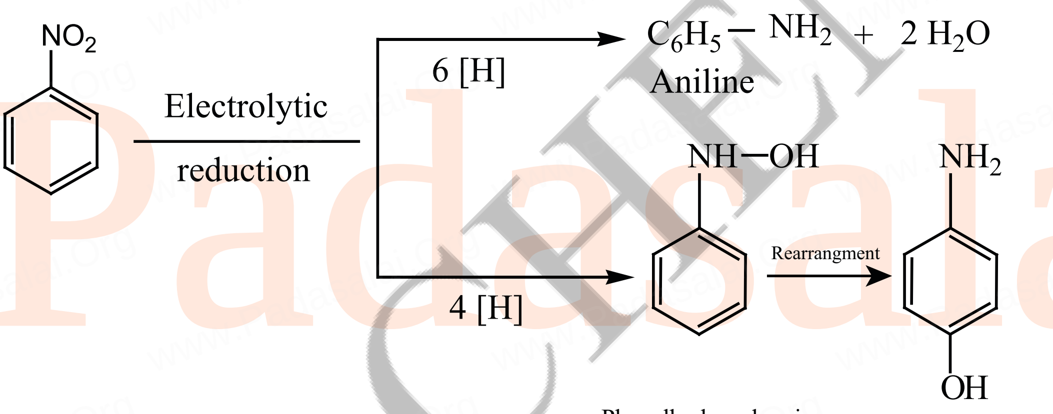
I) 2- Nitropropane boiled with HCl



$$(CH_3)_2CH-NO_2 \xrightarrow{\text{Boiled HCl}} (CH_3)_2C=O + N_2O + H_2O$$

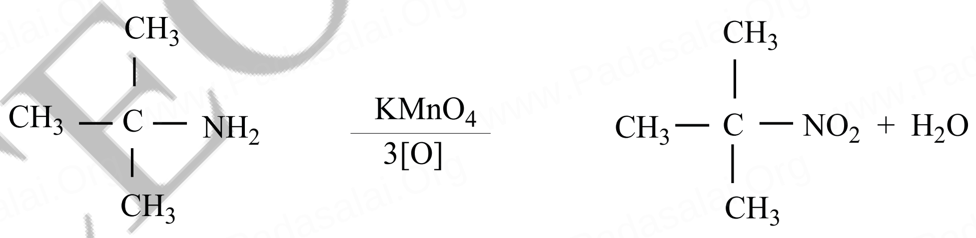
Acetone

II) Nitro benzene undergo electrolytic reduction in strongly acidic Medium



Phenylhydroxyl amine p-aminophenol

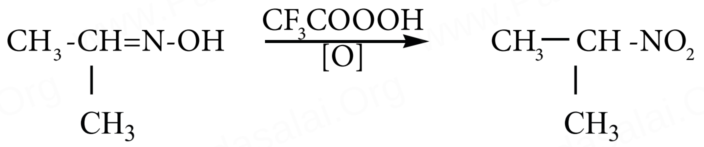
III) Oxidation of tert - butylamine with $KMnO_4$



$$(CH_3)_3C-NH_2 \xrightarrow[3[O]]{KMnO_4} (CH_3)_3C-NO_2 + H_2O$$

tert-butylamine 2 - methyl - 2 - nitro propane

IV) Oxidation of acetonoxime with trifluoroperoxy acetic acid



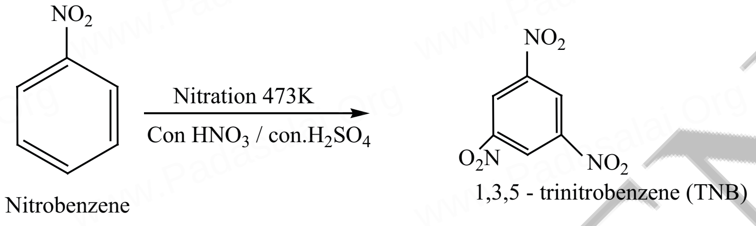
$$CH_3-\underset{\displaystyle CH_3}{CH}=N-OH \xrightarrow[\text{[O]}]{CF_3COOOH} CH_3-\underset{\displaystyle CH_3}{CH}-NO_2$$

Acetoneoxime 2- Nitropropane

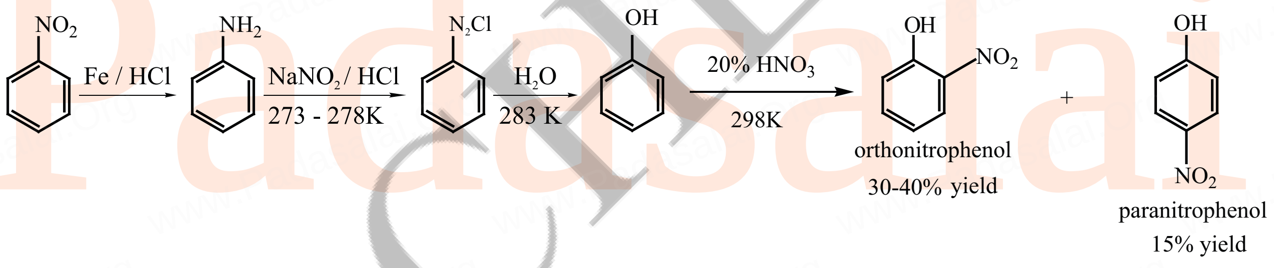
4. How will you convert nitrobenzene into

- **I. 1,3,5 trinitrobenzene**
- **ii. o and p - nitrophenol**
- **iii. m - nitro aniline**
- **iv. azoxy benzene**
- **v. hydroazobenzene**
- **vi. N - Phenylhydroxylamine**
- **vii. aniline**

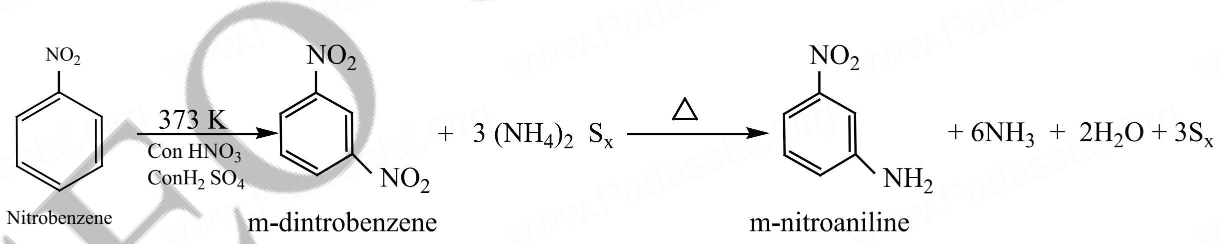
I. Conversion of nitrobenzene into 1,3,5 trinitro benzene



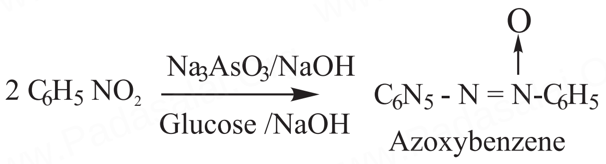
II. Conversion of nitrobenzene into o and p - nitrophenol



III. Conversion of nitrobenzene into m - nitroaniline



IV. Conversion of nitrobenzene into azoxybenzene



$$2\,C_6H_5\,NO_2 \xrightarrow[\text{Glucose /NaOH}]{Na_3AsO_3/NaOH} C_6N_5 - N = \overset{\overset{O}{\uparrow}}{N}\text{-}C_6H_5$$

Azoxybenzene

V. Conversion of nitrobenzene into Hydrazobenzene

In alkaline medium

$$\begin{tikzcd} 2\,C_6H_5NO_2 \arrow[r, "Zn / NaOH"] & C_6H_5-N=N-C_6H_5 \arrow[d, "2(H)"] \\ & C_6H_5-NH-NH\,C_6H_5 \end{tikzcd}$$

Hydrazobenzene

VI. Conversion of nitrobenzene to N - phenylhydroxylamine

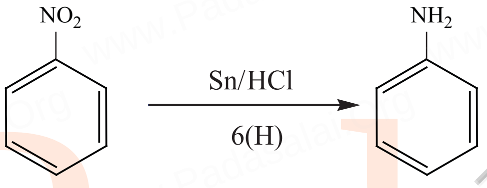
In neutral medium

$$C_6H_5-NO_2 \xrightarrow[4(H)]{Zn/NH_4Cl} C_6H_5-NH-OH$$

N Phenylhydroxylamine

VII. Conversion of nitrobenzene into aniline

In acidic medium



Aniline

5. Identify compounds A,B and C in the following sequence of reactions.

i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

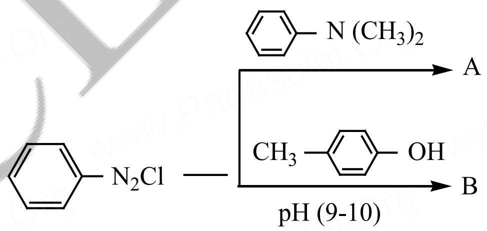
ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O / H^+} B \xrightarrow{NH_3} C$

iii) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

iv) $CH_3NH_2 \xrightarrow{CH_3Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

v) $C_6H_5NH_2 \xrightarrow[\text{pyridine}]{(CH_3CO)_2O} A \xrightarrow[H_2SO_4, 288K]{HNO_3} B \xrightarrow{H_2O / H^+} C$

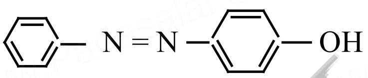
vi)



vii) $CH_3CH_2NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[ii)H_2O]{i)NaNO_2 / HCl} C$

Answer

i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273K]{HNO_2} \underset{\text{Benzene diazonium Chloride (B)}}{C_6H_5N_2Cl} \xrightarrow{C_6H_5OH}$



p- hydroxy azobenzene
(C)

ii) $C_6H_5N_2Cl \xrightarrow{CuCN} \underset{\substack{\text{Cyanobenzene}\\\text{(A)}}}{C_6H_5CN} \xrightarrow{H_2O / H^+} \underset{\substack{\text{Benzoic acid}\\\text{(B)}}}{C_6H_5COOH} \xrightarrow{NH_3} \underset{\substack{\text{Benzamide}\\\text{(C)}}}{C_6H_5CONH_2}$

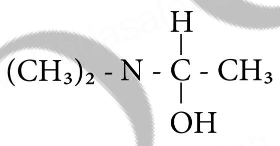
iii) $CH_3\,CH_2\,I \xrightarrow[-\,NaI]{NaCN} \underset{\substack{\text{(A)}\\\text{Ethylcyanide}}}{CH_3\,CH_2\,CN} \xrightarrow[OH^-]{\text{Partial hydrolysis}} \underset{\substack{\text{(B)}\\\text{Propanamide}}}{CH_3\,CH_2\,CONH_2} \xrightarrow{NaOH + Br_2} \underset{\substack{\text{(C)}\\\text{Ethylamine}}}{CH_3\,CH_2\,NH_2}$

iv) $CH_3\,NH_2 \xrightarrow{CH_3Br} \underset{\text{N, N - dimethylamine (A)}}{(CH_3)_2\,NH}$

$\Big\downarrow CH_3\,COCl$

$\underset{\text{N, N - dimethyl acetamide (B)}}{(CH_3)_2\,N - COCH_3}$

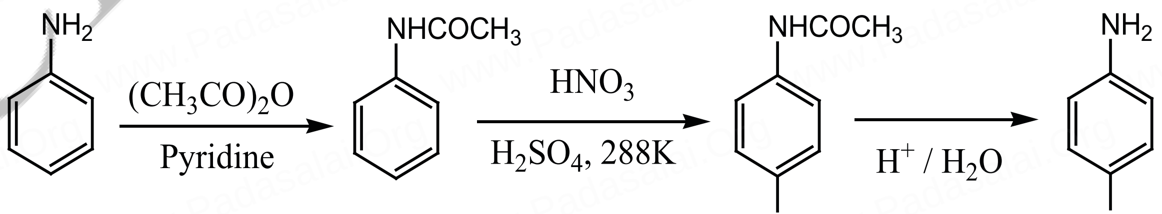
$\Big\downarrow B_2\,H_6$



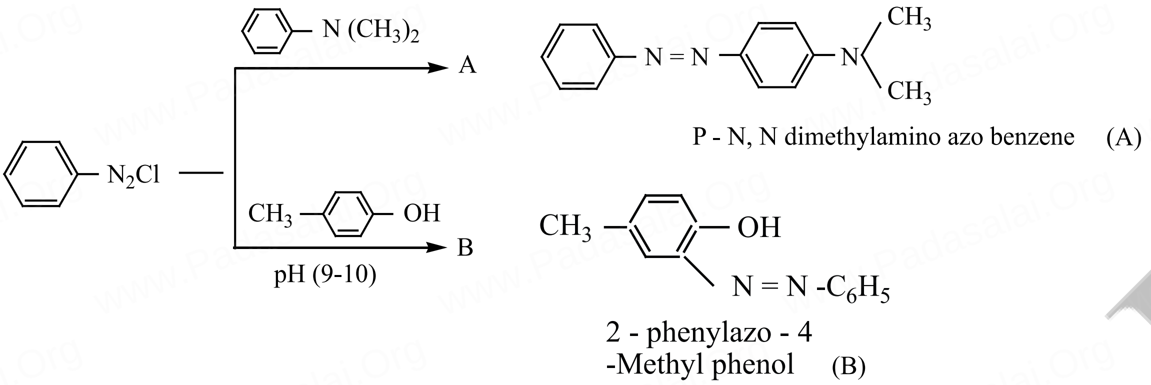
$$(CH_3)_2 - N - \overset{\displaystyle H}{\underset{\displaystyle OH}{C}} - CH_3$$

N, N dimethyl 2 hydroxy ethanamine (C)

v)



Acetanilide P-nitroacetanilide p-nitro aniline vi)



vii) $CH_3CH_2NC \xrightarrow{HgO} CH_3CH_2\text{-}N=C=O$

Ethylisocyanate (A)

$$\downarrow H_2O$$

$CH_3CH_2\text{-}NH_2 + CO_2$

Ethylamine (B)

$$\downarrow NaNO_2 / HCl, H_2O$$

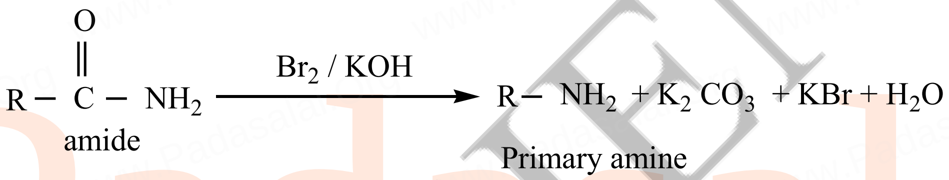
C_2H_5OH

(C) Ethanol

6. Write short notes on the following

- i. **Hofmann's bromamide 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**

i. Hofmann's bromamide reaction



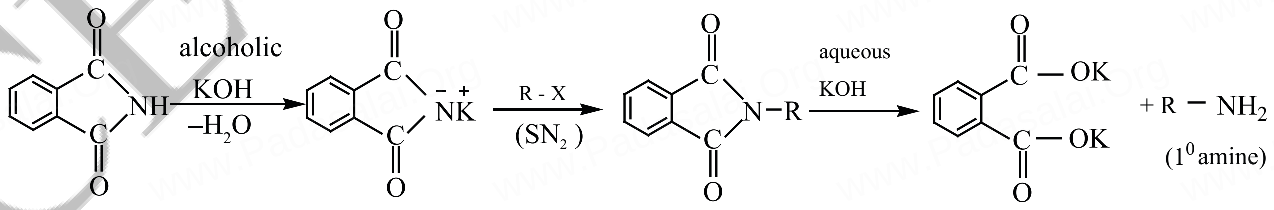
$$\underset{\text{amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{Br_2\,/\,KOH} \underset{\text{Primary amine}}{R-NH_2} + K_2CO_3 + KBr + H_2O$$

