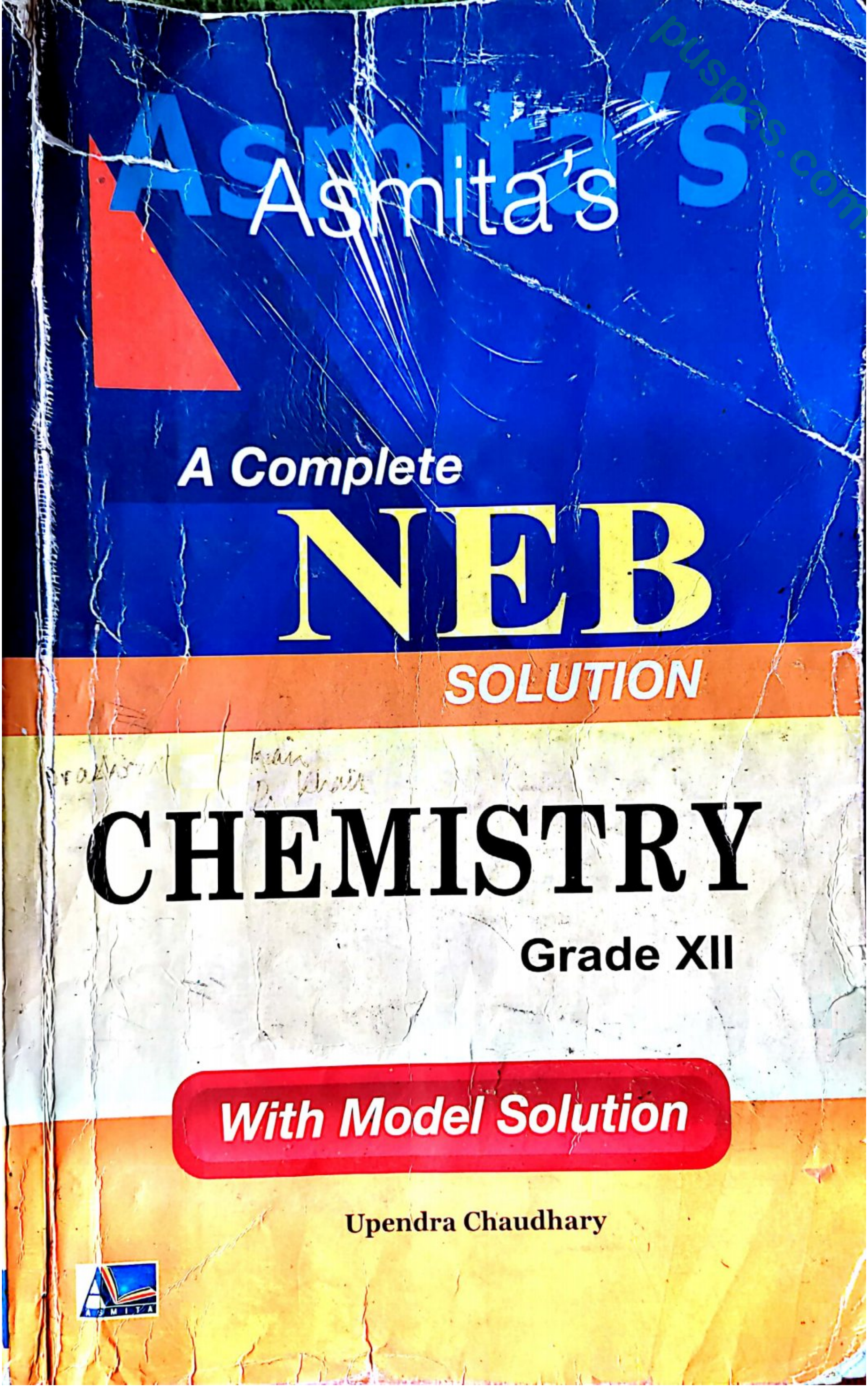

Asmita's

A Complete

NEB SOLUTION

Prashant Khair
D. Khair

CHEMISTRY

Grade XII

With Model Solution

Upendra Chaudhary

ASMITA

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GENERAL & PHYSICAL CHEMISTRY (SECTION A)

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Model Questions – Solution

Group A

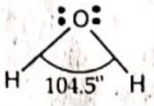
Attempt any FIFTEEN questions. **[15 × 2 = 30]**

1. Predict the structure of water molecule using VSEPR model.

According to VSEPR model, a molecule takes a shape that minimizes the repulsion between bonding pair i.e. bond pair and non-bonding i.e. lone pair of electron.

Lone pair- bond pair repulsion > bond pair – bond pair repulsion

In H_2O molecule, two lone pair of electrons and two bond pair of electrons are present. Due to the presence of lone pair of electrons on O- atom, the shape of water is angular or inverted V-shape.

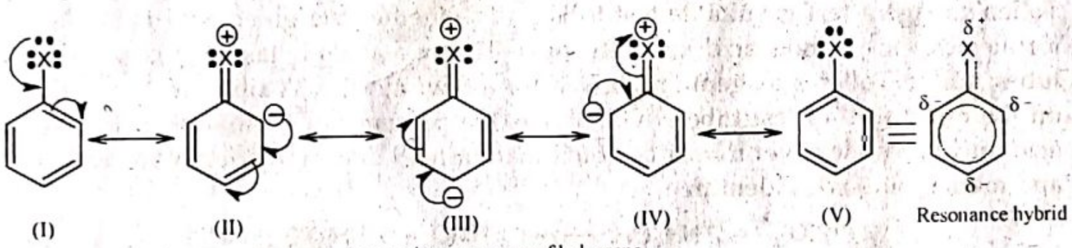


Angular or V-shape of H_2O

---

2. Why is it difficult to undergo nucleophilic substitution in haloarene?

Haloarene, the carbon attached with halogen is sp^2 hybridization and stabilized by resonance. Due to the resonance a double bond is developed between carbon and halogen atom and having lesser polarity of C–X bond.



Resonating structures of haloarene

Therefore, haloarene does not easily undergo nucleophilic substitution.

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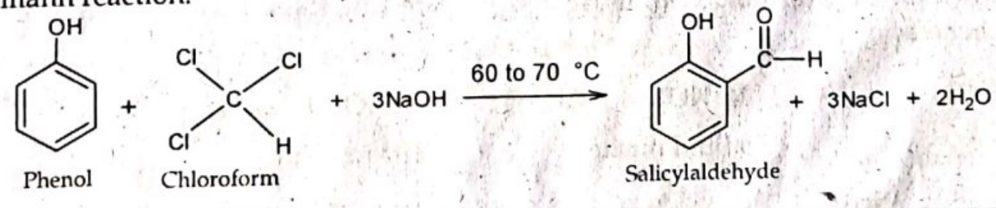
3. Give an example of Reimer Tiemann reaction.

When chloroform is heated with phenol and sodium hydroxide followed by hydrolysis, salicyaldehyde (o-hydroxy benzaldehyde) is formed. This reaction is known as Reimer-Tiemann reaction.



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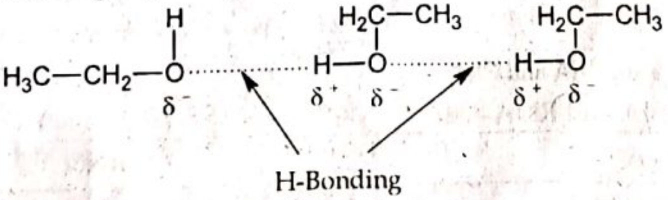
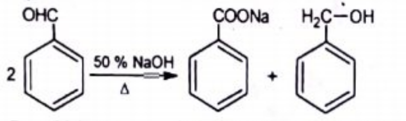
4. Why is the b.p. of ethanol higher than its isomer dimethyl ether?

Ethanol forms hydrogen bond whereas dimethyl ether does not form hydrogen bond. So, the ethanol has higher b.p. than dimethyl ether. We know that hydrogen bonded compound having higher b.p. than hydrogen non-bonded compound.



5. What happens when benzaldehyde is heated with aq. NaOH.

✎ When benzaldehyde is heated with aq. NaOH solution, sodium benzoate and benzyl alcohol is obtained. This reaction is called Cannizzaro's reaction.

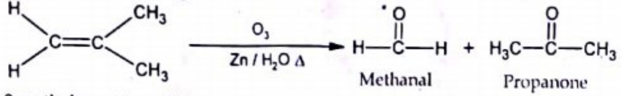


Benzaldehyde Sod. benzoate Benzyl alcohol

6. Suggest the structure of (A) in the reaction given below:

$$A \xrightarrow[Zn / H_2O]{O_3} \text{Methanal} + \text{Propanone}$$

✎ The compound A gives methanal and propanone on ozonolysis. So, the compound A must have alkene containing four carbons.



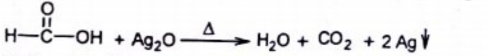
Methanal Propanone

2-methylprop-1-ene (A)

7. Give a chemical test to distinguish between methanoic acid and ethanoic acid.

✎ Tollen's reagent test is suitable test to identify whether the given acid is methanoic i.e. formic acid or ethanoic acid i.e. acetic acid. The two acids is taken in two separate test tubes, added Tollen's reagent and boiled for a few minutes. A silver mirror is deposited on the inner wall of test tube which shows the presence of methanoic acid. Methanoic acid only gives the silver mirror test but ethanoic acid does not give. In this way ethanoic and methanoic acid is identified.

$$2\,AgNO_3 + 2\,NH_4OH \longrightarrow Ag_2O + 2\,NH_4NO_3 + H_2O$$



$$H-\overset{\overset{O}{\|}}{C}-OH + Ag_2O \xrightarrow{\Delta} H_2O + CO_2 + 2\,Ag\downarrow$$

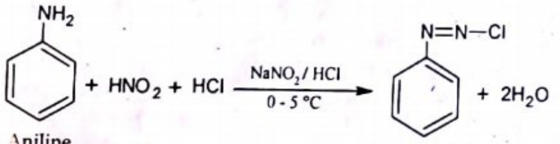
Methanoic acid Silver mirror

8. Write an example of diazotization reaction.

✎ Aniline reacts with nitrous acid at 0 - 5°C then diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

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

Sodium nitrite Nitrous acid



Aniline Benzene diazonium chloride

9. Give two differences between DNA and RNA.

✎ Difference between DNA and RNA are

DNA	RNA
It is deoxyribonucleic acid	It is ribonucleic acid
It is mainly found in chromosome.	It is mainly found in cytoplasm.