R = Alkyl (or) Aryl

ii. Ammonolysis

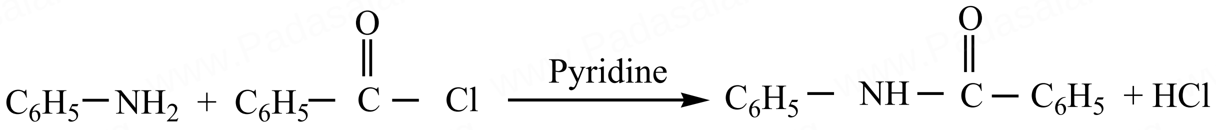
$$CH_3-Br \xrightarrow[\Delta]{\ddot{N}H_3} \underset{1^0\text{ - amine}}{CH_3-\ddot{N}H_2} \xrightarrow{CH_3\text{ - }Br} \underset{2^0\text{ - amine}}{(CH_3)_2\ddot{N}H} \xrightarrow{CH_3\,Br} \underset{3^0\text{- amine}}{(CH_3)_3\ddot{N}} \xrightarrow{CH_3\,Br} \underset{\text{Quarternary ammonium bromide}}{(CH_3)_4\overset{+}{N}\,Br^-}$$

iii. Gabriel phthalimide synthesis



Phthalimide Potassium phthalimide N - alkyl phthalimide Potassium pthalate

iv. Schotten – Baumann reaction



$$C_6H_5{-}NH_2 + C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow{\text{Pyridine}} C_6H_5{-}NH{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 + HCl$$

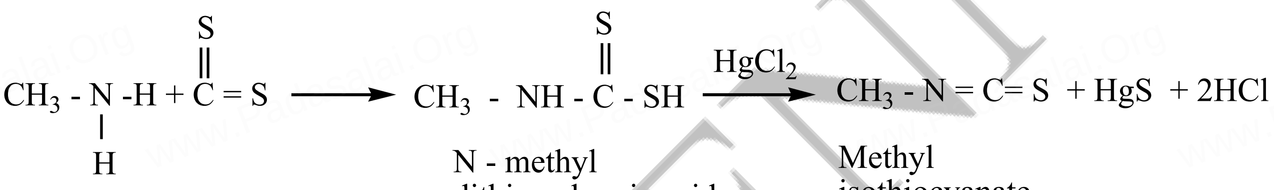
Aniline Benzoylchloride N - phenyl benzamide

v. Carbylamine reaction

$$C_2H_5 - NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5 - NC + 3KCl + 3H_2O$$

Ethylamine Chloroform Ethylisocyanide

vi. Mustard oil reaction



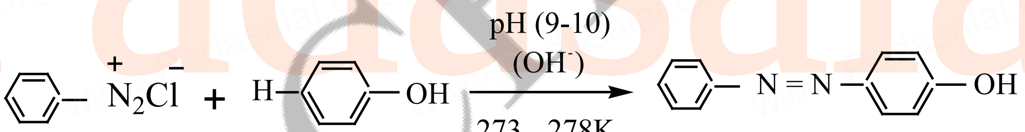
$$CH_3 - \underset{\underset{H}{|}}{N} - H + \overset{S}{\overset{\|}{C}} = S \longrightarrow CH_3 - NH - \overset{S}{\overset{\|}{C}} - SH \xrightarrow{HgCl_2} CH_3 - N = C = S + HgS + 2HCl$$

Methylamine

N - methyl dithiocarbamic acid

Methyl isothiocyanate (Mustard oil smell)

vii. Coupling reaction

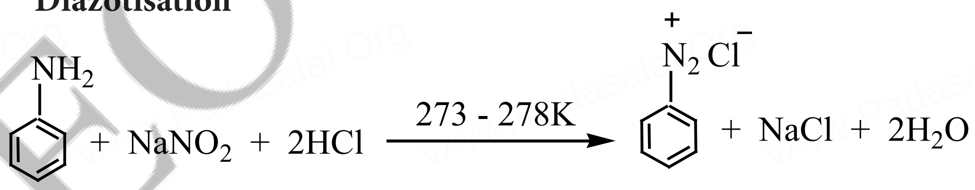


Benzene diazonium chloride

Phenol

p- hydroxy azobenzene (orange dye)

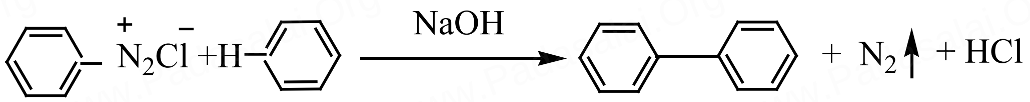
viii. Diazotisation



Aniline

Benzenediazonium chloride

ix. Gomberg reaction



Benzene diazonium chloride

Benzene

Biphenyl

7. How will you distinguish between primary, Secondary and Tertiary aliphatic amines.

S.No	Reagents	1°amine	2° amine	3° amine
1.	Nitrous acid (HNO_2)	Forms alcohols	Forms N-nitroso amine	Forms Salt
2.	Chloro form and KOH	forms carbylamine	No reaction	No reaction
3.	Acetylchloride	forms N-alkyl acetamide	forms N, N-dialkyl acetamide	No reaction
4.	CS_2 and $HgCl_2$	Forms alkyl isothiocyanate	No reaction	No reaction
5.	Alkyl halide	with three moles of Alkyl halides Quarternary ammonium salt is formed	with two moles of alkyl halides quarternary ammonium salt is formed	with one mole of alkyl halide quarternary ammonium salt is formed

8. Account for the following

i. Aniline does not undergo friedel craft's 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 & p - directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

Answers

1. Aniline is a lewis base. It donates its lone pair of electron on N atom to $AlCl_3$ (Lewis acid) and forms salt.

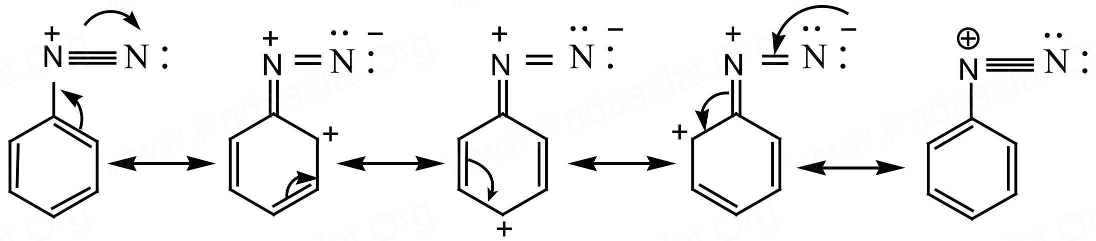
2. Which becomes strongly deactivating for electrophilic substitution reaction

$$C_6H_5\ddot{N}H_2 + AlCl_3 \longrightarrow C_6H_5\overset{+}{N}H_2\,AlCl_3^{-}$$

Lewis Base Lewis Acid

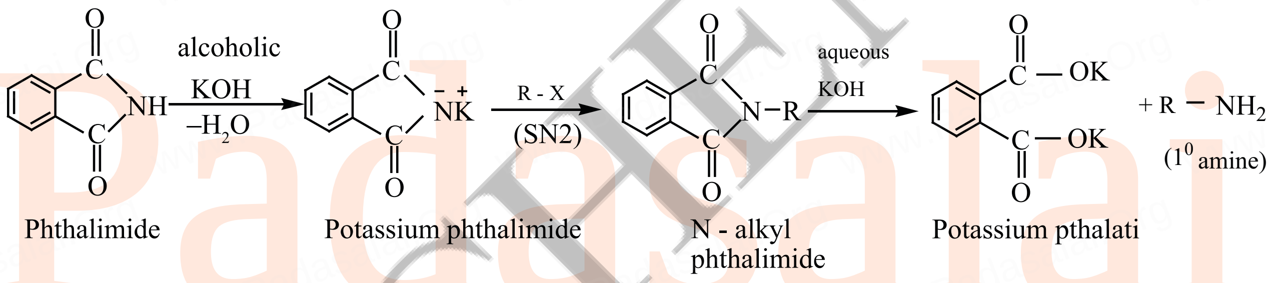
So Aniline does not undergo Friedel - Craft's reaction.

ii. The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring.



iii. 1) In aniline the lone pair of electron on the N-atom is delocalized over the benzene ring due do resonance. 2) In CH_3 NH_2, +I effect of CH_3 increases the electron density on the N - atom. Therefore aniline is a weaker base than methylamine and hence its pk_b value is more than that of methylamine

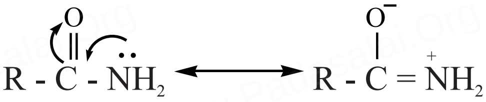
iv. Gabriel phthalimide synthesis is preferred only for 1^0 amines.



The 1^0 amine thus formed does not undergo further reaction to form 2^0 & 3^0 amines. Thus this method is used for preparation of 1^0 amines

V. When Ethylanmine is added to water forms intermolecular H - bonds with water. Aniline does not form H - bond due to the presence of a large hydrophobic - C_6H_5 group

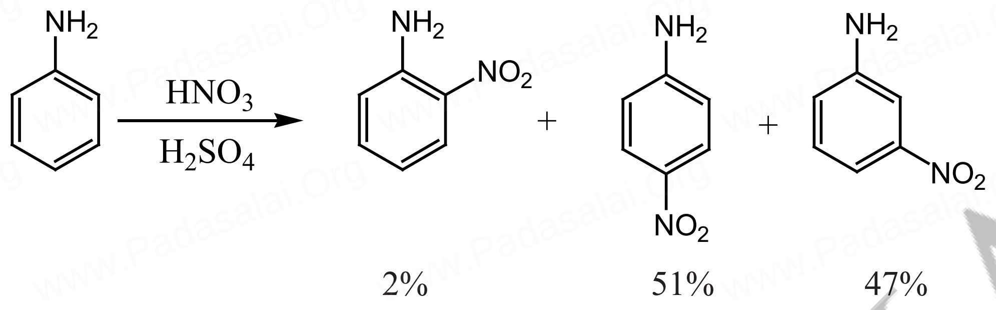
Vi. Amines are more basic than amides because in amines the lone pair of electrons is on nitrogen are available for protonation whereas in amides the electron pair on nitrogen is involved in resonance with C = O Group.



$$R - \overset{O}{\overset{\|}{C}} - \ddot{N}H_2 \longleftrightarrow R - \overset{O^-}{\overset{|}{C}} = \overset{+}{N}H_2$$

(Amide resonance Structure)

vii. In a strong acid medium aniline is protonated to form anilinium ion which is m - directing and hence m - nitro aniline is also formed.



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_6H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

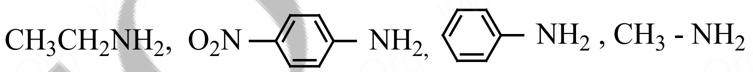
v. In decreasing order of the pK_b values

$C_2H_5NH_2$, $C_6H_5NHCH_3$,$(C_2H_5)_2NH$ and CH_3NH_2

vi. Increasing order of basic strength

$C_2H_5NH_2$,$C_6H_5N(CH_3)_2$,$(C_2H_5)_2$ NH and CH_3 NH_2

vii. In decreasing order of basic strength



Answers

i. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Solubility increases in the order in which molecular mass decreases.

ii. a) p – nitroaniline < aniline < p- toludine

The electron donating groups increases the basic strength of amines, electron withdrawing groups decreases the basic strength of amines

b) $p\text{-}Cl\text{-}C_6H_4\text{-}NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3$

Increase in basic strength is due to delocalization of lone pair of electrons on the N atom over the benzene ring.

iii. $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

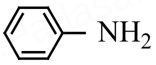
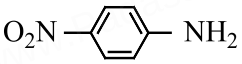
In gas phase, Basic strength mainly depends on the + I effect of alkyl groups.

iv. $(CH_3)_2NH, < C_2H_5NH_2 < C_6H_5OH,$

Amines form weaker H - bonding than phenol. 2^0 amines can form one H-bond due to NH group, whereas 1^0 amines form 2 H - bonds due to NH_2 group.

v. $C_6H_5NHCH_3 > C_6H_5NH_2 > CH_3NH_2 > (C_2H_5)_2NH$

vi. $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

vii. $CH_3 - NH_2 > CH_3CH_2NH_2, >$  $>$ 

10. How will you prepare propan - 1 - amine from

i) Butane nitrile

ii) Propanamide

iii) 1 - nitropropane

Answer

I) $CH_3 - CH_2 - CH_2 - CN \xrightarrow{H^+ / H_2O} CH_3 - CH_2 - CH_2 - CONH_2 \xrightarrow{Br_2 / KOH} CH_3 - CH_2 - CH_2 - NH_2$

butane nitrile — butanamide — Propane 1 - amine

II) $CH_3 - CH_2 - CONH_2 \xrightarrow[H_2O]{Li\,AlH_4} CH_3 - CH_2 - CH_2 - NH_2$

Propane 1 - amine

III) $CH_3 - CH_2 - CH_2 - NO_2 \xrightarrow[6\,(H)]{Fe/HCl \text{ or } H_2/Ni} CH_3 - CH_2 - CH_2 - NH_2$

Note: we can also use H_2 / Ni

11. Identify A,B,C and D

$CH_3\text{-}NO_2 \xrightarrow{Li\,AlH_4} A \xrightarrow{2CH_3CH_2Br} B \xrightarrow{H_2SO_4} C$

$\underset{}{CH_3\text{-}NO_2} \xrightarrow{Li\,AlH_4} \underset{(A)}{CH_3\;NH_2} \xrightarrow{2CH_3CH_2Br} \underset{(B)}{(CH_3\,CH_2)_2\,NCH_3} \xrightarrow{H_2SO_4} \underset{(\,C\,)}{[(CH_3\,CH_2)_2\,NHCH_3]^+\;HSO_4^-}$

12. How will you convert diethylamine into

i) N, N - diethylacetamide

ii) N - nitrosodiethylamine

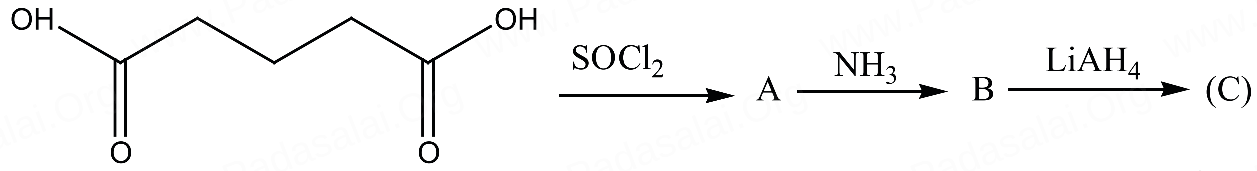
i) $(C_2\,H_5)_2\,NH + CH_3\,COCl \xrightarrow{Pyridine} (C_2\,H_5)_2\,N\text{-}CO\,CH_3 + HCl$