10. List two functions of proteins.

✎ Following are the two main functions:

i. It acts as biological catalyst in various metabolic processes in the living body.

ii. It helps in the synthesis of hormons. Example: glycoprotein is used in the synthesis of thyroxin.

11. Match the following:

A. Aspirin	**A. Antibiotic**
B. Dettol	**B. Antipyretic**
C. Paracetamol	**C. Antiseptic**
D. Chloromycetin	**D. Analgesic**

✎

A. Aspirin → D. Analgesic
B. Dettol → C. Antiseptic
C. Paracetamol → A. Antipyretic
D. Chloromycetin → B. Antibiotic

12. Name any two insecticides.

✎ Two insecticides are DDT and BHC.

13. X gram of $CaCO_3$ reacts completely with 20 mL of 1 molar HCl. Calculate the value of X.

✎ Here, 1M HCl = 1N HCl

So, 20 mL of 1M HCl = 20 mL of 1N HCl

Equivalent weight of $CaCO_3 = \frac{40 + 12 + 48}{2} = 50$

We know that,

1 g equivalent weight of acid = 1 g equivalent weight of base

or, 1000 mL of 1N HCl = 50 g equivalent weight of $CaCO_3$

or, 20 mL of 1N HCl = $\frac{50}{1000} \times 20 = 1$ g equivalent weight of $CaCO_3$

Therefore, the value of X = 1 gram.

14. State Faraday's Laws of Electrolysis.

✎ **Faradays Law of Electrolysis**

Michael Faraday's in 1833 introduced the quantitative aspect of the decomposition of electrolyte by passing an electric current through them. He established a relationship between the amount of the electricity passed and the amount of the substance deposited at the electrode. His result can be expressed in the form of two laws called Faradays law of electrolysis.

Faraday's First law of electrolysis

Statement: "The amount of substance deposited or liberated at electrode during electrolysis is directly proportional to the quantity of electricity passed through the solution"

Faraday's second law of electrolysis

Statement: If the same quantity of electricity is allowed to pass through the solutions of different electrolytes, then the amount of different substance or ions deposited or liberated at respective electrode are proportional to their chemical equivalent or equivalent weight.

15. Calculate the standard EMF of a cell from the half cell. Ag^+ / Ag and Ni^{+2} / Ni having standard reduction potential + 0.80 V and –0.25 V respectively.

✎ The reduction potential of two half cell reactions are

$Ag^+ + 1e^- \longrightarrow Ag\ [E^\circ = +0.80\ V]$
$Ni^{+2} + 2e^- \longrightarrow Ni\ [E^\circ = -0.25\ V]$

Here, the reduction potential of Ag^+ / Ag is more than that of Ni^{+2} / Ni. So, the reduction will occur at nickel electrode.

So, EMF of cell i.e. $E^ocell = E^o{}_{(cathode)} - E^o{}_{(anode)} = 0.80 - (-0.25) = +1.05$ V.

16. Define and give one example of Lewis base.

Lewis base: The species which is capable of donating a pair of electrons is known as Lewis base. Example: NH_3, RNH_2 etc.

17. What is the criteria for spontaneity of a reaction?

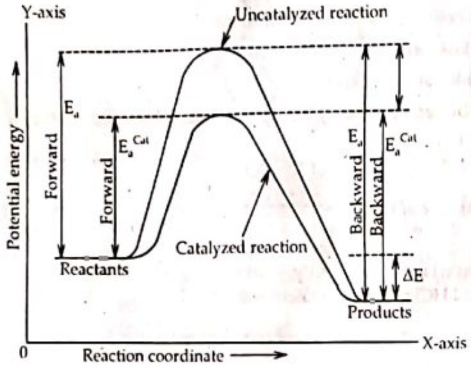
For spontaneity of a reaction

Free energy change should be negative i.e. ΔG = -ve (or < 0)

Entropy change should be positive i.e. ΔS = +ve (or > 0)

18. Draw energy profile diagram for catalyzed and uncatalyzed reaction.

The energy profile diagram of catalyzed and uncatalyzed reaction is



E_a(forward) = Forward reaction for uncatalyzed reaction

E_a(backward = Backward reaction for uncatalyzed reaction

E_a^{Cat}(forward) = For catalyzed reaction

E_a^{Cat}(backward) = For catalyzed reaction

19. Write two ways for prevention of corrosion.

Prevention from rusting

a. By galvanizing iron with Zn or Sn.

b. By covering iron surface with paint, coal tar, liquor etc.

20. Give two uses of Zinc.

Following are two uses:

i. It is used as galvanizing iron.

ii. It is used for the extraction of silver or gold.

Group 'B'

Attempt any FIVE questions. **[5×5 = 25]**

21. How is Diethyl ether prepared in the laboratory?

Principle: When excess of ethyl alcohol is heated with conc. H_2SO_4 at 140°C, diethyl ether is obtained.

$$\underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH} + H_2SO_4 \xrightarrow{100\ °C} \underset{\text{Ethyl hydrogen sulphate}}{H_3C-CH_2-HSO_4} + H_2O$$

$$\underset{\text{Ethyl hydrogen sulphate}}{H_3C-CH_2-HSO_4} + \underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH} \xrightarrow{140\ °C} \underset{\substack{\text{Diethyl ether}\\\text{(Ethoxyethane)}}}{H_3C-CH_2-O-CH_2-CH_3} + H_2SO_4$$

Procedure: 50 cc of conc. H_2SO_4 is gradually added with constant shaking to 100 cc of ethyl alcohol kept in the distillation flask. The mixture is heated on a water bath at 140°C, when ether begins to distill over. Alcohol is added in the distillation flask from the dropping funnel at nearly the same rate as that of the distillation, the temperature being maintained at 140°C.

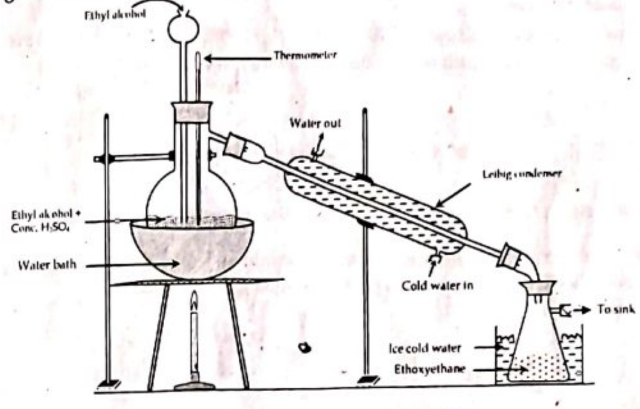


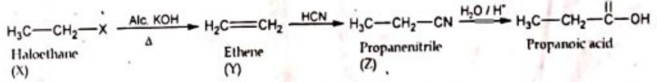
Figure: Laboratory preparation of diethylether

Purification: The distillate contains ether, ethyl alcohol, water and sulphur dioxide. It is first washed with dil. NaOH solution and then with water. The upper layer is separated and dried over anhydrous $CaCl_2$. It is then redistilled on a water bath pure ether passes over at 34 - 35°C.

22. A primary haloalkane (X) on dehydrohalogenation yields a compound (Y), which when reacted with HCN gives (Z). The compound Z on hydrolysis gives propanoic acid. Identify X, Y and Z.

The compound Z on hydrolysis gives propanoic acid. So, compound X contains two carbons. The primary haloalkane having two carbons is H_3C-CH_2-X

The complete reaction is given as:



$$\underset{\substack{\text{Haloethane}\\\text{(X)}}}{H_3C-CH_2-X} \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\substack{\text{Ethene}\\\text{(Y)}}}{H_2C=CH_2} \xrightarrow{\text{HCN}} \underset{\substack{\text{Propanenitrile}\\\text{(Z)}}}{H_3C-CH_2-CN} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{H_3C-CH_2-\overset{\overset{\large O}{\|}}{C}-OH}$$

The compounds are

X = Haloethane

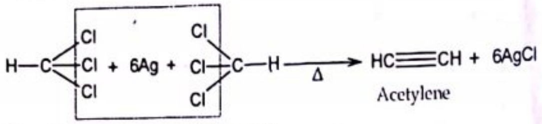
Y = Ethene

Z = Propanenitrile

23. What happens when:

a. The gas produced by heating chloroform with silver powder is passed into ammonical silver nitrate solution.

When chloroform is heated with silver powder, acetylene gas is obtained. Acetylene gas is passed through ammoniacal solution of silver nitrate,a white ppt of silver acetylide is obtained.



Acetylene

Chloroform Chloroform

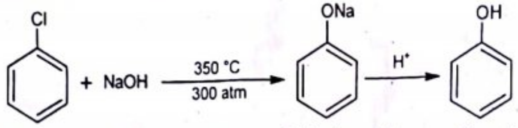
$CH{\equiv}CH + 2AgNO_3 + 2NH_4OH \longrightarrow Ag-C{\equiv}C-Ag\downarrow + 2NH_4NO_3 + 2H_2O$

Acetylene Silver nitrate Silver acetylide(White ppt)

---

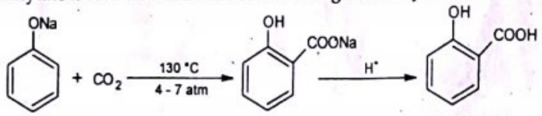
b. The product obtained by heating chlorobenzene with aq. NaOH is allowed to react with CO_2 at about 130°C under pressure.