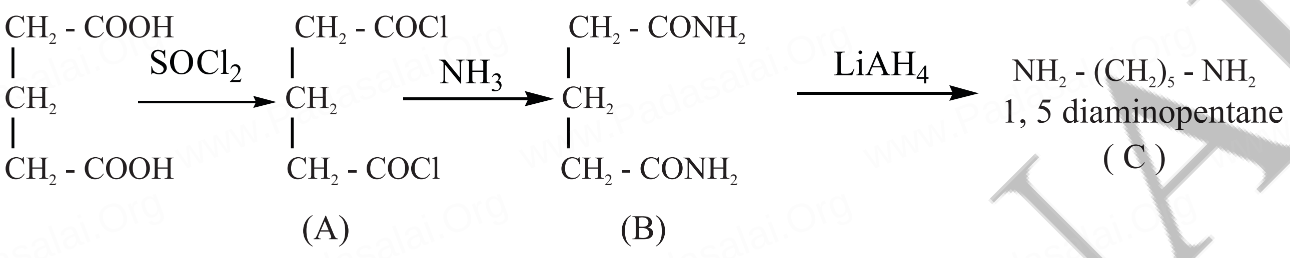
N, N - diethylacetamide

ii) $(C_2\,H_5)_2\,NH \xrightarrow[HNO_3]{NaNO_2 / Conc.\,HCl} (C_2\,H_5)_2\,N - N = O$

N - nitrosodiethylamine

13. Identify A, B and C





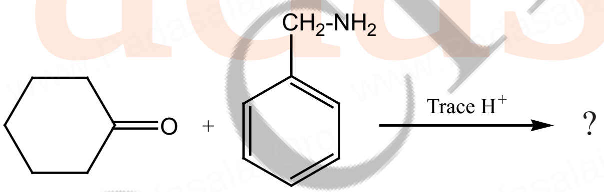
$$\begin{array}{l} CH_2-COOH\\ |\\ CH_2\\ |\\ CH_2-COOH\end{array} \xrightarrow{SOCl_2} \underset{(A)}{\begin{array}{l}CH_2-COCl\\ |\\ CH_2\\ |\\ CH_2-COCl\end{array}} \xrightarrow{NH_3} \underset{(B)}{\begin{array}{l}CH_2-CONH_2\\ |\\ CH_2\\ |\\ CH_2-CONH_2\end{array}} \xrightarrow{LiAH_4} \underset{(C)}{\underset{\text{1, 5 diaminopentane}}{NH_2-(CH_2)_5-NH_2}}$$

14. Identify A, B, C and D

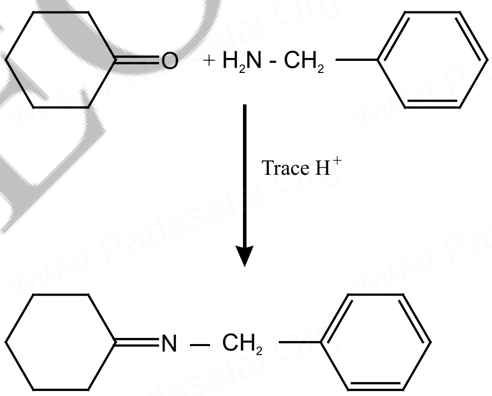
aniline+benzaldehyde $\longrightarrow A \xrightarrow[B]{con\ HNO_3} C+D$

$$C_6H_5NH_2 + C_6H_5CHO \longrightarrow \underset{(A)}{\underset{\text{Schiff's base}}{\underset{\text{benzalaniline}}{C_6H_5N=CH-C_6H_5}}} \xrightarrow[\underset{(B)}{H_2O}]{\text{Conc } HNO_3} \underset{(C)}{\underset{\text{Aniline}}{C_6H_5NH_2}} + \underset{(D)}{\underset{\text{benzaldehyde}}{C_6H_5CHO}}$$

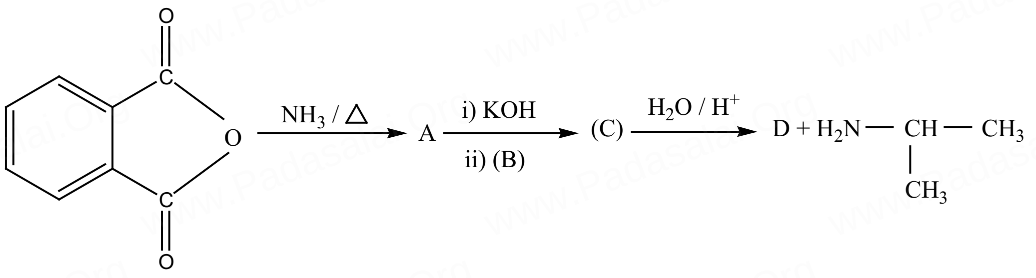
15. Complete the following reaction

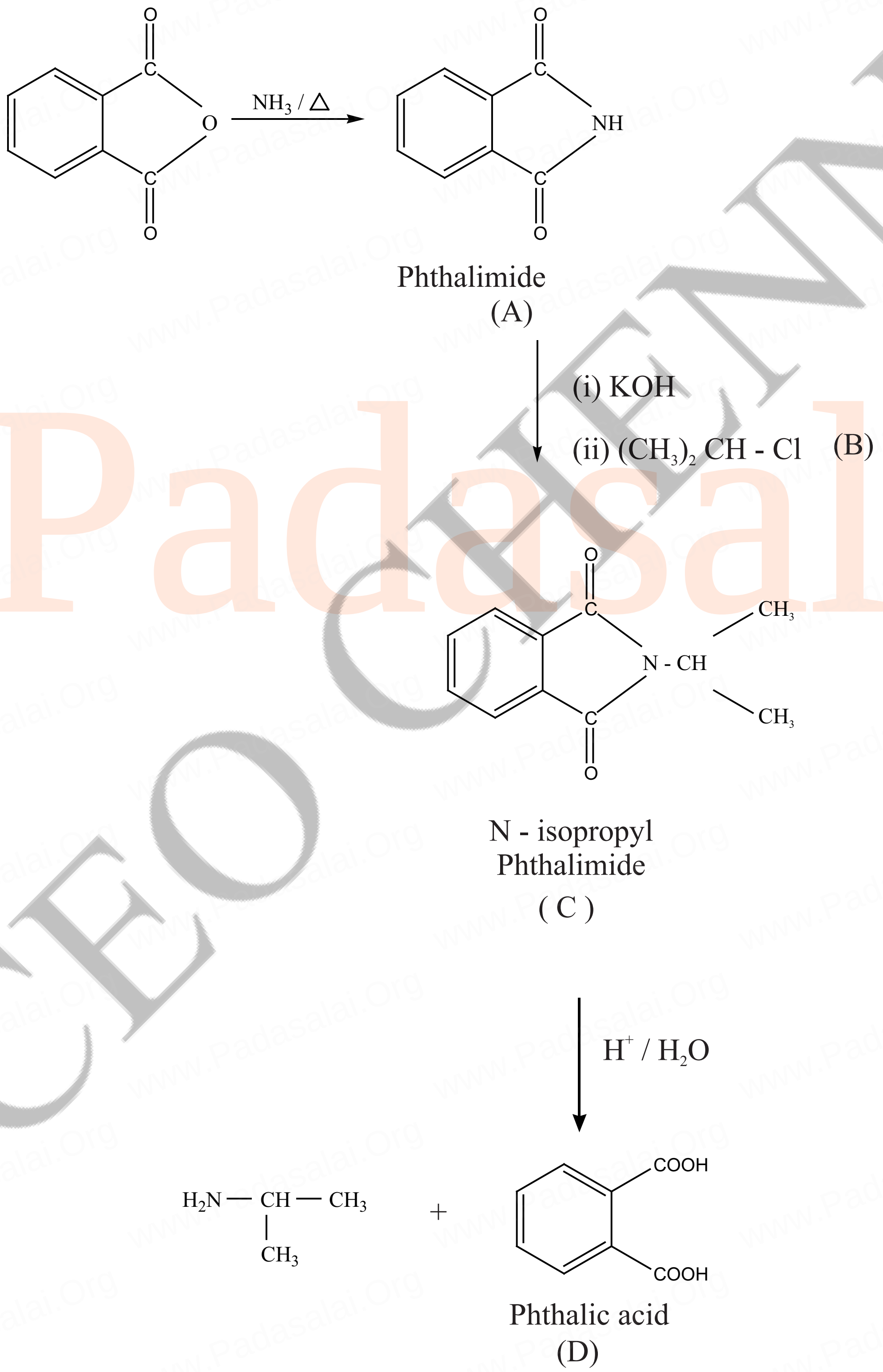


Answer

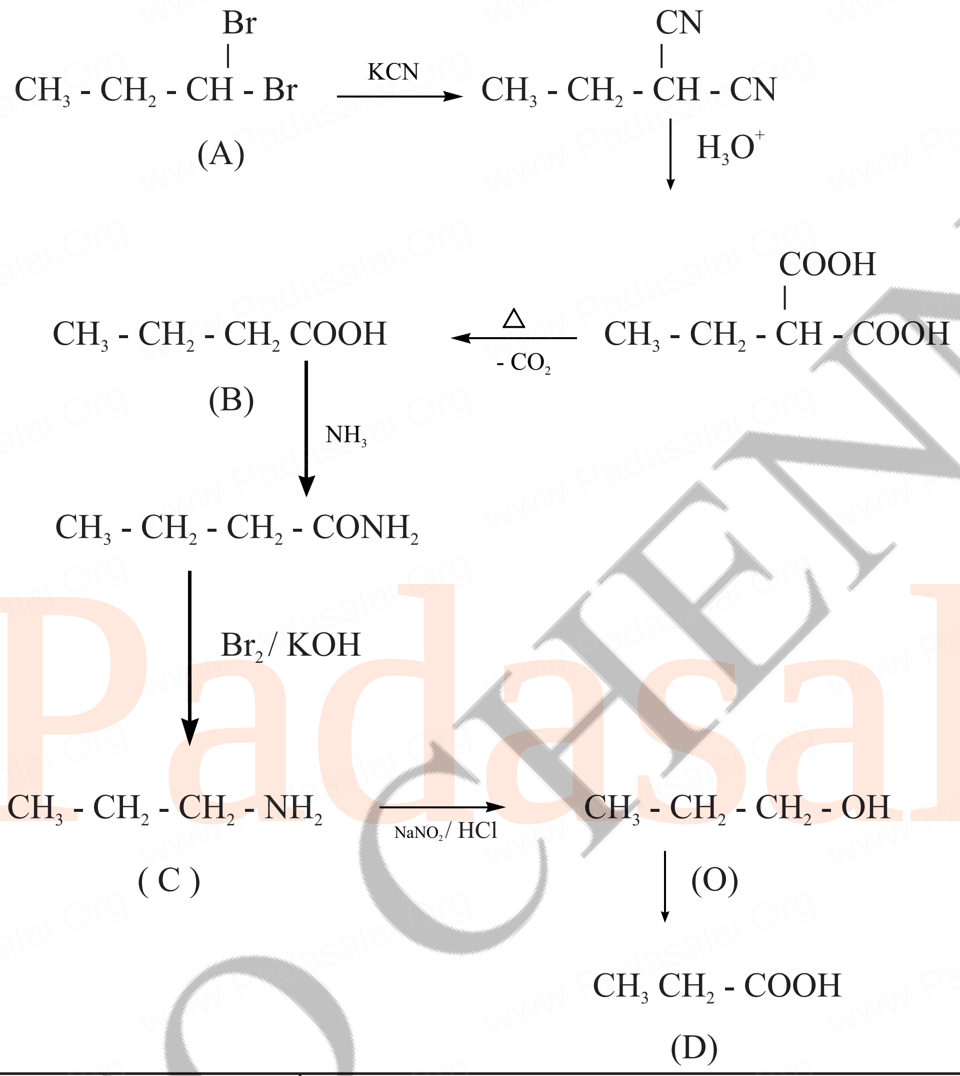


16. Predict A, B, C and D for the following reaction.



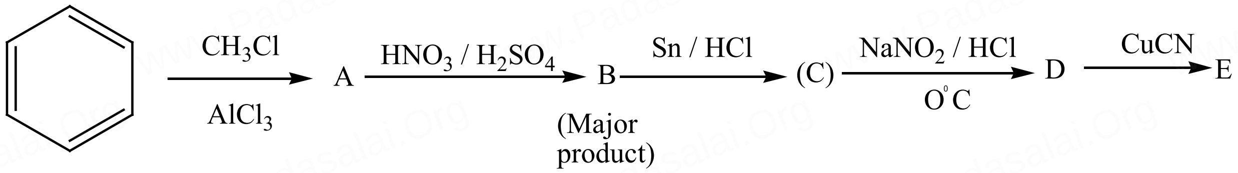


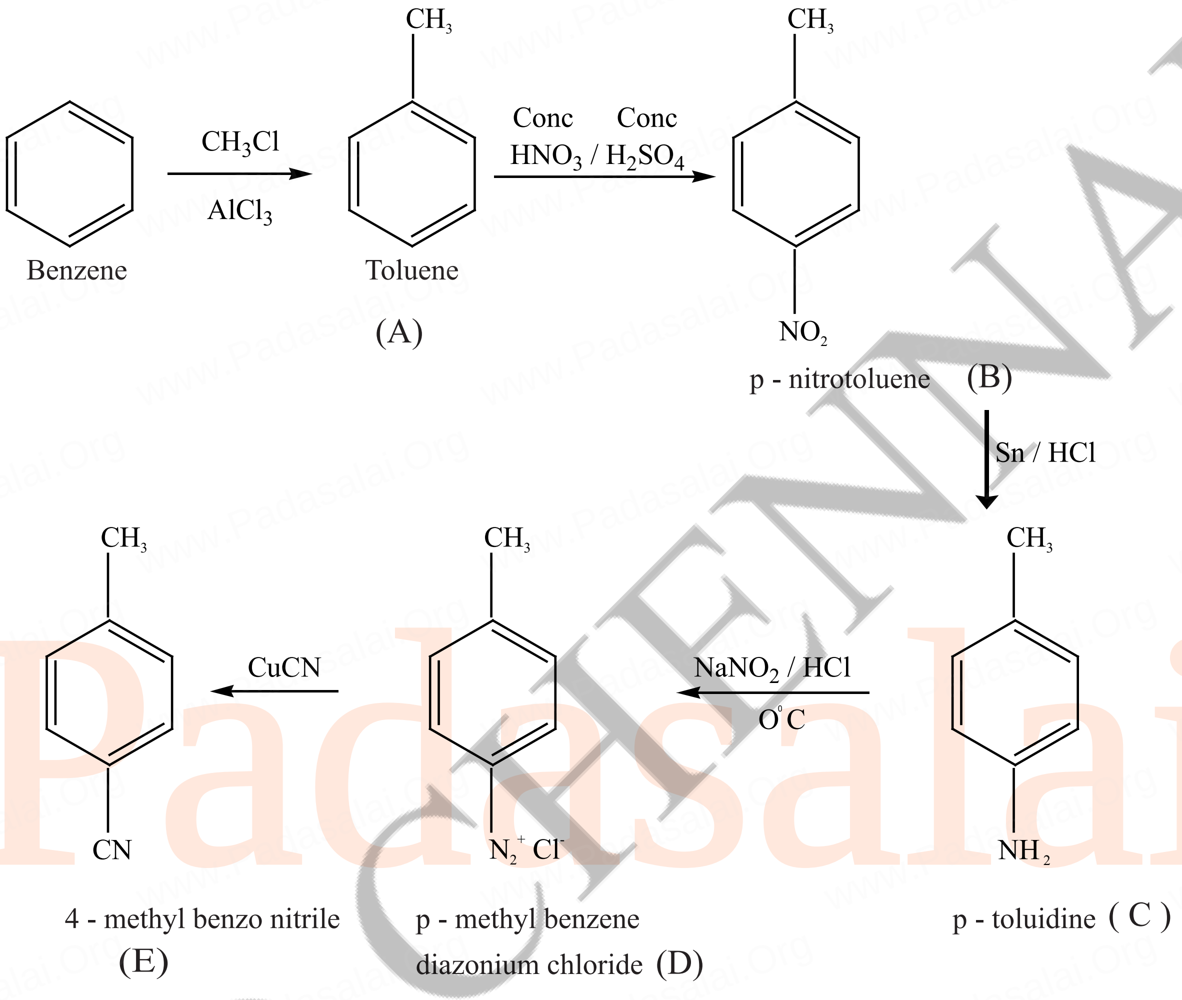
17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2. (B) on heating with liquid ammonia followed by treating with Br_2 / KOH gives (C) which on treating with $NaNO_2$ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.

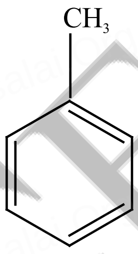


A	1, 1 dibromopropane
B	butanoic acid
C	1 - amino propane
D	Propanoic Acid

18. Identify A to E in the following frequency of reactions.

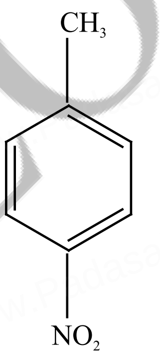






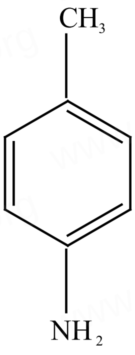
Toluene

(A)



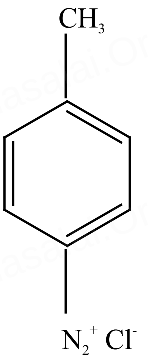
p - nitrotoluene

(B)



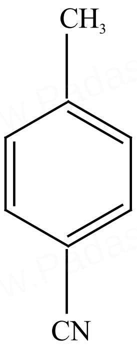
p - toluidine

(C)



p - methyl benzene diazonium chloride

(D)



4 - methyl benzo nitrile

(E)

II Evaluate Yourself

1. Write all possible isomers for the following compounds.

i) C_2H_5 -NO_2

ii) C_3H_7 -NO_2

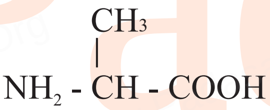
I) Possible isomers for C_2H_5 -NO_2

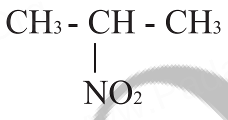
a) $CH_3 - CH_2 - NO_2$	Nitroethane
b) $CH_3 - CH_2 - O - N = O$	Ethyl nitrite
c) $H_2N - CH_2 - COOH$	Glycine

ii) Possible isomers for C_3H_7 - NO_2

a) $CH_3 - CH_2 - CH_2 - NO_2$ Nitro Propane

b) $CH_3 - CH_2 - CH_2 - O - N = O$ Propane - 1 - nitrite

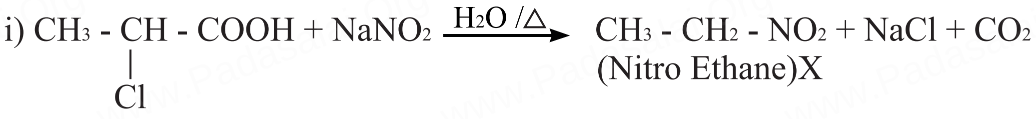
c) 
$NH_2 - \underset{}{\overset{CH_3}{\overset{|}{CH}}} - COOH$ Alanine

d) 
$CH_3 - \underset{\underset{NO_2}{|}}{CH} - CH_3$ 2 - Nitro Propane

2. Find out the product of the following reactions.


i) $CH_3 - \underset{\underset{Cl}{|}}{CH} - COOH \xrightarrow[\text{ii) } H_2O /\triangle]{\text{i) } NaNO_2}$?[X]

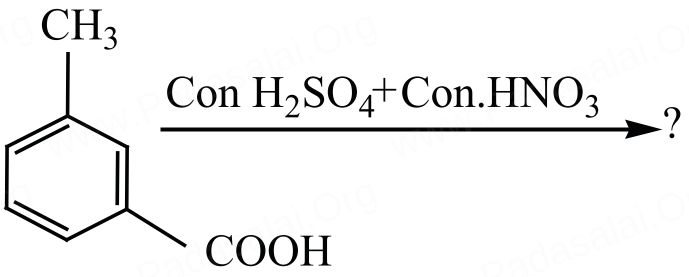
ii) $CH_3 - CH_2 - Br + NaNO_2 \xrightarrow{\text{alcohol} /\triangle}$?[Y]


i) $CH_3 - \underset{\underset{Cl}{|}}{CH} - COOH + NaNO_2 \xrightarrow{H_2O /\triangle} CH_3 - CH_2 - NO_2 + NaCl + CO_2$
(Nitro Ethane)X

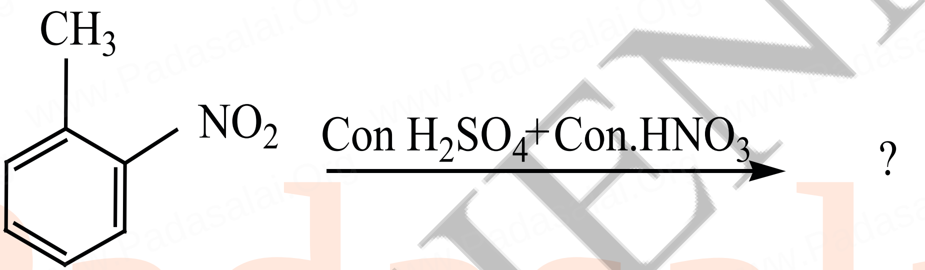
ii) $CH_3 - CH_2 - Br + NaNO_2 \xrightarrow{\text{alcohol} /\triangle} CH_3 - CH_2 - NO_2 + NaBr$
(Nitro Ethane) Y

3. Predict the major product that would be obtained on nitration of the following Compounds.

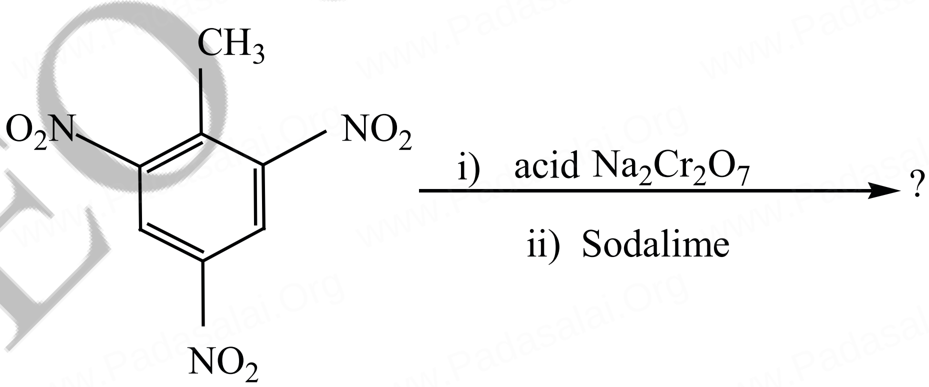
i)



ii)

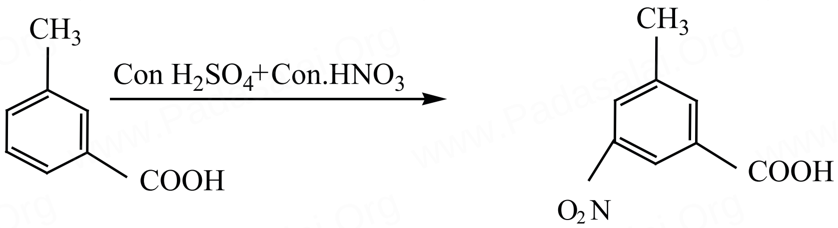


iii)

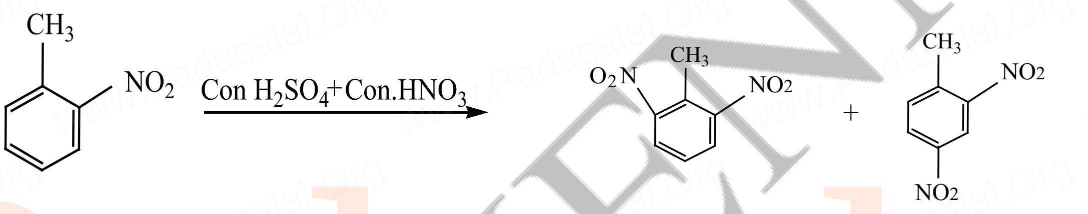


Answers

i)

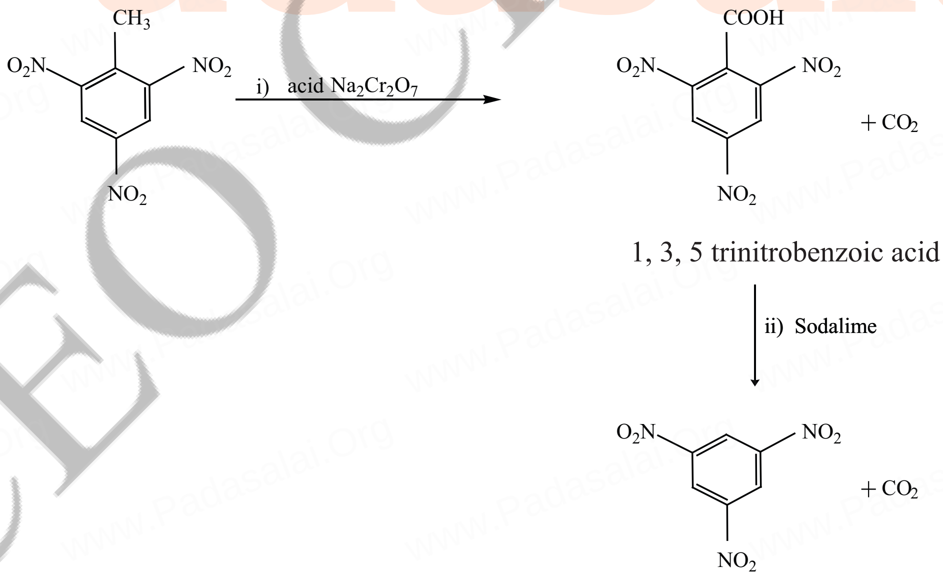


ii)



2, 6 dinitrotoluene 2, 4 dinitrotoluene

iii)

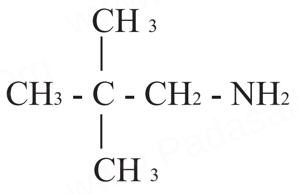


1, 3, 5 trinitrobenzene

4. Draw the structure of the following compounds

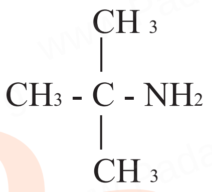
- i. **Neopentylamine**
- ii. **Tert – butylamine**
- iii. **α - amino propionaldehyde**
- iv. **Tribenzylamine**
- v. **N – ethyl – N – methylhexan – 3- amine**

i. Neopentylamine



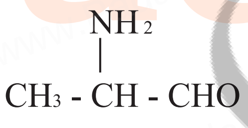
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - NH_2$$

ii. Tert – butylamine



$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - NH_2$$

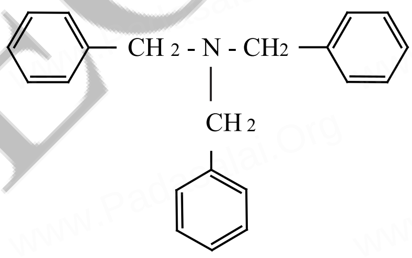
iii. α - amino propionaldehyde



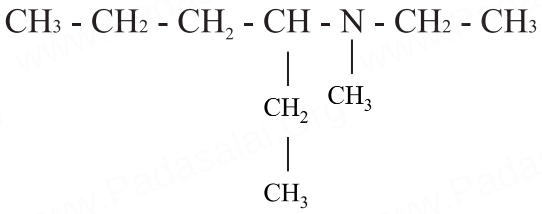
$$CH_3 - \overset{\overset{NH_2}{|}}{CH} - CHO$$

iv. Tribenzylamine

$(C_6H_5CH_2)_3N$

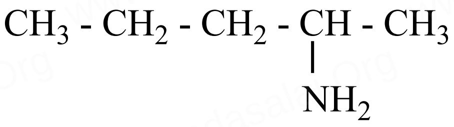
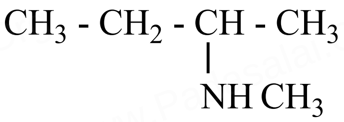
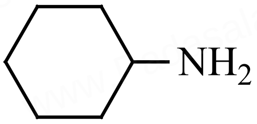
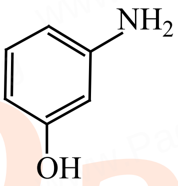
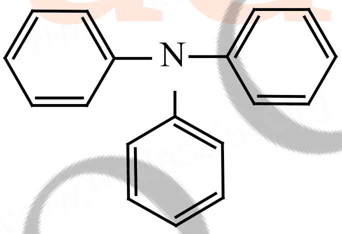


v. N – ethyl – N – methylhexan – 3- amine



$$CH_3 - CH_2 - CH_2 - \underset{\underset{\underset{CH_3}{|}}{CH_2}}{\underset{|}{CH}} - \underset{\underset{CH_3}{|}}{N} - CH_2 - CH_3$$

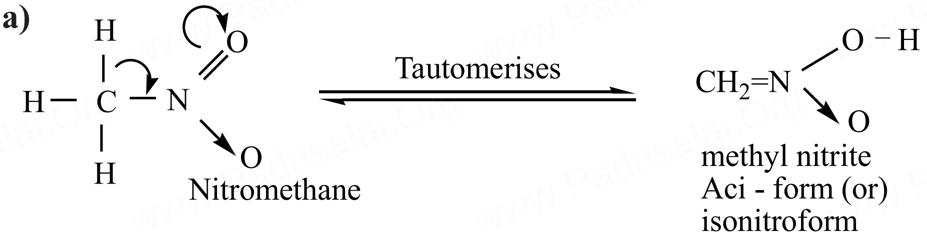
5. Give the correct IUPAC names for the following amines