➣ When chlorobenzene is heated with aq. KOH at 350°C and 300 atm pressure, sodium phenoxide is formed which on acidification to form phenol.



Chlorobenzene Sod. phenoxide Phenol

Sodium phenoxide is heated with carbon dioxide at 130°C under 4 - 7 atm pressure, sodium salicylate is formed which on acidification gives salicylic acid.



Sod. phenoxide sod. salicylate Salicylic acid

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24. For the reaction 2A + B ⟶ C, the following data were obtained.

Expt. No.	Initial concⁿ of [A]° mol / L	Concⁿ of [B]° mol/L	Initial rate of reaction Mol L⁻¹ s⁻¹
1	0.1	0.2	3×10^2
2	0.3	0.4	3.6×10^3
3	0.3	0.8	1.44×10^4

a. Find the order of reaction with respect of A, B and overall.

b. What are the units of rate constant of the reaction?

Solution

Given,

Reaction $2A + B \longrightarrow C$

Rate = $k[A]^m[B]^n$

Therefore,

$3 \times 10^2 = k[0.1]^m[0.2]^n$ ... (i)

$3.6 \times 10^3 = k[0.3]^m[0.4]^n$ ... (ii)

$1.44 \times 10^4 = k[0.3]^m[0.8]^n$ ... (iii)

Dividing equation (iii) by (ii) then we get

$$\frac{1.44 \times 10^4}{3.6 \times 10^3} = \frac{k[0.3]^m[0.8]^n}{k[0.3]^m[0.4]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

∴ $n = 2$

The reaction is second order with respect to B.

Again, dividing equation (ii) by (i) we get,

$$\frac{3.6 \times 10^3}{3 \times 10^2} = \frac{k[0.3]^m[0.4]^n}{k[0.1]^m[0.2]^n}$$

or, $12 = 3^m 2^n$ [n = 2]

or, $12 = 3^m 2^2$

or, $12 = 3^m . 4$

or, $3^1 = 3^m$

∴ $m = 1$

The reaction is 1st order with respect to A.

Hence,

The reaction is 1st order with respect to A.

The reaction is 2nd order with respect to B.

Overall order is (2 + 1) = 3 (3rd order)

Units of Rate constant

$$k = \frac{Rate}{[A]^1[B]^2} = \frac{mol\ s^{-1}L^{-1}}{mol\ L^{-1}(mol\ L^{-1})^2} = mol^{-2}\,L^{+2}\,s^{-1}$$

---

25. 0.05 g of impure $CaCO_3$ is dissolved into 20 mL of $\frac{N}{5}$ [f = 1.05] HCl solution and excess of HCl solution needs 30 mL of $\frac{N}{10}$ [f = 1.15] NaOH solution for complete neutralization. Find the percentage purify of $CaCO_3$.

Solution

20 mL of $\frac{N}{5}$ (f=1.05) HCl = 4.2 mL of 1N HCl

30 mL of $\frac{N}{10}$ (f=1.15) NaOH = 3.45 mL of 1N NaOH

According to volumetric analysis principle

1000 mL of 1N NaOH neutralizes 1000 mL of 1N HCl

So, 3.45 mL of NaOH must neutralizes 3.45 mL of 1N HCl

The volume of HCl left = (4.2 - 3.45) = 0.75 mL of 1N HCl which was already neutralized by 0.05 g of $CaCO_3$.

Now,

0.75 mL of 1N HCl is neutralized by 0.05 g of $CaCO_3$

1000 mL of 1N HCl is neutralized by $\frac{0.05 \times 1000}{0.75} = 66.66$ g

But actually,

1000 mL of 1N HCl requires = 50 g $CaCO_3$ i.e. equivalent weight

The weight of impure $CaCO_3$ = (66.66 - 50) = 16.66 g

% impurity = $\frac{16.66}{66.66} \times 100 = 24.99$ %

% purity = (100 - 24.99) = 75.01 %

Therefore, % purity of $CaCO_3$ = 75.01 %

---

26. Define Gibb's free energy and derive an expression to show the relation between ΔG, ΔH and ΔS.

➣ **Gibb's Free energy:** Any part of energy which can be converted into useful work is called Gibb's free energy. It is denoted by the symbol G. its relation with E,H,S and T are given by the following equation.

G = H - TS

If the system is changed from one state to another state then

$G_1 = H_1 - T_1S_1$ ... (i)

$G_2 = H_2 - T_2S_2$ ... (ii)

The change of free energy is given by

$G_2 - G_1 = (H_2 - H_1) - (T_2S_2 - T_1S_1)$

If the system is carried out at constant temperature then $T_1 = T_2 = T$

$\therefore \Delta G = \Delta H - T\Delta S$ ... (iii)

The equation (iii) is called Gibb's Helmholtz equation and useful for predicting the spontaneity of a process.

From 1st law of thermodynamics

$\Delta Q = \Delta E + \Delta W$

or, $\Delta Q = \Delta E + W_{exp} + W_{useful}$

or, $\Delta Q = \Delta E + P\Delta V + W_{useful}$ $[W_{exp} = P\Delta V]$

or, $\Delta Q = \Delta E + W_{useful}$ $[\Delta E = P\Delta V = \Delta H]$

or, $\Delta Q = \Delta H + W_{useful}$ ... (iv)

We know that,

$$\Delta S = \frac{\Delta Q_{rev}}{T}$$

$\Delta Q = T\Delta S$

Equation (iv) becomes

$T\Delta S = \Delta H + W_{useful}$

$\Delta H - T\Delta S = - W_{useful}$

or, $\Delta G = - W_{useful}$

27. How is mercury extracted in pure form from its sulphide ore?

Extraction: Mercury is extracted from cinnabar ore by carbon reduction process. This process consists of the following steps:

a. **Concentration of cinnabar ore by froth floatation process:** Cinnabar is a sulphide ore and hence it is concentrated by froth floatation process.

b. **Roasting of the concentrated ore:** The concentrated ore is roasted in air when it gets oxidized to HgO and portion decomposes to Hg and O_2.

$$2HgS + 3O_2 \xrightarrow{\Delta} 2HgO + 2SO_2\uparrow$$

$$2HgO \xrightarrow{\Delta} 2Hg + O_2\uparrow$$

c. **Smelting in a shaft furnace:** The roasted ore is mixed with coke and the mixture are heated in a shaft furnace to about 1000°C. Under this condition, HgO gets reduced to Hg.

$$HgO + C \longrightarrow Hg + CO$$

The vapours of Hg and CO are led into a tank containing water where mercury vapours condenses to form liquid mercury.

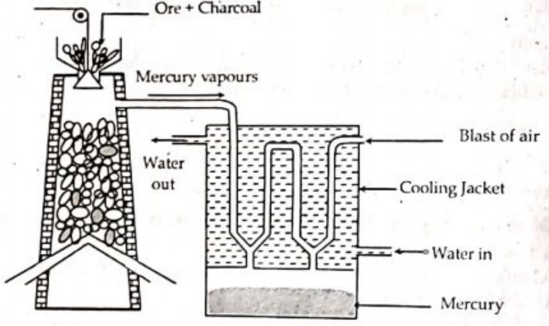


Fig: Shaft furnace

d. **Purification:** Mercury contains some solid as well as soluble base-metals impurities. It is purified in following steps:

i. **Filtration through chamois leather:** Impure mercury is filtered through a chamois leather bag when mercury filters out and solid impurities remain in the bag.

ii. **Treatment with 5% HNO_3:** The filtered mercury is treated with 5% HNO_3 when most of the base metals impurities dissolve in HNO_3 but mercury does not dissolve. This mercury is separated, washed with water and dried.

iii. **Distillation in vacuum:** The dry mercury is distilled in vacuum when very pure mercury is obtained.

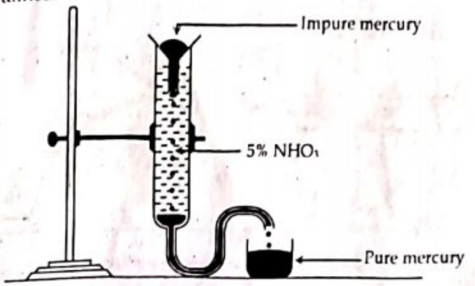


Fig: Purification of mercury

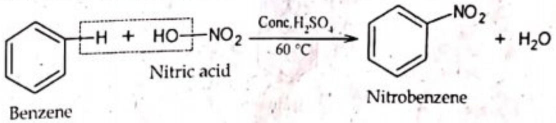
Group 'C'

Attempt any TWO questions. **[2×10 = 20]**

28. How is nitrobenzene prepared in laboratory? Give its reduction in different media.

Laboratory preparation of nitrobenzene:

Theory: It is prepared in the laboratory by the nitration of benzene with a mixture of conc. HNO_3 and conc.H_2SO_4 at ordinary temperature.



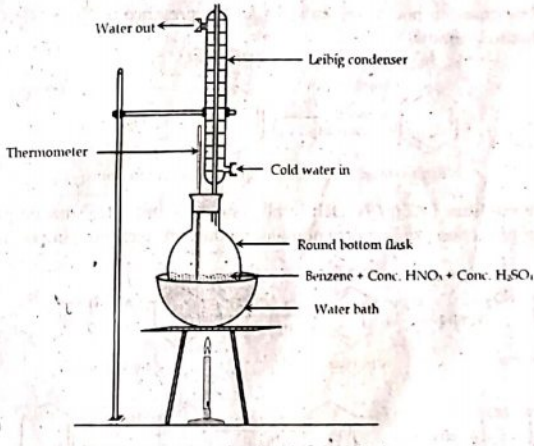


Fig: Laboratory preparation of nitrobenzene (reflux)

Procedure: 60 mL of conc. H_2SO_4 and 60 mL conc. HNO_3 is taken in a round bottom flask and the flask is cooled by immersing in cold water then 50 mL benzene is added in small amount and the mixture is shaked in every addition. The mixture is heated in water ba at 60°C for 60 minutes, pale yellow oily layer with bitter almond odour appears on th surface. The flask is cooled and the mixture is transferred into cold water. The layer o nitrobenzene is separated by using separating funnel.

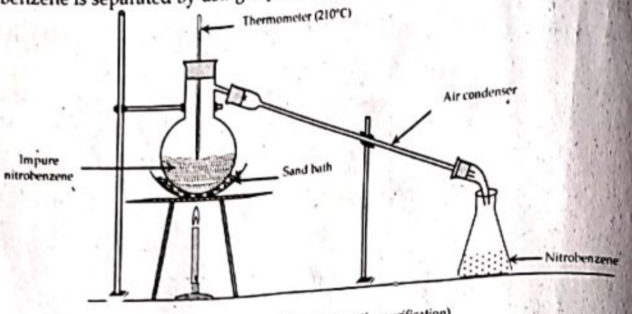
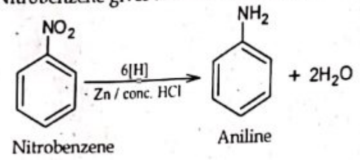


Figure: Distillation of nitrobenzene (for purification)

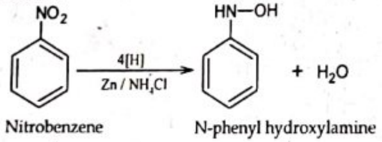
Purification: Thus the obtained nitrobenzene is washed with Na_2CO_3 and water seve times and dried over anhydrous $CaCl_2$. The nitrobenzene is distilled by using a condenser to get pure nitrobenzene. Thus, the obtained pure nitrobenzene has boili point 210°C.

Reduction of nitrobenzene in different medium:

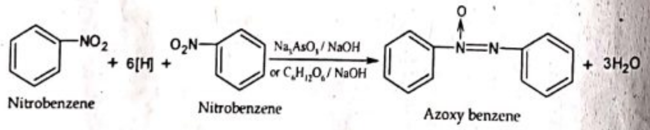
a. **In acidic medium:** Nitrobenzene gives aniline in acidic medium.

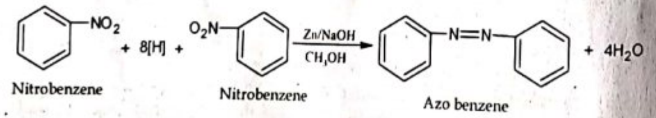


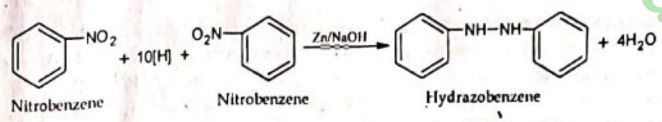
b. **In neutral medium:** In neutral medium i.e. in the presence of Zn + NH_4Cl then gives N-phenyl hydroxylamine.



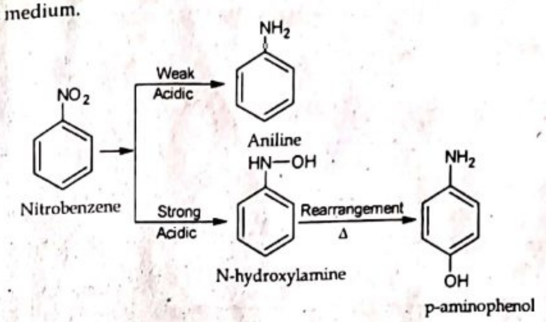
c. **In alkaline medium i.e.Zn / NaOH:** In alkaline medium, nitrobenzene gives different bimolecular reduction product depending upon the nature of reducing agent used.







d. **Electrolytic reduction:** Nitrobenzene on electrolytic reduction gives different products in different medium.



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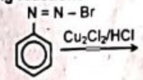
29. a. **Write the major product of following reactions:**

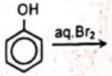
(i) $CH_3COOH \xrightarrow[\Delta]{P_2O_5}$

(ii)

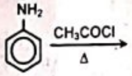


(iii) $CHCl_3 \xrightarrow{Conc.\ HNO_3}$

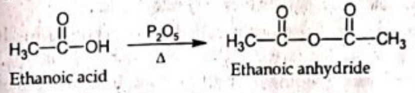
(iv)



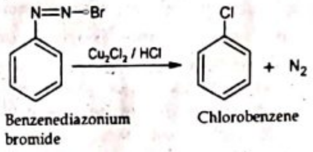
(v)



i.



ii.



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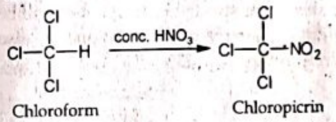

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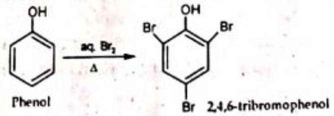
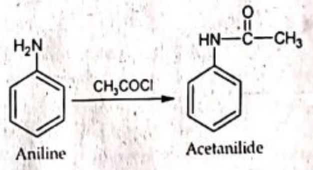


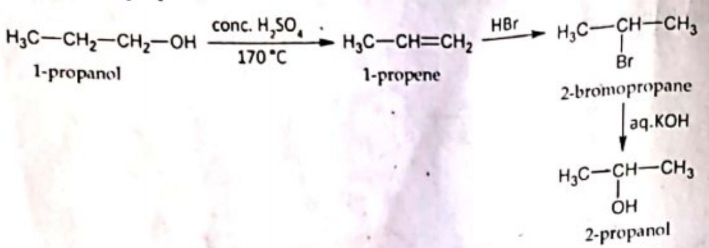
v.



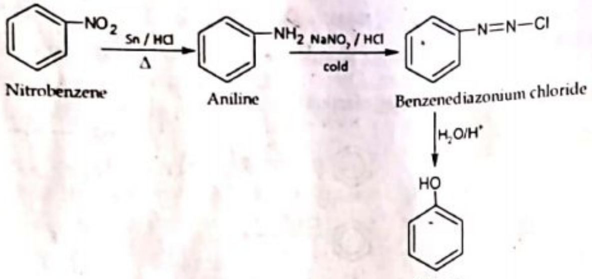
b. How would you convert?
- i. 1 – Propanol into 2 – propanol
- ii. Nitrobenzene into phenol

➢ Conversion:

i. 1-propanol to 2-propanol



ii. Nitrobenzene to phenol:



30. a. Define specific conductance and molar conductance. How do they vary with dilution?

➢ **Specific conductance:** The reciprocal of specific resistance is called specific condunce. It is denoted by kappa (κ)

Molar conductance: The conductance of certain volume of solution containing 1 mole of solute when the whole solution is placed between two parallel electrodes of 1 cm apart is called molar conductace.

Variation of specific (κ) conductances with dillution: With increase in dilution, the specific conductance will decrease. It is due to decrease in number of ions per cm^3. The decrease in specific conductance will be sharp or abrupt for strong electrolyte but will be gradual for weak electrolyte. With increase in dilution, degree of dissociation will also increase which is not possible in case of strong electrolyte.

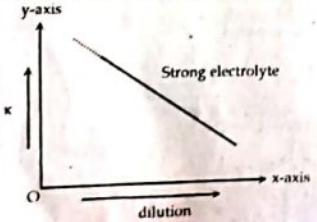


Fig: Variation of specific conductance (κ) with dilution

Effect of dilution on molar conductance (μ): With increase in dilution, the molar Conductance will increase. The increase in molar conductance with increase in dilution will be sharp for weak electrolyte and will be slow for strong electrolyte. The value of conductance depends on (i) number of ions (ii) speed of ions.

In case of strong electrolyte the increase in molar conductance is only due to increase in speed of the ions because with increase in dilution force of attraction between ions will decrease.

In case of weak electrolyte, the increase in molar conductance with increase in dilution is sharp. It is because of no. of ions will also increase.

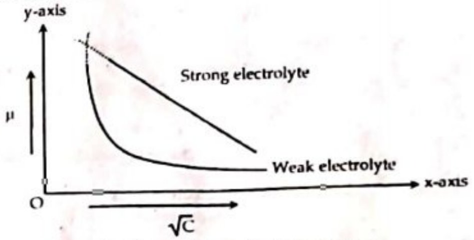


Fig: Variation of molar conductance (μ) with dilution

b. Find the pH of 0.01M acetic acid solution. (Given Ka = 1.85 × 10^{-5})

➢ CH_3COOH ionizes as

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	+ H^+
Initially	C	0	0
At equilibrium	(1-α)C	αC	αC (Let α is degree of ionization)

Applying Law of mass action

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \text{ ....(i}$$

Here, $\alpha C = [H^+] = [CH_3COO^-]$

$(1-\alpha)C = [CH_3COOH] = 0.01M$

$Ka = 1.85 \times 10^{-5}$

Putting the value in the above equation (i) we get

$$Ka = \frac{\alpha^2C^2}{(1-\alpha)C} = \frac{\alpha^2C}{(1-\alpha)}$$

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

or, $1.85 \times 10^{-5} = \frac{[H^+][H^+]}{[0.01]}$

or, $[H^+]^2 = 1.85 \times 10^{-5} \times 0.01$

or, $[H^+] = \sqrt{1.85 \times 10^{-7}} = 4.30 \times 10^{-4}$

We know that

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

$pH = -\log[4.30 \times 10^{-4}]$

$pH = 3.36$

Hence, pH of 0.01 M CH_3COOH is 3.36

31. Write short note on any TWO:

a. Characteristics of Transition elements.

➢ **Transition elements:** Those elements which have partially filled d-orbitals in metallic state is called transition elements.