	Answers
i)  $CH_3 - CH_2 - CH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - CH_3$	Pentan - 2 amine
ii)  $CH_3 - CH_2 - \underset{\substack{\vert \\ NH\,CH_3}}{CH} - CH_3$	N - methyl - butan - 2 - amine
iii) 	Cyclohexan - 1 - amine
iv) 	3 - amino phenol
v) 	N, N diphenyl benzenamine

III Additional Questions

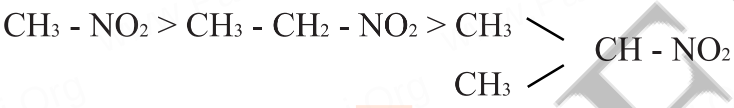
1. a) Write the tautomers of Nitromethane. b) Why tertiary nitro alkanes do not exhibit tautomerism?

a)



b) Tertiary nitro alkanes do not exhibit tautomerism due to absence of α - H atom

2. Compare the acid strength of the following compounds i) Nitro methane ii) Nitro ethane iii) 2 - nitro propane



$$CH_3-NO_2 > CH_3-CH_2-NO_2 > (CH_3)_2CH-NO_2$$

When the number of alkyl group attached to α - carbon increases, acidity decreases, due to + I effect

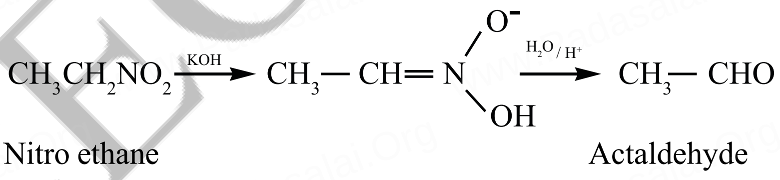
3. What is chloropicrin ? How is it prepared? Give its uses?

i) CCl_3NO_2 is chloropicrin (Trichloro nitro methane)

ii) $CH_3NO_2 + 3Cl_2 \xrightarrow{NaOH} CCl_3NO_2 + 3HCl$

iii) It is used as an insecticide.

4. Explain - Nef Carbonyl Synthesis

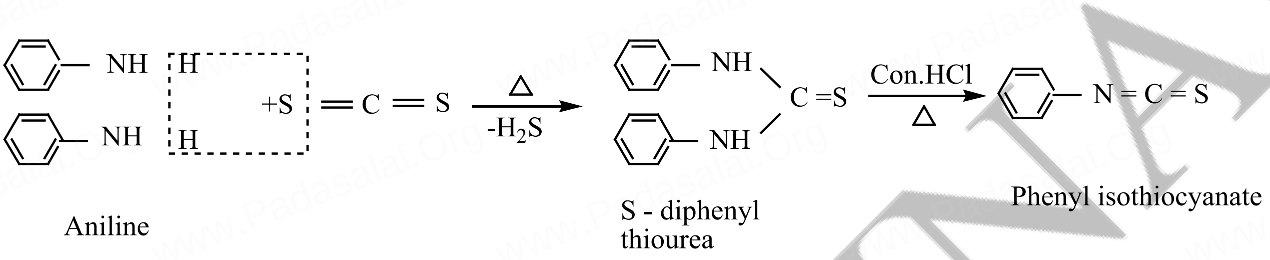


5. Amines are basic. Justify this statement?

The lone pair of electrons on nitrogen atom in amines makes it basic. Amines reacts with mineral acid to form salt.

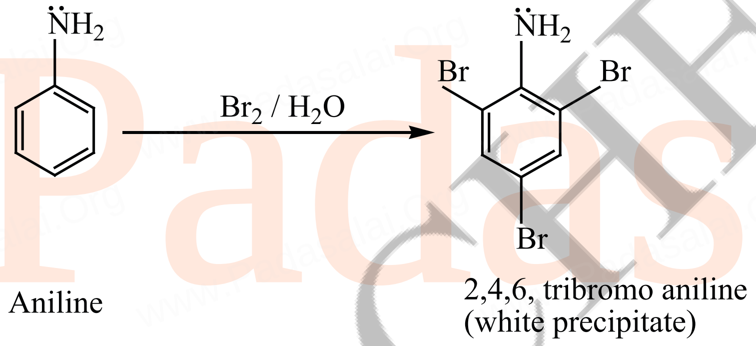
$$R - \ddot{N}H_2 + HCl \rightleftharpoons R - \overset{+}{N}H_3Cl^-$$

6. Explain the action of CS_2 with aniline (or) Mustard Oil Reaction

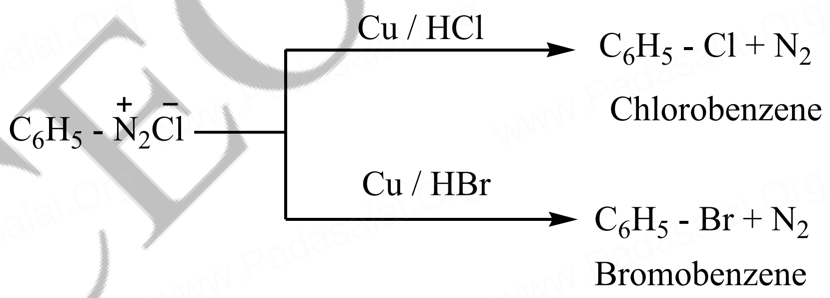


7. Give a test for aniline?

With bromine water aniline forms white precipitate of 2,4,6 Tribromo aniline



8. Explain Gattermann reaction



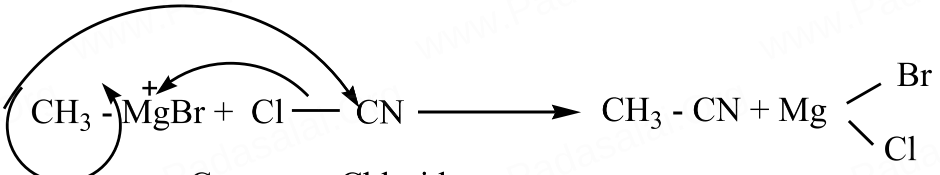
9. Convert Benzene diazonium chloride into phenol

$$C_6H_5\text{-}N_2Cl + H_2O \xrightarrow[283K]{\triangle} C_6H_5 - OH + N_2 + HCl$$

Benzene diazonium Chloride

Phenol

10. Starting from methyl magnesium bromide, how would you obtain ethane nitrile



Cyanogen Chloride

methyl magnesium bromide

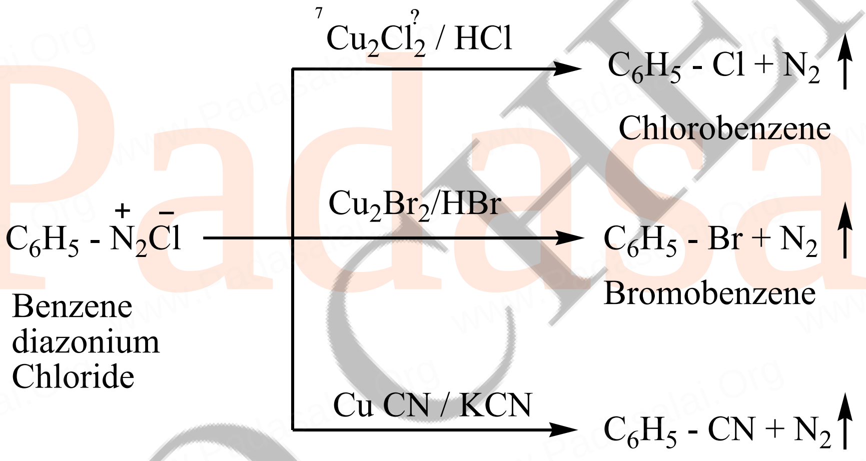
ethanenitrile

11. Convert methyl isocyanide to methyl cyanide

$$CH_3 - N \equiv C \xrightarrow[250^0C]{Heat} CH_3 - C \equiv N:$$

Methyl isocyanide Methylcyanide

12. Write sandmeyer reaction



Chlorobenzene

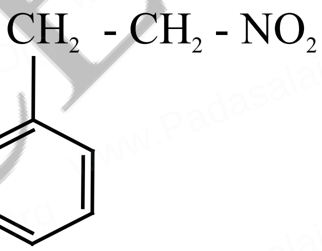
Benzene diazonium Chloride

Bromobenzene

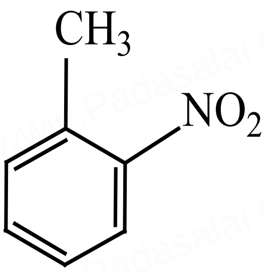
Cyanobenzene

13. Write the IUPAC names for the following structure.

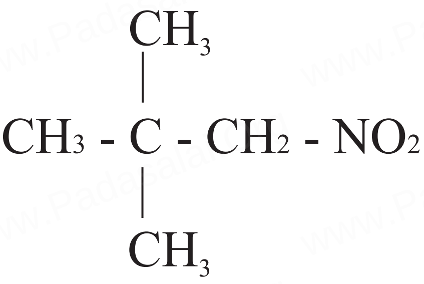
a)



b)



c)



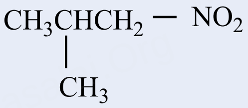
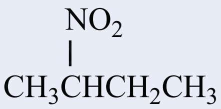
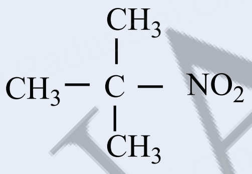
$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - NO_2$$

Ans: IUPAC Name
2 - Phenyl - 1 - nitroethane

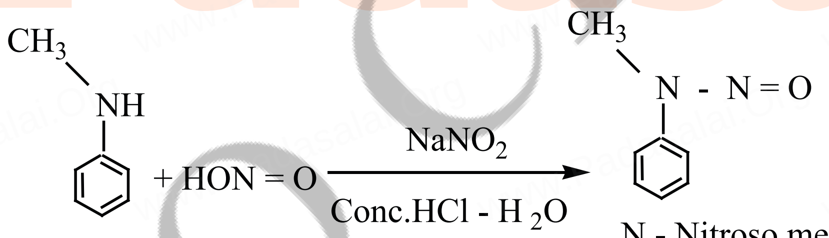
2, 2 - dimethyl - 1- nitro propane

2 - nitro - 1 - methyl benzene

14. Explain the isomerism exhibited by nitro alkanes in $C_4H_9NO_2$

Isomerism	Structural formula of isomers
Chain isomerism: They differ in the length of carbon chain.	$CH_3CH_2CH_2CH_2 - NO_2$ 1 - nitrobutane and  $\underset{\displaystyle CH_3}{\underset{\displaystyle \vert}{CH_3CH}}CH_2 - NO_2$ 2 - methyl - 1-nitropropane
Position isomerism: They differ in the position of nitro group.	$CH_3CH_2CH_2CH_2 - NO_2$, 1 - nitrobutane  $CH_3\overset{\displaystyle NO_2}{\overset{\displaystyle \vert}{C}}HCH_2CH_3$ 2 - nitrobutane and  $CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\vert}{\underset{\vert}{C}}}} - NO_2$ 2 - methyl - 2- nitro propane
Functional isomerism: Nitroalkanes exhibit functional isomerism with alkylnitrites	$CH_3CH_2CH_2CH_2 - NO_2$ 1 - nitrobutane and $CH_3CH_2CH_2CH_2 - O - N = 0$ butyl nitrite

15. Write Libermann's nitroso test



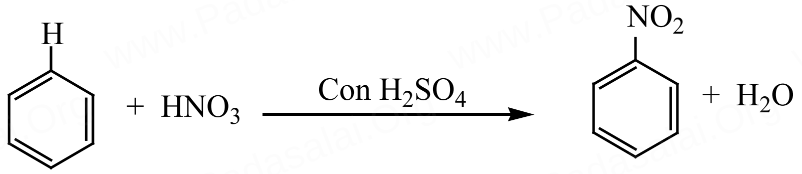
N - methylaniline

N - Nitroso methyl phenyl amine (yellow oil)

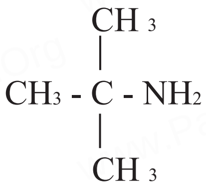
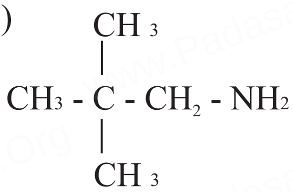
16. What is Oil of mirbane? How is it prepared

i) Oil of mirbane is nitro benzene

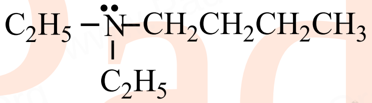
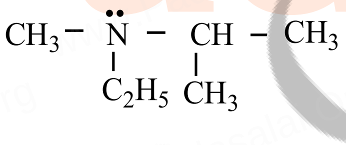
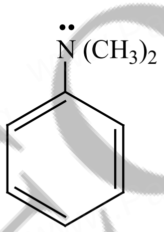
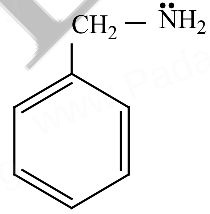
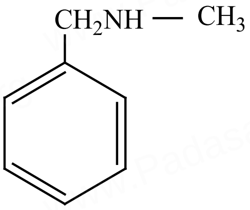
ii) Preparation



17. Classify the following as 1^0 2^0 & 3^0 amines

	Answer
i)  $CH_3-C(CH_3)_2-NH_2$	1^0
ii)  $CH_3-C(CH_3)_2-CH_2-NH_2$	1^0
iii) $CH_3-CH_2-NH-CH_3$	2^0
iv) $CH_3-CH_2-N(CH_3)_2$	3^0

18. Write the IUPAC names for the following structures

	Answer
a)  $C_2H_5-\ddot{N}(C_2H_5)-CH_2CH_2CH_2CH_3$	N - N - diethyl butan - 1 - amine
b)  $CH_3-\ddot{N}(C_2H_5)-CH(CH_3)-CH_3$	N - ethyl N - methyl propan - 2 - amine
c) 	N , N - dimethylbenzenamine
d) 	Phenyl methanamine
e) 	N - methyl phenyl methanamine

19. Write Baltz - Schiemann reaction

$$C_6H_5-\overset{+}{N}_2\overset{-}{Cl} + \underset{\text{Fluoroboric acid}}{HBF_4} \longrightarrow \underset{\text{Benzenediazonium fluoroborate}}{C_6H_5-\overset{+}{N}_2\overset{-}{BF_4}} \xrightarrow{\triangle} \underset{\text{Fluorobenzene}}{C_6H_5-F} + BF_3 + N_2$$

20. Write the structures for the following

a) Benzene Carbonitrile

b) 3-Cyanobutanoicacid

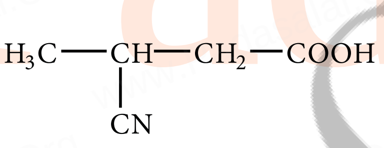
c) 2-Bromo-3-chloro-3- methyl pentanenitrile.