General properties:

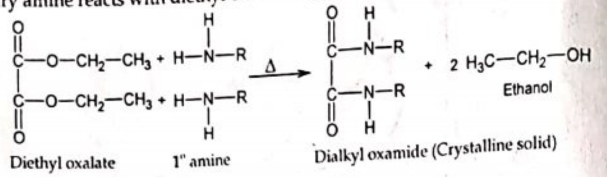
i. Transition elements have high melting and boiling point.

ii. Salts of transition elements are coloured in the solid state.

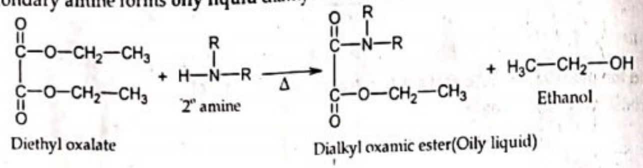
iii. The compounds of transition elements show paramagnetic behavior.
iv. Transition elements exhibit variable oxidation states.
v. Transition elements have ability to act as catalyst in different chemical reactions.

b. Hoffmann's method of separation of mixture of amines.

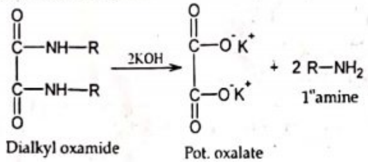
Separation of primary, secondary and tertiary amines by Hoffmann's method:
Given mixture of primary, secondary and tertiary amine is heated with diethyl oxalate.
Primary amine reacts with diethyl oxalate to give crystalline solid dialkyl oxamide.



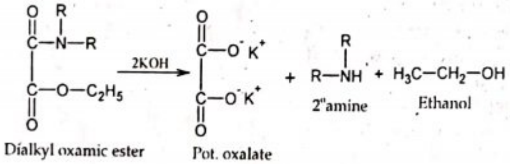
Secondary amine forms **oily liquid** dialkyl oxamic ester.



Tertiary amine **does not** react with diethyl oxalate.
The reaction mixture containing dialkyl oxamide, dialkyl oxamic ester, tertiary amine and ethyl alcohol is first filtered and solid product of dialkyl oxamide is separated. Dialkyl oxamide is heated with aq. KOH to recover primary amine.



The remaining mixture of dilakyl oxamic ester, tertiary amine and ethyl alcohol is subjected to fractional distillation. Tertiary amine is distilled out first. The residual dialkyl oxamic ester is heated with aq.KOH to recover secondary amine and ethyl alcohol in different fractions.



In this way, the given mixture of 1°,2°,3° amines are separated out by Hoffmann's method.

c. Manufacture of steel by open-hearth process.

Open- Hearth process: In this process , a mixture of cast iron,steel ,iron ore and lime is charged in a open hearth furnace.The furnace is lined with dolomite or silica depending upon the nature of impurities present in cast iron. The mixture and air is passed through the furnace at 1500°C. The impurities are oxidized by iron ore and removed as slag or gases.

$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$
$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
$10Fe_2O_3 + 6P \longrightarrow 20Fe + 6P_2O_5$
$2P_2O_5 + 6CaO \longrightarrow 2Ca_3(PO_4)_2$
$2P_2O_5 + 6MgO \longrightarrow 2Mg_3(PO_4)_2$
$2Fe_2O_3 + 3Si \longrightarrow 4Fe + 3SiO_2$
$SiO_2 + CaO \longrightarrow CaSiO_3$
$Fe_2O_3 + 3Mn \longrightarrow 2Fe + 3MnO$
$MnO + SiO_2 \longrightarrow MnSiO_3$

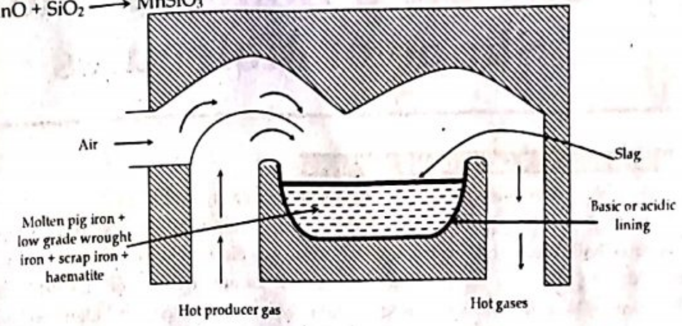


Fig: Open Hearth Furnace

Advantage of the open hearth process over Bessemer converter process:

i. Better quality of steel can be manufactured.
ii. Large quantity of steel can be manufactured in once operation.
iii. Low quality of iron ore or cast iron can be directly used.
iv. The temperature can be controlled.

d. Application of common ion effect in qualitative analysis.

Following are the some important application:

In the purification of NaCl: When HCl gas is passed in a saturated solution of impure NaCl, pure NaCl crystals precipitate out. This happens because [Na^+] and [Cl^-] are maximum in the saturated solution of NaCl. On bubbling HCl into it the concentration of Cl^- ion increases due to dissolution of HCl in solution. Hence, [Na^+] [Cl^-] becomes larger than the solubility product of NaCl. Hence, NaCl precipitates out. It must be noted that a substance precipitates from its solution when its ionic product exceeds its solubility product.

Precipitation of soap: When excess of NaCl is added to a solution of a soap which is RCOONa, the concentration of the common Na^+ ion increase too much so that [$RCOO^-$] [Na^+] becomes greater than solubility product of RCOONa (soap). Hence, soap precipitates out.

Precipitation of sulphides of group (II) in salt analysis: When H_2S gas is passed in an acidified solution of cupric salt, lead salt, Cd-salt, Bi-salt, Hg(ic) salt, stannous salt, As-salt and Sb-salt, their sulphides are precipitated because the product of the concentration of these metal ions and S^{--} ions exceeds the solubility product of CuS, PbS, CdS, Bi_2S_2, HgS, SnS, As_2S_3 and Sb_2S_3 respectively.

Precipitation of hydroxides of group (IIIA) in salt analysis: When NH_4Cl and NH_4OH solution are added to solution of a salt mixture containing Fe^{3+},Cr^{3+},Al^{3+},Mg^{2+},Ni^{2+},Zn^{2+}, Co^{2+},Mn^{2+} ions, only $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$ are precipitated in Group (IIIA) but those of Mg^{2+},Ni^{2+},Zn^{2+},Co^{2+},Mn^{2+} are not precipitated. This is because of the fact that ionic products exceed the solubility products of $F(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$, but ionic products do not exceed solubility product of $M(OH)_2$ Where, M = Ni,Co, Mn,Zn, Mg.

❑❑❑

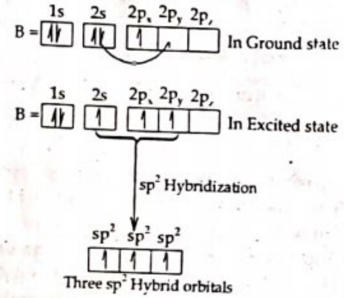
Unit 1

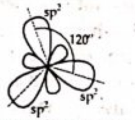
Chemical Bonding and Shape of Molecules

VERY SHORT ANSWER QUESTIONS [2 MARKS]

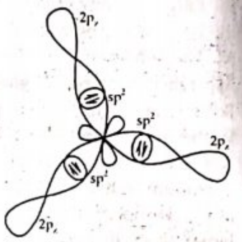
1. **2076 Set B Q.No. 1 How would you confirm that B in BF_3 gets sp^2 hybridization?** [2

The central atom Boron has one half filled orbital in ground state ($1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$) bu it has three half filled orbital in excited state since one electron is promoted from 2s to 2p orbital during chemical combination. Hence, one 2s and two 2p orbital undergo sp hybridization to form three sp^2 hybrid orbital of equivalent energy and identical shape & size which takes trigonal planar geometry with bond angle 120°.





Three sp² hybrid orbitals
Trigonal geometry



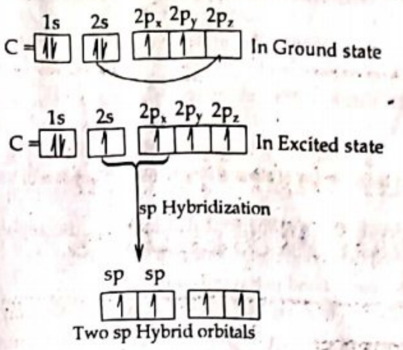
Orbital picture of BF_3

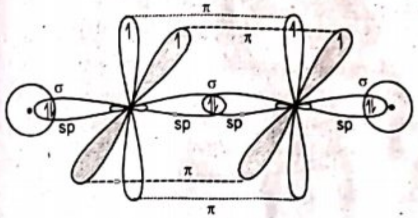
Each half filled sp^2 hybrid orbital of boron overlaps with half filled $2p_z$ orbital of three fluorine atom to form three covalent bonds.

2. **2076 Set C Q.No. 1 C in C_2H_2 gets sp hybridization, why?** [2]

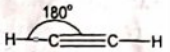
Each carbon has two half filled orbitals in ground state ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$). It has four unpaired electrons in excited state since one electron is promoted from 2s to empty 2p orbital during chemical reaction ($1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$). One 2s and one 2p orbitals undergoes sp hybridization to form two sp hybrid orbitals of equivalent energy and identical shape which has linear geometry and bond angle 180°.

One half filled sp hybrid orbital of carbon atom overlaps with another half filled sp hybrid orbital to form sigma bond. The remaining half filled sp hybrid orbital of each carbon atom overlaps with half filled orbital of hydrogen to form sigma bond. The unhybridized orbital of carbon atom forms pi bond.





π
Orbital picture of ethyne



Linear shape of ethyne

3. **2075 GIE Q.No. 1 State any two proper conditions for hybridization. What is the mode of hybridization of C in C_2H_2?** [1+1]

The necessary conditions for hybridization:

i. The orbitals taking part in hybridization must have only a small difference of enthalpies.

ii. The orbitals undergoing hybridisation generally belong to the valence of the atom. The mode of hybridization of C in C_2H_2 is sp-hybridization.

4. **2075 Set A Q.No. 1 Predict the mode of hybridization of B in BF_3. Mention any two features of this hybridization.** [1+1]

The central atom B in BF_3 has sp^2 hybridization. Two important features of sp^2 hybridization are:

i. Bond angle of sp^2 hybrid orbitals is 120°.

ii. sp^2 hybrid orbital having 33 % s-character and 66 % p-character.

5. **2075 Set B Q.No. 1 Predict the mode of hybridization.** [1+1]

i. **carbon in ethyne** ii. **oxygen in water**

i. The hybridization of carbon in ethyne is sp-hybridization

ii. The hybridization of oxygen in water is sp^3-hybridization

6. **2074 Supp. Q.No. 1 Write two important features of hybrid orbitals.** [2]

Following are two important features of hybrid orbitals:

i. They have same shape and same energy.

ii. They are equivalent and symmetrical.

7. **2074 Set A Q.No. 1 Which kinds of hybridization results into tetrahedral geometry? Give an example of such hybridization.** [1+1]

sp^3 hybridization results into tetrahedral geometry. Example: methane (CH_4)

8. **2074 Set B Q.No. 1 Which kinds of hybridization results into linear geometry. Give an example of such hybridization. [1+1]**

sp hybridization results into linear geometry. Example: Ethyne (C_2H_2) has sp hybridization.

9. **2073 Supp Q.No. 1 What kinds of hybridization results into trigonal planar geometry. Give an example of it. [1+1]**

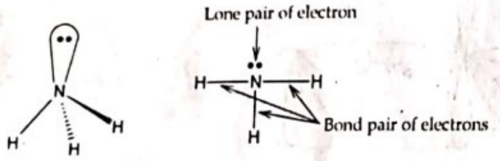
sp^2 hybridization results into trigonal planar geometry. Example: ethene ($CH_2=CH_2$)

10. **2073 Set C Q.No. 1 How would you predict the geometry of ammonia molecule on the basis of VSEPR theory? [2]**

According to VSEPR model, a molecule takes a shape that minimizes the repulsion between bonding pair i.e. bond pair and non-bonding i.e. lone pair of electron.

Lone pair- bond pair repulsion > bond pair - bond pair repulsion

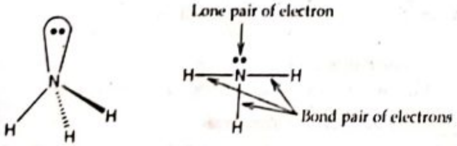
In NH_3 molecule, three bonding pair of electrons and one lone pair of electron are present. Due to the presence of lone pair of electron the regular tetrahedral structure of NH_3 is distorted to give triangular pyramidal shape and having bond angle 106°45′. This gives the maximum stability between the bond pair and lone pair of electrons.



Pyramidal shape of NH_3

11. **2073 Set D Q.No. 1 Ammonia molecule has got trigonal pyramidal geometry even though nitrogen of ammonia gets sp^3 hybridization. Give reason. [2]**

The central atom N has one lone pair and three bonding electrons. Three bonding electrons are shared with three hydrogen atom to form three bond pair electrons. According to VSEPR theory, lone pair - bond pair repulsion is greater than bond pair - bond pair repulsion. Due to the unequal repulsion, tetrahedral geometry is distorted and changed into trigonal pyramidal geometry.



Pyramidal shape of NH_3

12. **2072 Supp. Q.No. 1 Predict the mode of hybridization in the central atom of the molecules having (i) trigonal plannar (ii) tetrahedral structure with an example of each. [1+1]**

i. **Trigonal plannar:** *The mode of hybridization in central atom is sp^2. Example: BF_3*

ii. **Tetrahedral:** *The mode of hybridization in central atom is sp^3. Example: CH_4*

13. **2072 Set C Q.No. 1 Define hybridization and write any two features of tetrahedral hybridization. [1+1]**

Hybridization:

The process of mixing of dissimilar atomic orbital of same atom giving rise to equal number of a new set of orbital having same energy is known as hybridization.

Features of tetrahedral hybridization

Two important features of tetrahedral hybridization are:

a. Carbon atoms are sp^3 hybridization.

b. The bond angles are 109.5°.

14. **2072 Set D Q.No. 1 What are the features of tetrahedral hybridization? Write an example of it.**

Following are the features of tetrahedral hybridization

a. Carbon atoms are sp^3 - hybridization

b. The bond angles are 109.5°

Example: Methane (CH_4), the central carbon atom is sp^3 hybridization.

15. **2072 Set E Q.No. 1 State the mode of hybridization in B of BF_3 and C of C_2H_6. [1+1]**

The mode of hybridization in B of BF_3 is sp^2 hybridization and mode of hybridization in C of C_2H_6 is sp^3.

16. **2071 Supp. Q.No. 1 Which kind of hybridization results into tetrahedral geometry? Mention any one character of such hybridization. [2]**

sp^3 hybridization have tetrahedral geometry. sp^3 hybridization is formed by mixing of one s-orbital and three p-orbital. The characteristics of sp^3 hybrid orbital: It has bond angle 109.5° and tetrahedral shape.

17. **2071 Supp. Q.No. 1 What is the mode of hybridization in carbon of acetylene? Write any two correct features of this hybridization. [1+1]**

The mode of hybridization in carbon of acetylene is sp.

Two important features of sp-hybridization are:

i. The bond angles are 180°.

ii. The shape sp-hybridization is linear. sp-hybridized orbital possess 50% s-character and 50% p-character.

18. **2071Set-C Q.No. 1 Predict the geometry of molecules having: [1+1]**

a. sp^3 hybridization

b. sp hybridization with an example of each.

a. **sp^3 hybridization:** The molecules having sp^3 hybridization generally possess tetrahedral shape. Example: CH_4 molecule.

b. **sp hybridization:** The molecules having sp hybridization generally possess linear shape. Example: C_2H_2 molecule.

19. **2071 Set D Q.No. 1 Write any two features of sp^3 hybrid orbital with an example. [2]**

Two features of sp^3 hybrid orbital are:

i. The bond angle of sp^3 hybrid orbital is 109.5° and tetrahedral shape.

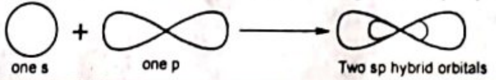
ii. sp^3 hybridized orbital possesses 25 % s-character and 75 % p-character.

Methane molecule has sp^3 hybrid orbital.

20. **2070 Set C Q.No. 1 What is meant by hybrid orbital? Write an example of it. [2]**

Hybrid orbital: The process of mixing of dissimilar atomic orbitals of same atom giving rise to equal number of a new set of orbitals having same energy is known as hybridization and new orbital is called hybrid orbital.

Example: Mixing of one s-orbital with one p-orbital to give two sp- hybrid orbital.



21. **2070 Set D Q.No. 1 Why do NH_3 and BF_3 have dissimilar geometries? [2]**

In NH_3 molecule, the cetntaral atom N has one lone pair and three bonding electrons. These three bonding electons is shared by three hydrogen atom to form three bonding pair of electons. But in the case of BF_3 molecule, central atom do not have lone pair electron and only form three covalent with three F atom. Due to the lone pair and bond pair repulsion, geometry of NH_3 and BF_3 are different.

22. 2069 Supp. Set B Q.No. 1 **State the mode of hybridization of C_2H_6 and mention any two features of this hybridization.** **[2]**

✍ Ethane molecule i.e. C_2H_6 has sp^3 hybridization. Two feature of sp^3-hybridization are:

i. The bond angle of sp^3 hybrid orbital is 109.5° and tetrahedral shape.

ii. sp^3 hybridized orbital possesses 25% s-character and 75 % p-character.

23. 2069 Set A Q.No. 1 **Nitrogen of ammonia gets sp^3 hybridization but ammonia molecule has trigonal pyramid geometry. Give reason.** **[2]**

✍ Please refer to 2073 Set D Q.No. 1

24. 2069 Set B Q.No. 1 **What is the mode of hybridization of B in BF_3? Write any two important features of this hybridization.** **[2]**

✍ Please refer to 2075 Set A Q.No. 1

25. 2068 Q.No. 1 **Write any two important characters of tetrahedral hybridization.** **[1+1]**

✍ Following are two important characters:

i. Carbon atoms are sp^3-hybridization.

ii. The bond angles are 109.5°

26. 2067 Q.No. 1 **Mention one example of each:** **[1+1]**

i. **Tetrahedral Hybridization** ii. **Trigonal Hybridization**

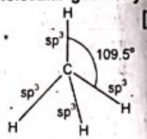
✍

i. In methane (CH_4), the central carbon atom is sp^3-hybridization i.e. tetrahedral shape.

ii. In boron trifluoride (BF_3), the central boron atom has trigonal hybridization.

27. 2066 Q. No. 1 **What is the mode of hybridization of the central atom whose molecular geometry is tetrahedral? And, give an example of its.** **[2]**

✍ If the molecule has molecular geometry of tetrahedral, the central atom of that molecule is sp^3 hybridization. Example: In CH_4 molecule, the central carbon atoms are in sp^3 hybridization and having bond angle 109.5°.



28. 2065 Q.No. 1 **Predict the mode of hybridization in** **[2]**

i. **C of C_2H_4** ii. **B of BF_3**

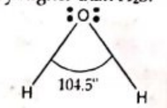
✍

i. The mode of hybridization in C of C_2H_4 is sp^2 hybridization.

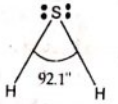
ii. The mode of hybridization in B of BF_3 is also sp^2 hybridization.