Answer

a) Benzene Carbonitrile

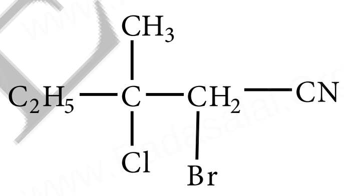
C_6H_5-CN

b) 3-Cyanobutanoicacid



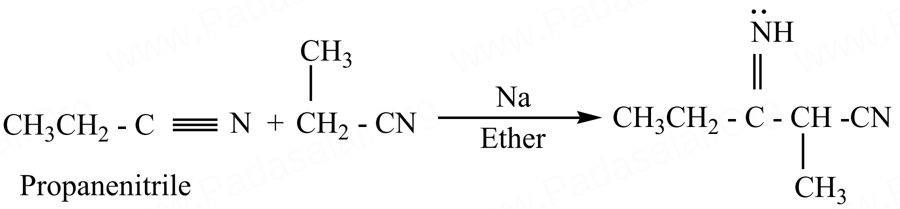
$$H_3C-\underset{\underset{\displaystyle CN}{|}}{CH}-CH_2-COOH$$

c) 2-Bromo-3-chloro-3- methyl pentanenitrile.



$$C_2H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\underset{\underset{\displaystyle Br}{|}}{CH_2}-CN$$

21. Write Thorpe - nitrile Condensation



$$CH_3CH_2-C\equiv N + \overset{CH_3}{\overset{|}{CH_2}}-CN \xrightarrow[Ether]{Na} CH_3CH_2-\overset{\ddot{N}H}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CN$$

Propanenitrile

3 - imino - 2- methyl pentanenitrile

22. What are the uses of aliphatic nitro alkanes

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.

23. Mention the uses of nitrobenzene

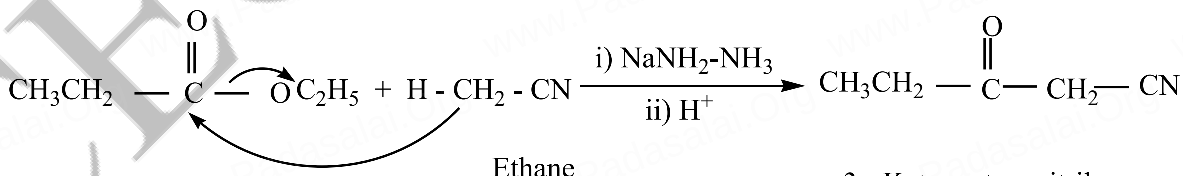
1 Nitrobenzene is used to produce lubricating oils in motors and machinery.

2 It is used in the manufacture of dyes, drugs, pesticides, synthetic rubber, aniline and explosives like TNT, TNB.

24. Write the uses of mitomycin

1. Mitomycin C, anticancer agent used to treat stomach and colon cancer, contains an aziridine ring.
2. The aziridine functional group participates in the drug's degradation by DNA, resulting in the death of cancerous cells.

25. Leavine and Hauser acetylation



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H-CH_2-CN \xrightarrow[ii)\ H^+]{i)\ NaNH_2\text{-}NH_3} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CN$$

Ethyl Propionate

Ethane nitrile

3 - Ketopentanenitrile

26. Aryl amines cannot be prepared by Gabriel phthalimide synthesis. Give reasons?

1. Aryl halide is resonance stabilized having partial double bond character between C - X , and cannot be cleaved.

BIOMOLECULES

I. Text Book Questions:

1. What type of linkages hold together monomers of DNA?

- Monomers of DNA are linked together by phospho diester bond between 5’OH group of one nucleotide and 3’OH group on another nucleotide.

2. Give the difference between primary and secondary structure of proteins.

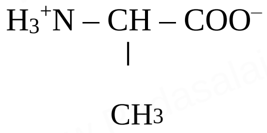
S.no	Primary	Secondary
1	It is the relative arrangement of amino acids in the polypeptide chain	The amino acids in the polypeptide chain forms highly regular shapes through the hydrogen bond between carbonyl oxygen and amine hydrogen.
2	It is essential as even small changes can alter the overall structure and function of a protein.	$\propto$ - helix and β – strands or sheets are two most common sub – structures formed by proteins.

3. Name the Vitamins whose deficiency cause i) rickets ii) scurvy

i) Rickets - Vitamin D

ii) Scurvy - Vitamin C

4. Write the Zwitter ion structure of alanine.



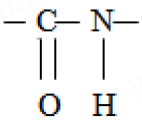
$$H_3^+N - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COO^-$$

5. Give any three difference between DNA and RNA.

S.no	DNA	RNA
1	It is mainly present in nucleus, mitochondria and chloroplast	It is mainly present in cytoplasm, nucleolus and ribosomes.
2	It contains deoxyribose sugar	It contains ribose sugar
3	Base pair A=T G $\equiv$ C	Base pair A=U C $\equiv$ G
4	Double stranded molecules	Single stranded molecules
5	It’s life time is high	It is short lived.
6	It is stable and not hydrolysed easily by alkalies.	It is unstable and hydrolysed easily by alkalies.
7	It can replicate itself	It cannot replicate itself.It is formed from DNA

6. **Write a short note on peptide bond**.

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



$$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$$

7. **Give two difference between Hormones and Vitamins.**

S.no	Hormones	Vitamins
1	Hormone is an organic substance that is secreted by one tissue. It limits the blood stream and induces a biological response in other tissues.	Vitamins are organic compounds that cannot be synthesized by our body and must be obtained through diet.
2	Endocrine glands, which are special groups of cells, make hormones.	They are essential for the normal growth and maintenance of our health
3	Eg. Insulin	Eg. Vitamin A,B,C,D,E and K.

8. **Write a note on denaturation of Proteins.**

- Each protein has a unique three dimensional structure formed by interactions.
- These interactions can be disturbed when the protein is exposed to a higher temperature.
- The process of losing its higher order structure without losing the primary structures is called denaturation.
- When a protein denatures, its biological function is lost.

Eg. Coagulation of egg white by action of heat.

9. **What are reducing and non- reducing sugars.**

Reducing sugars:

- These are carbohydrates which contain free aldehyde or ketonic group.
- Reduces Fehling's solution and Tollen's reagent. Eg. Glucose.

Non - reducing sugars:

- They do not have free aldehyde group.
- They do not reduce Tollen's reagent and Fehling's solution.

Eg. Sucrose

10. Why carbohydrates are generally optically active.

- ❖ Carbohydrates are optically active as they have one or more chiral carbons.

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11. Classify the following into monosaccharides, oligosaccharides and polysaccharides.

i) Starch - polysaccharides
ii) Fructose - monosaccharides
iii) Sucrose - oligosaccharides (disaccharides)
iv) Lactose - oligosaccharides (disaccharides)
v) Maltose - oligosaccharides (disaccharides)

12. How are vitamins classified.

Vitamins are classified into two groups based on their solubility.

i) Fat soluble Vitamins – They do not dissolve in water.
   - ❖ Vitamin A, D, E and K.

ii) Water soluble Vitamins - They are readily soluble in water
   - ❖ Vitamins B(B_1, B_2, B_3, B_5, B_6, B_7, B_9 and B_{12}) and Vitamin C

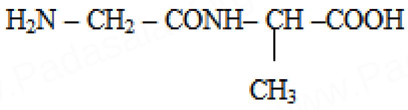
13. What are hormones? Give examples.

- ❖ Hormone is an organic substance that is secreted by one tissue.
- ❖ It limits the blood stream and induces a physiological response in other tissues.
- ❖ Endocrine glands, which are special groups of cells make hormones
- ❖ It is an intercellular signaling molecule.
- ❖ Eg. Insulin, estrogen.

14. Write the structure of all possible dipeptides which can be obtained from glycine and alanine.

They form two dipeptides namely glycylalanine and alanylglycine.

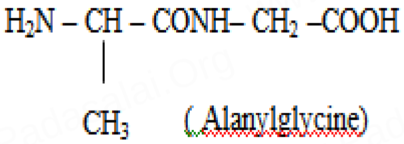
i)



$H_2N-CH_2-CONH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(Glycylalanine)

ii)



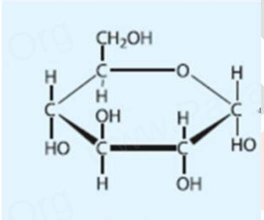
$$H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CONH-CH_2-COOH$$

(Alanylglycine)

15. Define enzymes.

- ❖ All biochemical reactions occur in the living systems are catalysed by the catalytic proteins called Enzymes.
- ❖ Enzymes are biocatalysts that accelerate the reaction rate in the orders of 10^5 and also make them highly specific. Eg. Sucrase

16.Write the structure of α – D(+) glucophyranose.



α-D-glucose
(α–D-Glucopyranose)

17. What are the different types of RNA which are found in cell?

RNA molecules are classified into three major types.

1. Ribosomal RNA (rRNA)
2. Messenger RNA (mRNA)
3. Transfer RNA (tRNA)

18. Write a note on formation of α-helix.

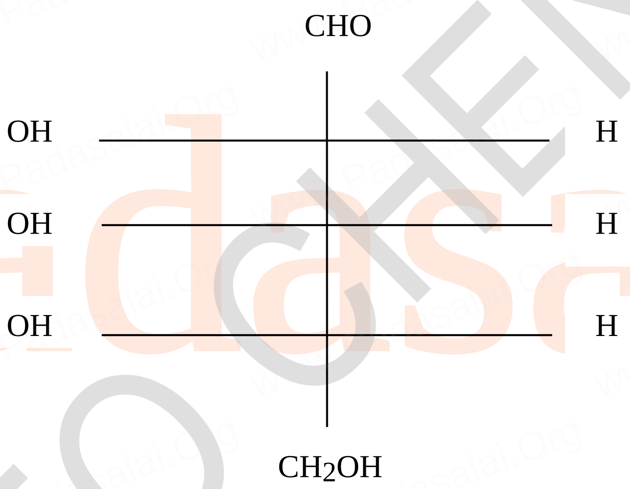
- ❖ In the α-helix sub-structure, the amino acids are arranged in a right handed helical structure.
- ❖ They are stabilised by the hydrogen bond between the carbonyl oxygen of one amino acid with amino hydrogen of the fifth residue.
- ❖ The side chains of the residues protrude outside of the helix.

- Each turn contains 3.6 residues and is about 5.4 A° long.
- The amino acid proline produces a kink in the helical structure and often called as helix breaker due to its rigid cyclic structure.

19. What are the functions of lipids in living organisms.

- Lipids are the integral component of cell membrane.
- The main function of triglycerides(lipids) in animals is as an energy reserve.
- They act as protective coating in aquatic organisms.
- Lipids of connective tissues give protection to internal organs.
- Lipids help in the absorption and transport of fat soluble vitamins.
- Essential for activation of enzymes such as lipases.
- Act as emulsifier in fat metabolism.

20. Is the following sugar, D- sugar or L – sugar?



L - Sugar

Additional questions and Answers.

1. What are monosaccharides? Give example.

Monosaccharides are carbohydrates that cannot be hydrolysed further and are also called simple sugars.
General formula $C_n(H_2O)_n$
Eg: glucose, fructose

2. What are disaccharides? Give example.

Disaccharides are sugars that yield two molecules of monosaccharides on hydrolysis catalysed by dilute acid or enzyme.
General formula $C_n(H_2O)_{n-1}$.
Eg: Sucrose, Lactose

3. What are polysaccharide? Give example.

Polysaccharide consists of large number of monosaccharide units bonded together by glycosidic bonds.Since, they do not have sweet taste polysaccharides are called as non-sugars.

Eg: starch, cellulose

4. What is mutarotation

- The specific rotation of pure α- and β-(D) glucose are 112° & 18.7°
- When a pure form of any one of these sugars is dissolved in 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**.

5. What is epimerization.

- 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.

6. Sucrose is called as invert sugar? Why?

- 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.

7. Write a short note on the structure of sucrose (or) sucrose is a non-reducing sugar. Justify.

- 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.

8. What is glycosidic linkage?

- In disaccharides two monosaccharide's are linked by *oxide linkage* called '*glycosidic linkage*'.
- It is formed by the reaction of the anomeric carbon of one monosaccharide with a hydroxyl group of another monosaccharide.

9. Lactose is a reducing sugar? Justify.

- In lactose the β-D–galactose and β-D–glucose are linked by β-1,4 glycosidic bond.
- The aldehyde carbon is not involved in the glycosidic bond
- It retains its reducing property and is called a reducing sugar.

10. Maltose acts as a reducing sugar justify.

- 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.

11. Write a note on a starch.

- Starch is used for energy storage in plants.
- It is a polymer of glucose in which glucose molecules are linked by α (1,4) glycosidic bonds
- They are separated into two fractions,
  1. water soluble amylose - 20 %
  2. water insoluble amylopectin - 80%

12. Write two difference between Amylose and Amylopectin

S.No	Amylose	Amylopectin
1	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. At branch points, new chains of 24 to 30 glucose molecules are linked by α (1,6)glycosidic bonds.
2	Gives blue colour with iodine solution.	Gives purple colour with iodine solution.
3	Starch contains 20% amylose which is water soluble	Starch contains 80% amylopectin which is water insoluble

13.Write the importance of carbohydrates?

- Carbohydrates, widely distributed in plants and animals, act mainly as energy sources and structural polymers
- Carbohydrate is stored in the body as glycogen and in plant as starch.
- Carbohydrates such as cellulose which is the primary components of plant cell wall, is
- used to make paper, furniture and cloths.
- Simple sugar glucose serves as an instant source of energy.
- Ribose sugars are one of the components of nucleic acids.

- ❖ Modified carbohydrates such as hyaluronate (glycosaminoglycans) act as shock absorber and lubricant.

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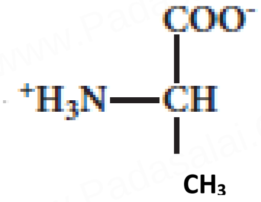
14. What is isoelectric point.

- ❖ 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.

15.What are Zwitter ions?

- ❖ 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.



Zwitter Ion

16.How are proteins classified? Explain.

Proteins are classified into two major types.

1. Fibrous proteins
2. Globular proteins

1.Fibrous proteins

- ❖ Fibrous proteins are linear molecules similar to fibres.
- ❖ 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

2.Globular proteins

- ❖ They 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 Example: myoglobin

17. Give the importance of proteins.

- ❖ All biochemical reactions occur in the living systems are catalysed by the catalytic proteins called enzymes.
- ❖ Proteins such as keratin, collagen act as structural back bones.
- ❖ Antibodies help the body to fight various diseases.
- ❖ They are used as messengers to coordinate many functions. Insulin and glucagon control the glucose level in the blood.

- ❖ They act as receptors that detect presence of certain signal molecules and activate the proper response.
- ❖ They are also used to store metals such as iron (Ferritin).

18. Give the catalytic activity of the following enzymes i) Carbonic anhydrase ii) Sucrase ii) Lactase.

(i) Carbonic anhydrase - Catalyses the interconversion of carbonic acid to water and carbon dioxide.