29. 2064 Q.No. 1 **Why is H-O-H bond angle in water molecule comparatively higher than H-S-H bond angle in H_2S molecule?** **[2]**

✍ In both molecules i.e. H_2O and H_2S, the central atom O- and S- are sp^3 hybridized orbital and both atom having two bond pair and two lone pair of electrons. O- atom has smaller size and higher electronegativity than S-atom, due to this reason bond pair in H_2O are closer to the oxygen atom and repulsion between them are large. In the case of H_2S, larger size and low electronegativity of S-atom than O-atom. The bond pair in H_2S, the bond pair are away from the central atom. Therefore, the bond angle in water molecule is comparatively higher than H_2S.



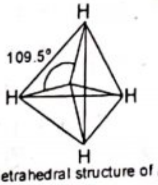
Closer bond pair and larger repulsion



Farther bond pair and smaller repulsion

30. 2063 Q.No. 1 **Define hybridization. Draw the orbital picture of a hydrocarbon showing tetrahedral structure.** **[2]**

✍ **Hybridization:** The process of mixing of dissimilar atomic orbitals of same atom giving rise to equal number of a new set of orbitals having same energy is known as hybridization. Methane shows tetrahedral structure and orbital picture of methane is



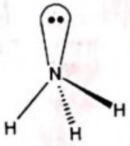
Tetrahedral structure of methane

31. 2062 Q.No. 1 **How do you predict the molecular geometry of NH_3 based on VSEPR model?** **[2]**

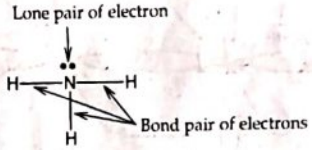
✍ According to VSEPR model, a molecule takes a shape that minimizes the repulsion between bonding pair i.e. bond pair and non-bonding i.e. lone pair of electron.

Lone pair- bond pair repulsion > bond pair – bond pair repulsion

In NH_3 molecule, three bonding pair of electrons and one lone pair of electron are present. Due to the presence of lone pair of electron the regular tetrahedral structure of NH_3 is distorted to give triangular pyramidal shape and having bond angle 106°45′. This gives the maximum stability between the bond pair and lone pair of electrons.

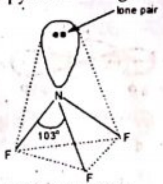


Pyramidal shape of NH_3

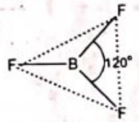


32. 2061 Q.No. 1 **The bond angle at the central atom in NF_3 is 103°, whereas in BF_3 is 120°. What factor accounts for the difference in bond angles?** **[2]**

✍ Due to the presence of lone pair of electrons in cental atom N in NF_3, the lone pair – bond pair repulsion is greater than bond pair repulsion. The shape of NF_3 is pyramidal trigonal geometry. Due to the absence of lone pair of electron B in BF_3, there is only bond pair – bond pair repulsion and having triangular geometry with bond angle 120°. Therefore, NF_3 has pyramidal trigonal and BF_3 has triangular geometry.



pyramidal trigonal shape



Triangular geometry

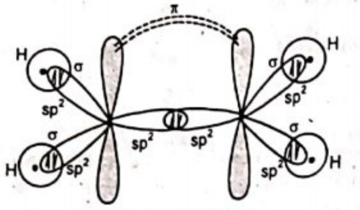
33. 2060 Q.No. 1 **How would you interpret that all four C – H bonds of methane are identical?** **[2]**

✍ All the four carbon atoms in methane are sp^3 hybridization which are directed towards the four corners of regular tetrahedral having bond angle of 109.5°. Each bond is formed by the head to head overlapping of sp^3 hybrid orbital of carbon atom and s-orbital of hydrogen. Therefore, all the four C–H bond in methane are identical.

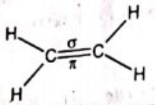
Tetrahedral structure of methane

34. **2059 Q.No. 1** **Draw the molecular orbital picture of ethene.**

Molecular orbital picture of ethene is given as



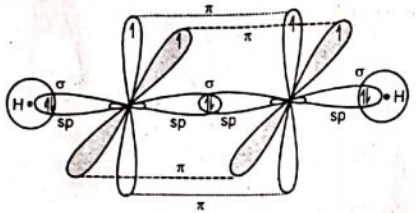
Orbital picture of Ethene



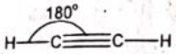
Trigonal palanar geometry

35. **2058 Q.No. 1** **Draw the orbital picture of ethyne indicating sigma and pi bonds.**

Orbital picture of ethyne indicating sigma and pi-bonds is given as:



Orbital picture of ethyne



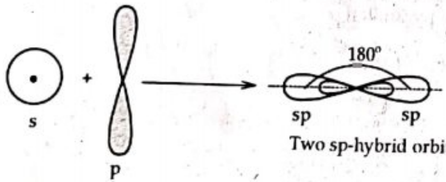
Linear shape of ethyne

36. **2057 Q.No. 1** **How do you predict the molecular geometry of NH_3 based on VSEPR model?** [2

Please refer to 2073 Set C Q.No. 1

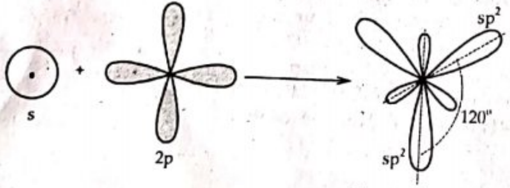
37. **2056 Q.No. 1** **Draw the shapes of sp and sp² hybrid orbitals.** [2]

Shape of sp hybrid orbital: When one s-orbital and one p-orbital are mixed together then two sp-hybrid orbital is formed. The shape of sp-hybrid orbital is linear i.e. bond angle 180°.



Two sp-hybrid orbital

Shape of sp² hybrid orbital: When one s-orbital and two p-orbital are mixed together then three sp²-hybrid orbital is formed. The shape of sp²-hybrid orbital is trigonal i.e. bond angle 120°.



Three sp²-hybrid orbital

38. **2053 Q.No. 2** **Identify the hybridization of the indicated atom in each of the following molecules.** [2]

a. Be in BeF_2
b. B in BF_3
c. N in NH_3

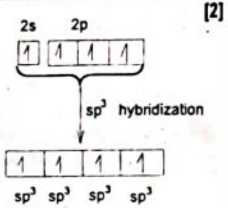
a. Hybridization of Be in BeF_2 is sp-hybrsidization.
b. Hybridization of B in BF_3 is sp²-hybridization.
c. Hybridization of N in NH_3 is sp³-hybridization.

39. **2052 Q.No. 1** **Predict the structure of methane based on hybridization.** [2]

The electronic configuration of central atom C in methane is

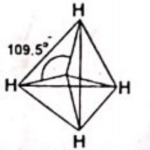
$C_6 = 1s^2 2s^2 2p^2$ [Ground state]

The p-orbital is empty. During bond formation, carbon atom absorbs energy and one 2s electron gets promoted to 2p orbital.



$C_6 = 1s^2 2s^1 2p^3$ [Excited state]

These four sp³-hybrid orbitals overlap with 1s-orbital of 4 hydrogen atoms to give a methane molecule. These four bonds are directed towards the corners of a regular tetrahedral with bond angle of 109.5°.

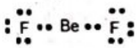


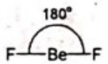
Tetrahedral structure of methane

SHORT ANSWER QUESTIONS [5 MARKS]

40. **2056 Q.No. 24** **Using VSEPR theory, explain the shapes of BeF_2 and BF_3.** [5]

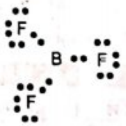
In BeF_2 molecule, the central atom Be have two valence electrons. These two electrons are shared by two F atoms and two bond pair of electrons are formed around the central atom Be. According to VSEPR theory, these two bond pair of electrons is arranged in such a way that there must be minimum repulsion. These two bond pair is in 180° apart from each other. The geometry of BeF_2 is linear.

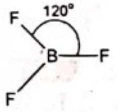




Shape: Linear

In BF_3 molecule, the central atom B has three valence electrons. These three electrons are shared by three F atom to form three bond pair of electrons. They have equal force of repulsion among each other and are oriented in triangular geometry with bon angle 120°.

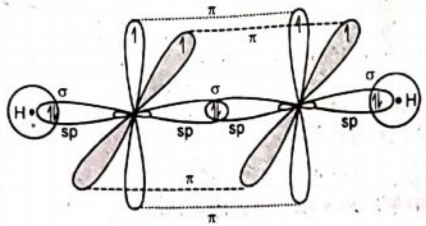


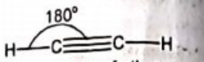


Shape: Triangular

41. **2055 Q.No. 23** **Explain the state of hybridization in ethyne molecule.** [5]

The central carbon atom in ethyne is sp-hybridization. One s-orbital and one p-orbital of the excited carbon atom hybridize to form two sp-hybrid orbital. Two sp-hybrid orbitals are inclined to each other at right angle i.e bond angle 180°. In ethyne, each carbon atom forms two sigma bond using sp-hybrid orbital and two pi bonds are formed by using unused p-orbitals of carbon atom. The orbital picture of ethyne is



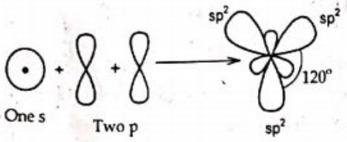


Linear shape of ethyne

Orbital picture of ethyne

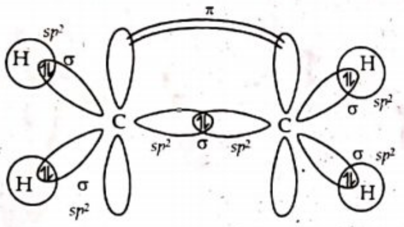
42. **2054 Q.No. 24 What do you understand by sp^2 hybridization? Using any example explain the molecular geometry involved.** **[5]**

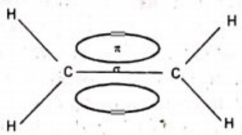
sp^2-hybridization: When one s-orbital and two p-orbital mix together to form three sp^2-hybrid orbital, is called sp^2-hybridization. The three hybrid orbitals are oriented to the three conrers of a tiangle having an angle of 120° to one another.