(ii) Sucrase - Catalyses the hydrolysis of sucrose to fructose and glucose.

(iii) Lactase enzyme - Hydrolyses the lactose into its constituent monosaccharides, glucose and galactose.

19. What are the components of nucleic acids?

The three components of nucleic acids

(i) Nitrogenous base

(ii) Pentose sugar

(iii) Phosphate group

20. Human cannot use cellulose as food? Why?

Human cannot use cellulose as food because our digestive system do not contain the necessary enzymes (glycosidases or cellulases) that can hydrolyse the cellulose.

21. What are nucleoside and nucleotide.

Sugar + Base $\longrightarrow$ Nucleoside

Nucleoside + Phosphate $\longrightarrow$ Nucleotide

22. Give the Biological functions of nucleic acids.

(i) Energy carriers (ATP)

(ii) Components of enzyme cofactors (Eg. FAD)

(iii) Chemical messengers. (Eg. Cyclic AMP)

23. What are the types of RNA? Write its functions. Explain.

Types of RNA

i. Ribosomal RNA (rRNA)

- ❖ rRNA is mainly found in cytoplasm and in ribosomes.
- ❖ It contains 60% RNA and 40% protein.
- ❖ Protein synthesis takes place at this site.

ii. Messenger RNA (mRNA)

- ❖ It is present in small quantity and very short lived.
- ❖ The synthesis of mRNA from DNA strand is called transcription.
- ❖ It carries genetic information from DNA to the ribosomes for protein synthesis.

iii. Transfer RNA (tRNA)

- ❖ Molecules have lowest molecular weight of all nucleic acids.
- ❖ They carry amino acids to the sites of protein synthesis on ribosomes.

24.Elucidate the structure of glucose.

(i) Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$

(ii) 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.

(iii) Glucose reacts with hydroxylamine to form oxime and with HCN to form cyanohydrins. The above reactions indicate the presence of carbonyl group in glucose.

(iv) Glucose gets oxidized to gluconic acid with mild oxidizing agents like bromine water It shows that the carbonyl group is an aldehyde group and it occupies one end of the carbon chain.

(v) When oxidised using strong oxidising agent such as conc. nitric acid gives glucaric acid (saccharic acid).It shows that the other end is occupied by a primary alcohol group.

(vi) 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.

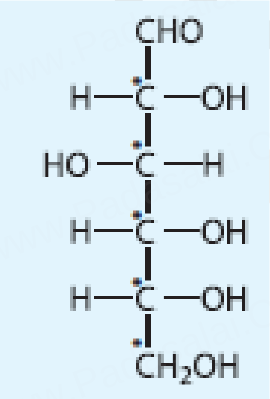
(vii) Glucose forms penta acetate with acetic anhydride suggesting the presence of five alcohol groups.

(viii) 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 hydroxyl groups are attached to five different carbon atoms.
- ❖ Sixth carbon is an aldehyde group.

(ix) The glucose is referred to as D(+) glucose as it has D configuration and is dextrorotatory.

Structure of D(+) glucose



25. What are anomers

- ⇨ In the formation of cyclic structure of glucose, the achiral aldehyde carbon in it is converted to 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.

26. Elucidate the structure of fructose.

1) Elemental analysis and molecular weight determination of fructose show that it has the molecular formula $C_6H_{12}O_6$.

2) On reduction with concentrated HI and red phosphorus, fructose gives a mixture of n hexane and 2–iodohexane indicating that the six carbon atoms are bonded linearly

3) Fructose reacts with NH_2OH and HCN. It shows the presence of a carbonyl groups in the fructose.

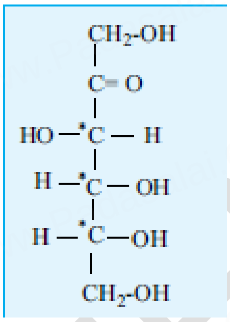
4) Fructose reacts with acetic anhydride in the presence of pyridine to form penta acetate. This reaction indicates the presence of five hydroxyl groups in a fructose molecule.

5) Fructose is not oxidized by bromine water. This rules out the possibility of presence 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.In the above reaction new asymmetric carbon is formed at C-2. This confirms the presence of a keto group.

7) On oxidation with nitric acid, it gives glycolic acid and tartaric acids which contain smaller number of carbon atoms than in fructose.This shows that a keto group is present in C-2. It also shows that 1° alcoholic groups arepresent at C- 1 and C- 6.

The structure of fructose is



27. Write a note on DNA finger printing.

- DNA fingerprinting is also called DNA typing or DNA profiling.
- The DNA finger print is unique for every person.
- It 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.

28 Explain the method of DNA finger printing.

- The extracted DNA is cut at specific points along the strand with restriction of enzymes.
- It 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.
- 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 between individuals

UNIT 15 CHEMISTRY IN EVERDAY LIFE

I. EVALUATION – SHORT ANSWER QUESTIONS

1. Which chemical is responsible for the antiseptic properties of dettol?

(i) Chloroxylenol,
(ii) terpineol

2. What are antibiotics?

The medicines that have the ability to kill the pathogenic bacteria are grouped as antibiotics.
Example: (i) Penicillins (ii) amoxicillin (iii) cefpodoxime

3. Name one substance which can act as both analgesic and antipyretic.

(i) Aspirin (ii) paracetamol

4. Write a note on synthetic 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***
(i)	Anionic detergent	Sodium Lauryl sulphate (SDS)
(ii)	Cationic detergent	n- hexaadecyltrimethyl ammonium chloride
(iii)	Non – ionic detergent	pentaerythrityl stearate

5. How do antiseptics differ from disinfectants?

Antiseptics	**Disinfectants**
⇨ Stop or slow down the growth of micro organisms.	⇨ Stop or slow down the growth of micro organisms.
⇨ Applied to living tissue	⇨ Generally used on inanimated objects.
Example (i) Hydrogen peroxide (ii) Povidine – Iodine (iii) Benzalkonium chloride	Example (i) Chlorine compounds (ii) Alcohol (iii) Hydrogen peroxide

6. What are food preservatives?

Preservatives are capable of inhibiting retarding or arresting the process of fermentation acidification or other decomposition of food by growth of microorganisms.

Examples:

<u>ACETIC ACID</u>

i. Acetic acid is used as a preservative for the preparation of pickles.
ii. Sodium metasulphite is used as a preservative for fresh vegetables and fruits.
iii. Benzoic acid, sorbic acid and their salts are potent inhibitors of a number of fungi, yeast and bacteria.

7. Why do soaps not work in hard water?

Ca^{2+} and Mg^{2+} ions present in hard water reacts with soaps to produce insoluble calcium or magnesium salts of fatty acids.

These insoluble salts separate as scum, and get on the fabrics of the clothes.

8. What are drugs? How are they classified?

A drug is substance that is used to modify or explore physiological systems or pathological states for benefit of the recipient. It is used for the purpose of diagnosis, prevention cure or relief of a disease.

Classification of drugs:

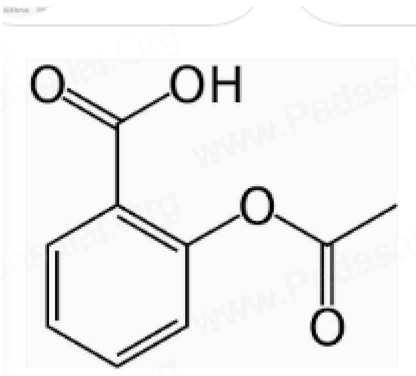
Classification based on

i. The chemical structure
ii. Pharmacological effect
iii. Target system (drug action)
iv. Site of action (molecular target)

9. How the tranquilizers work in body?

- ➩ They are neurologically active drugs.
- ➩ They acts on the central nervous system by blocking the neuro transmitter dopamine in the brain.
- ➩ They are used in the treatment of stress, anxiety, depression, sleep disorders and severe mental diseases like schizophrenia.

10. Write the structural formula of aspirin.



11. Explain the mechanism of cleansing action of soaps of detergents

- ➩ 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 non polar portion is hydrophobic while the polar end is hydrophilic. The hydrophobic hydrocarbon portion is soluble in oils and greases, but not in water.
- ➩ The hydrophilic carboxylate group is soluble in water.
- ➩ 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 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.
  Eg. Sodium Palmitate

Detergents:

- ➩ 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.

12. Which sweetening agents are used to prepare sweets for a diabetic patient?

i) Saccharin ii) Aspartarme iii) Sucralose iv) Alitame are artificial sweeteners.

13. What are narcotic and non-narcotic drugs. Give examples

Narcotic drugs relieve pain and produce sleep. These drugs are addictive. In poisonous dose, these produces coma and ultimately death.

i) **Narcotic drugs Uses:**

- ⇨ Used for either short – term or long term relief of severe pain.
- ⇨ Mainly used for post operative pain, pain of terminal cancer.
- ⇨ Example: Morphine, Codeine.
- ⇨ Non narcotic drugs are Analgesics reduce the pain without causing impairment of consciousness.
- ⇨ They alleviate pain by reducing local inflammatory responses.

ii) **Non-narcotic drugs Uses:**

i. Used for short – term pain
ii. Relief and for modest pain like headache, muscle strain, bruising (arthritis)
Example: paracetamol, Asprin

14. What are antifertility drugs? Give examples

Antifertility drugs are synthetic hormones that suppresses ovulation (or) fertilisation.
Uses: used in birth control pills.

Example:

- ❖ **Synthetic oestrogen**
  i. Ethynylestradiol
  ii. Menstranol

- ❖ **Synthetic progesterone**
  i. Norethindrone
  ii. Norethynodrel

15. Write a note on co- polymer

A polymer containing two or more different kinds of monomer units is called a co-polymer.

Example:

i. Buna –S(SBR rubber) contains styrene and butadiene monomer units.
ii. Buna –N, Nylon – 6, 6

16. What are bio degradable polymers? Give examples.

- ⇨ The materials that are readily decomposed by microorganisms in the environment are called biodegradable.

Examples:

- ❖ Poly hydroxy butyrate (PHB)
- ❖ Polyglycolic acid (PGA)
- ❖ Polylactic acid (PLA)

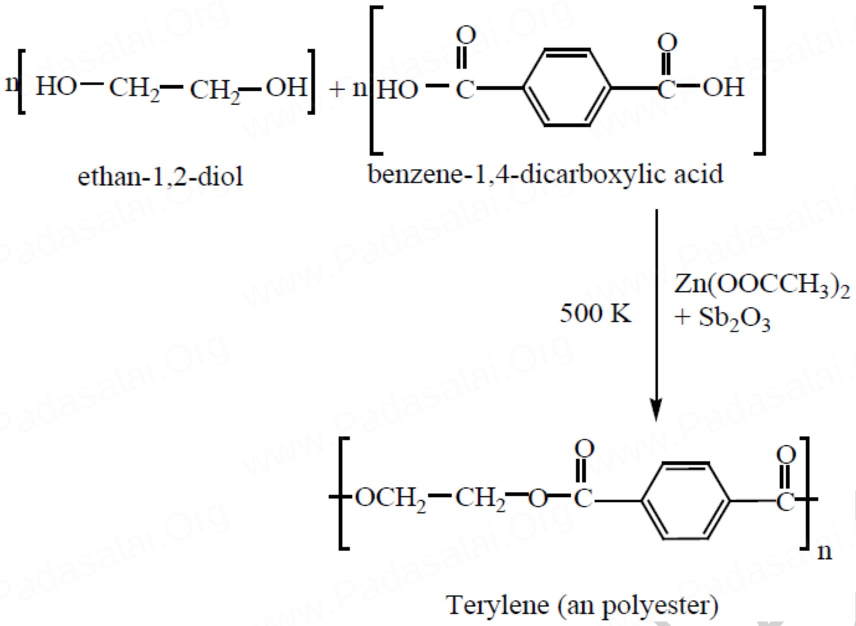
Uses:

In medical field such as

- ❖ Surgical sutures
- ❖ Plasma substitute

17. How is terylene prepared?

The monomers are ethylene glycol and terephthalic acid these monomers are mixed and heated at 500K in the presence of zinc acetate and antimony trioxide catalyst, terylene is formed.



Uses:

- blending with cotton or wool fibres.
- glass reinforcing materials in safety helmets.

18. Write a note on vulcanization of rubber?

- Natural rubber is not so strong or elastic, the properties of natural rubber can be modified by the process 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.

- Ratio of sulphur controls the properties of rubber.

Sulphur Ratio	Properties of rubber
1-3%	soft and stretchy
3 -10%	harder but flexible

19. Classify the following as linear, branched or cross linked polymers.

a) Bakelite b) Nylon c) polythene

a)	Bakelite	- cross linked polymers
b)	Nylon	- linear polymers
c)	Polyethene	- linear polymers.

20. Differentiate thermoplastic and thermosetting.

S.No	Thermoplastic	Thermosetting
1	Linear polymers	Cross linked polymers
2	They become soft on heating and hard on cooling.	Don't become soft on heating but set to an infusible mass upon heating.
3	They can be remoulded	They cannot be remoulded
4	Example: Polyethene, PVC, Polystrene	Example: Bakelite, Melamine, formaldehyde.

Additional questions:

1. **Explain the terms (i) drug (ii) medicine (iii) chemotherapy**

(i) Drug:

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.

(ii) Medicine:

The drug which interacts with macromolecular targets such as proteins to produce a therapeutic and useful biological response is called medicine.

(iii) Chemotherapy:

The specific treatment of a disease using medicine is known as chemotherapy.

2. **Define the term therapeutic index?**

Therapeutic index is defined as the ratio between the maximum tolerated dose of a drug (above which it becomes toxic) and the minimum curative dose (below which the drug is ineffective). Higher the value of therapeutic index, safer is the drug.

3. **Write short notes on (i) antagonists (ii) agonists**

- ⇨ Antagonist is drug which block the message by binding to the receptor side and inhibits to natural function.
- ⇨ Agonists are drugs which mimic the natural messenger by switching on the receptor.

4. **Explain the action of antagonist and agonist with examples.**

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).

Antagonist is a drug, morphine, which is used as a pain killer, binds to the opioid receptors and activates them. This suppress the neuro transmitters that causes pain.

5. **Explain Anaesthetics with example.**

Anaesthetics are two types. They are (i) Local Anaesthetics (ii) General Anaesthetics.

Types	Mode of action	Uses	Example
Local anaesthetics	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.	They are often used during minor surgical procedures.	(i) Procaine **(Ester-linked local)** (ii)Lidocaine **(Amide-linked)**
General Anaesthetics	Cause a controlled and reversible loss of consciousness by affecting central nervous system	They are often used for major surgical procedures.	(i) Propofol (Intravenous) (ii) Isoflurane (Inhalational)

6. What are antacids? Give examples?

Antacids 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.

Examples:

(i) Milk of Magnesia,
(ii) calcium bicarbonate,
(iii) Aluminium hydroxide

7. **What are Antihistamines? Give examples.**

Antihistamines block histamine release from histamine-1 receptors.

Uses:

To provide relief from the allergic effects.

Examples:

(i)Cetirizine, (ii) levocetirizine

8. Write short notes on Antioxidant with example.

- ⇨ Antioxidants are substances which retard the oxidative deteriorations of food. Food containing fats and oils are 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.

Example:

Sulphur dioxide and sulphites are used as as antioxidants and enzyme inhibitors.

9. **Define saponificaiton.**

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..

10. Define TFM value.

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 76% TFM,
  Grade-2 soaps 70% TFM
  Grade-3 soaps 60% TFM

11. Explain the types of polyethene (LDPE, HDPE)

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.

$$n\,CH_2 = CH_2 \xrightarrow[1000\ atm]{200^\circ - 300^\circ C} \left(CH_2 - CH_2 \right)_n$$

ethene Polythene

Uses:

(i) insulators for cables, making toys etc…

HDPE:

The polymerization of ethylene is carried out at 373K and 6 to 7 atm pressure using Zeiglar – Natta catalyst [$TiCl_4$ +$(C_2H_5)_3$ Al] HDPE has high density and melting point and it is used to make bottles, pipes etc..,

12. How Teflon is prepared?

The monomer is tetrafluroethylene when heated with oxygen (or) ammonium persulphate under high pressure, Teflon is obtained.

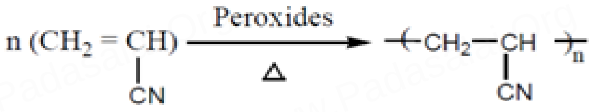
$$n\,CF_2{=}CF_2 \xrightarrow{\Delta} \left(CF_2 - CF_2 \right)_n$$

Uses:

coating articles and preparing non – stick utensils.

13. **How orlon (PAN) is prepared?**

It is prepared by the addition polymerisation of vinylcyanide (acrylonitrile) using a peroxide initiator.



$$n\,(CH_2 = \underset{CN}{CH}) \xrightarrow[\Delta]{Peroxides} \left(CH_2 - \underset{CN}{CH} \right)_n$$

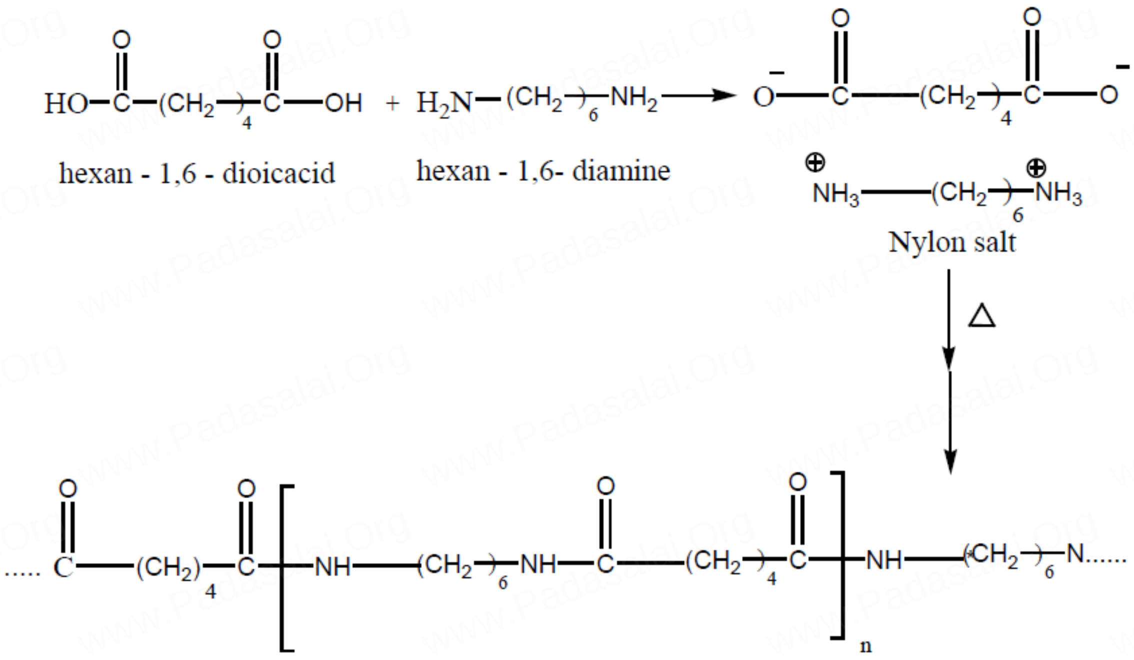
Prop - 2-enenitrile PAN

Uses:

It is used as a substitute of wool for making blankets, sweaters etc.,

14. **How Nylon 6,6 is prepared? Give its use**.

Nylon – 6,6 can be prepared by mixing equimolar adipic acid and hexamethylene – diamine in equimolar proportion to form a nylon salt which on heating eliminate a water molecule to form amide bonds.



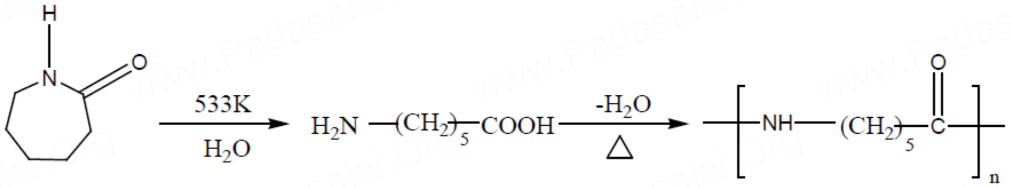
Poly (hexamethyleneadipamide)
Nylon 6,6

Uses:

It is used in textiles, manufacture of cards etc…

15. How Nylon-6 is prepared? Give its uses.

Capro lactum (monomer) on heating at 533K in an inert atmosphere with traces of water gives ∈ amino caproic acid which polymerises to give nylon – 6



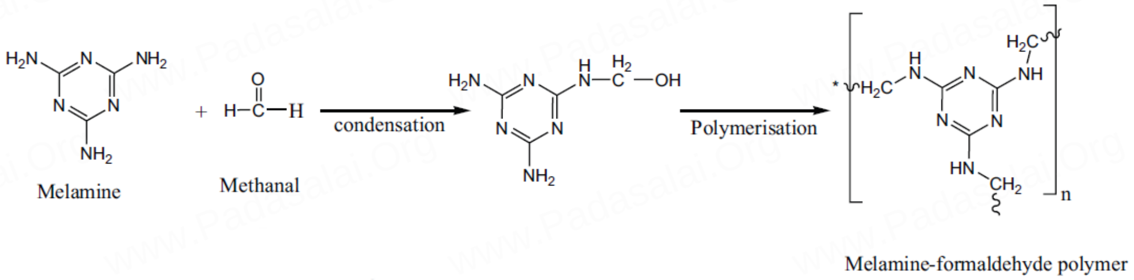
Nylon -6

Uses:

It is used in the manufacture of tyrecords fabrics etc….

16. How is melamine prepared? Give its uses

The monomers are melamine and formaldehyde. These monomers undergo condensation polymerisation to form melamine formaldehyde resin.

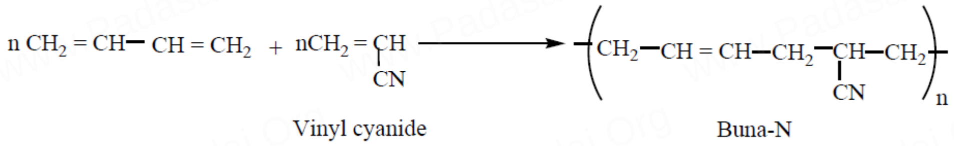


Usage:

It is used for making unbreakable crockery.

17. How Buna-N rubber prepared? Mention its uses.

It is a co-polymer of acrylonitrile and buta-1,3-diene.

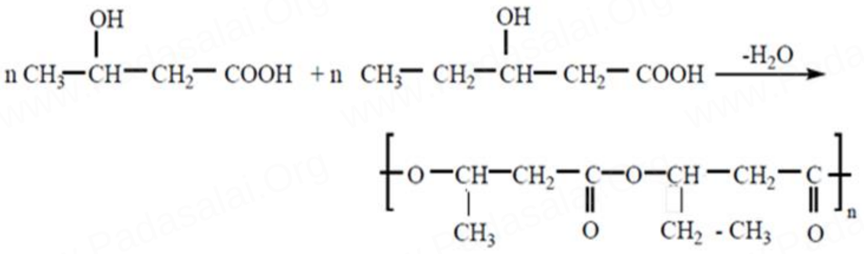


Uses:

It is used in the manufacture of hoses and tanklinings.

18. How PHBV polymer is prepared? Mention its uses.

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.

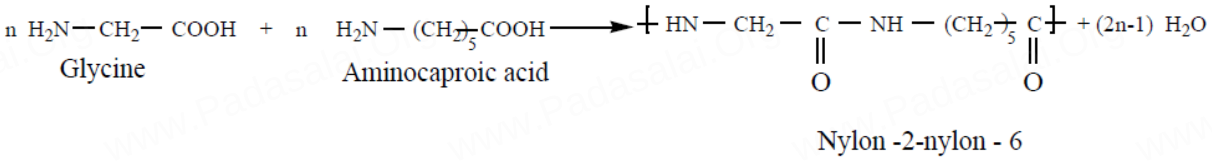


Uses:

It is used in orthopaedic devices, and in controlled release of drugs.

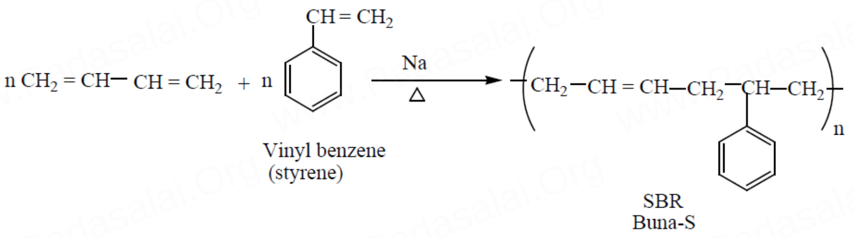
19. How Nylon -2 - Nylon-6 is prepared?

- ⇨ It is a co – polymer which contains polyamide linkages.
- ⇨ It is obtained by the condensation polymersiation of the monomers, glycine and ∈ - amino caproic acid.



20. How Buna-S rubber is prepared?

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.

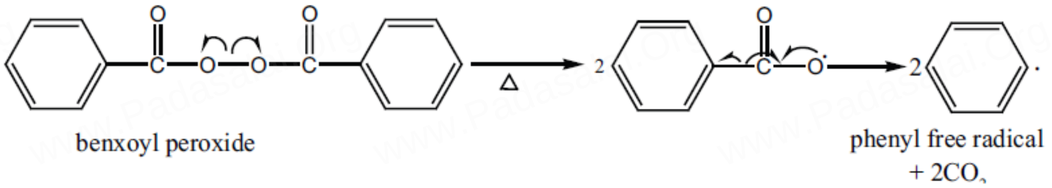


21. **Explain the mechanism followed in free radical polymerization**.

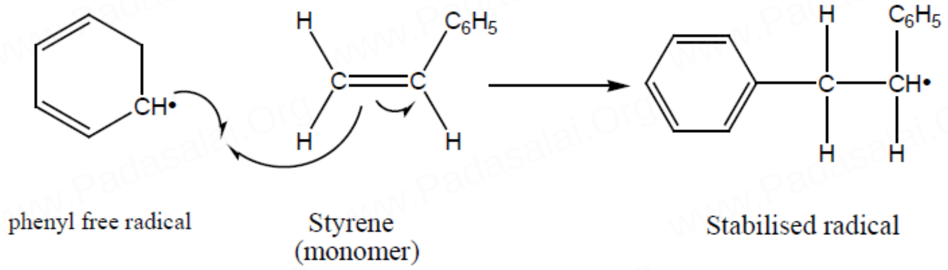
When alkenes are heated with free radical initiator such as benzyl peroxide, they undergo polymerisation reaction.

For example preparation of polystyrene from styrene.

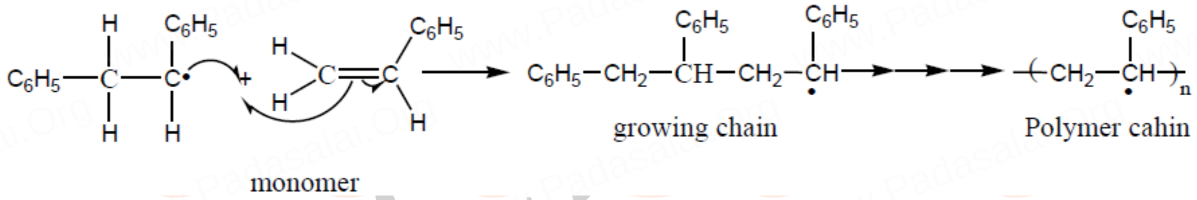
1. initiation – formation of free radical



2. Propagation step



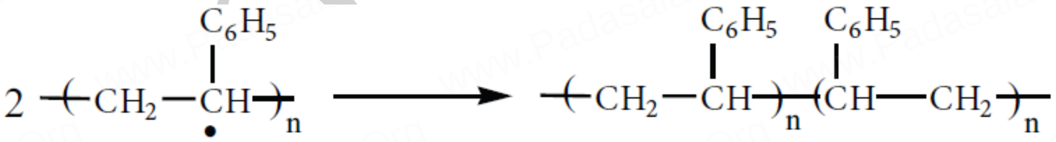
The stabilized radical attacks another monomer molecule to give an elongated radical



Chain growth will continue with the successive addition of several thousands of monomer units.

Termination:

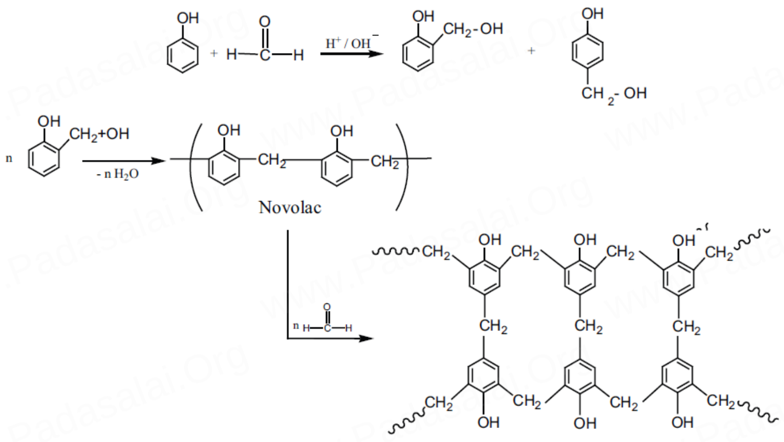
In termination step coupling of two monomers, to form polystyrene polymer.



$$2\,\left(\mathrm{CH_2-\overset{C_6H_5}{\underset{\bullet}{C}H}}\right)_n \longrightarrow \left(\mathrm{CH_2-\overset{C_6H_5}{C}H}\right)_n\left(\mathrm{\overset{C_6H_5}{C}H-CH_2}\right)_n$$

22. **Explain the 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.
- ⇨ In this preparation 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:

(i) Navolac is used in paints.

(ii) Soft bakelites are used for making glue for binding laminated wooden planks and in varnishes.

(iii) Hard bakelites are used to prepare combs, pens etc..