Three sp^2 hybrid orbital

Ethene molecule has sp^2 hybridization. In ethene molecule the three sp^2 hybrid orbitals form sigma bonds, while the unused p-orbital will form π bond. The orbital picture of ethene molecule is





Orbital picture of ethene

WRITE SHORT NOTES ON:(5 MARKS)

43. **2061 Q.No. 31(iv) / 2055 Q.No. 31(a) VSEPR model** **[5]**

Valence shell electron pair repulsion theory is also called VSEPR theory. This theory was given by Sidgwick and Powell. This theory describes the influence of lone pair of electrons to the bonding electrons and also predicts the shape of molecule. This theory is based on the number of valence of electrons present in the central atom of a molecule.

Statement: "A molecules take a shape that minimizes the repulsion between the bonding and non-bonding pair of electrons".

Following are the postulates of VSEPR theory:

a. In any covalent molecule, there is a central atom around which other atoms are arranged.

b. The shape of molecule is determined by the number of electrons pair presents in the valence shell of the central atom.

c. If the central atom of a molecule is surrounded by electron pairs of dissimilar atoms then the molecules will have irregular geometry due to different repulsive interaction.

d. If the central atom in a molecule is surrounded by both lone pair and bond pair of electron then the molecules will have irregular geometry due to different repulsive interaction.

e. The order of repulsion between electrons pair are:
Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

f. The magnitude of repulsion between bonding pair of electrons depend upon the electronegativity difference between central atom and other atom.

g. Triple bond have more repulsive force than double bond and double bond have more repulsive than single bond.

□□□

Unit 2

Volumetric Analysis

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 2 Distinguish between decinormal and decimolar solution.** [2]

✍ Following are the difference between decinormal and decimolar solution:

Decinormal solution	Decimolar solution
1. The solution in which one tenth gram equivalent of solute is dissolved to prepare one litre solution.	1. The solution in which one tenth mole of solute is dissolved to prepare one litre solution.
2. It is denoted by $\frac{N}{10}$	2. It is denoted by $\frac{M}{10}$
3. Example: 4 g NaOH solution is dissolved to prepare 1 L solutioen, the strength of solution is decinormal.	3. Example: 9.8 g of sulphuric acid is dissolved to prepare 1 L solution, the strength of solution is decimolar.

2. **2076 Set C Q.No. 2 Distinguish between titration error and normality factor.** [2]

✍ Following are the difference between titration error and normality factor.

Titration error	Normality factor
The difference between the equivalence point and the measured end point is called titration error.	It is defined as the ratio of observed weight of solute to the theoretical weight of solute required to prepare a solution of desired normality.

3. **2075 GIE Q.No. 2 Differentiate between end point and equivalence point of a reaction.** [1+1]

✍ Following are the difference between end point and equivalence point.

End Point	Equivalence Point
1. The point in a titration at which the reaction between two solutions is complete as shown by indicator.	1. The point at which one gram equivalent of a substance completely reacts with one gram equivalent of another substance is called equivalence point.
2. It must be in acid base solution.	2. It may or may not in acid base solution.

4. **2075 Set A Q.No. 2 Differentiate between normality and molarity.** [2]

✍ Following are the difference between normality and molarity:

Normality	Molarity
The number of gram equivalent of solute is present in one litre of it's solution is called normality.	The number of gram mole of solute is present in one litre of it's solution is called molarity.
It is denoted by 'N'	It is denoted by 'M'

5. **2075 Set B Q.No. 2 Distinguish between Primary standard solution and secondary standard solution.** [1+1]

✍ Following are the distinction between primary standard solution and secondary standard solution:

Primary standard solution	Secondary standard solution
It is prepared by dissolving pure substance which is not affected in its composition for a long time.	It is prepared by neuträlizing against the primary standard solution.
Example: Oxalic acid, Na_2CO_3, $AgNO_3$, KCl etc.	Example: NaOH, HCl, H_2SO_4, HNO_3, $KMnO_4$ etc.

6. **2074 Supp. Q.No. 2 Define the terms:** [1+1]
   i. **Primary standard solution**
   ii. **Acidimetry**

✍

i. **Primary standard solution:** The substances whose standard solution can be prepared directly by dissolving the known weight of substance in certain volume of solution is called primary standard substance and the solution made from primary standard substance is called primary standard solution. Example: solution of oxalic acid.

ii. **Acidimetry:** The method of determining the strength of acid by titrating it with the known volume of standard alkali solution is called acidimetry.

7. **2074 Set A Q.No. 2 Define the terms;** [1+1]
   i. **Normality factor**
   ii. **Secondary standard solution**

✍

i. **Normality factor:** Normality factor (f) is the ratio of observed weight of substance and theoretical weight of substance.

$$\text{Normality factor (f)} = \frac{\text{Observed weight}}{\text{Theoretical weight}}$$

ii. **Secondary standard solution:** The solution whose strength is to be determined with the help of primary standard solution is called secondary standard solution.

8. **2074 Set B Q.No. 2 How is end point differed from equivalence point?** [2]

✍ Please refer to 2075 GIE Q.No. 2

9. **2073 Supp Q.No. 2 What is the importance of calculating normality factor of solutions during titration?** [2]

✍ In order to minimize the experimental error, normality factor of solution is calculated during titration. Normality factor (f) is the ratio of observed weight of substance and theoretical weight of substance.

$$\text{Normality factor (f)} = \frac{\text{Observed weight}}{\text{Theoretical weight}}$$

10. **2073 Set C Q.No. 2 Define the terms:** [1+1]
    i. **Normality factor**
    ii. **Secondary standard solution.**

✍

i. **Normality factor:** The ratio of actual weight of substance taken to the theoretical weight of substance to be taken is called normality factor. It is denoted by symbol 'f'.

$$\text{Normality factor (f)} = \frac{\text{Weight taken}}{\text{Weight to be taken}}$$

ii. **Secondary standard solution:** The solution whose strength is to be determined with the help of primary standard solution is called secondary standard solution.

11. 2073 Set D Q.No. 2 Why is crystal oxalic acid regarded as a good substance for the preparation of primary standard solution? **[2]**

Oxalic acid is regarded as primary standard substance because it is available in pure state, non-toxic, high equivalent weight, non hygroscopic and deliquescent. So, it is used for the preparation of primary standard solution in titration.

12. 2072 Supp. Q.No. 2 How would you convert 500 cc of 2MH_2SO_4 into **[1+1]**

i. Gram/liter **ii. Normality**

Given,

Volume of H_2SO_4 = 500 cc

Molecular weight of H_2SO_4 = 98

Equivalent weight of H_2SO_4 = 49

Molarity of H_2SO_4 = 2M

i. Gram/L = Molarity x Molecular weight = 2 × 98 = 196 g/L

ii. $\text{Normality} = \dfrac{\text{Gram/L}}{\text{Equivalent weight}} = \dfrac{196}{49} = 4\text{ N}$

13. 2072 Set C Q.No. 2 Distinguish between end point and equivalence point of reaction. **[1+1]**

Please refer to 2075 GIE Q.No. 2

14. 2072 Set D Q.No. 2 Which one has higher concentration and why?

a. 80 g / litre NaOH solution and 3 M NaOH solution. **[1]**

b. 5.3 g / litre Na_2CO_3 and $\frac{N}{10}$ Na_2CO_3 solution. **[1]**

a. Given,

g/litre of NaOH = 80 g/litre

Equivalent weight of NaOH = 40 = Molecular weight

We known that,

$$\text{Normality} = \frac{\text{g/litre}}{\text{Equivalent weight}} = \frac{80}{40} = 2\text{ N of NaOH}$$

Given, molarity of NaOH = 3M = 3N of NaOH

Hence, concentration of 3M NaOH is higher than 80 g/litre NaOH solution.

b. Given,

g/litre of Na_2CO_3 = 5.3 g/litre

Molecular weight of Na_2CO_3 = 106

Equivalent weight of Na_2CO_3 = 53

We know that

$$\text{Normality} = \frac{\text{g/litre}}{\text{Equivalent weight}} = \frac{5.3}{53} = 0.1\text{ N of } Na_2CO_3$$

Given, the normality of $Na_2CO_3 = \frac{N}{10} = 0.1$ N

Hence, the concentration of both 5.3 g/litre Na_2CO_3 and $\frac{N}{10}$ Na_2CO_3 are same.

15. 2072 Set E Q.No. 2 A sample of Na_2CO_3 weighing 0.53 g is added to 101 mL of 0.1N H_2SO_4 solution. Will the resulting solution be acidic, basic or neutral? **[2]**

Given, weight of Na_2CO_3 = 0.53 g

Equivalent weight of Na_2CO_3 = 53

From normality solution,

1000 mL of Na_2CO_3 of 1 N requires 53 g of Na_2CO_3.

100 mL of Na_2CO_3 of 0.1 N requires 0.53 g of Na_2CO_3

For complete neutralization

100 mL of Na_2CO_3 of 0.1 N = 100 mL of H_2SO_4 of 0.1 N

We know that,

Equal volume of acid neutralizes equal volume of base, if acid and base have the same normality. So, 100 mL of H_2SO_4 of 0.1 N neutralize 100 mL of Na_2CO_3 of 0.1 N. Thus, 1 mL of acid is left unreacted and the resulting solution must be acidic.

16. 2071 Supp. Q.No. 2 Calculate the normality and molarity of 5% of NaOH solution. **[1+1]**

Given, 5% NaOH solution means 5 g of NaOH is dissolved in 100 cc of solution.

Given weight of NaOH = 5 g

Volume of solution = 100 cc

Equivalent weight = Molecular weight of NaOH = 40

We know that,

$$\text{Normality (N)} = \frac{\text{No. of g equivalent weight of solute}}{\text{Volume of solution in litre}} = \frac{\dfrac{\text{Weight of solute}}{\text{Equivalent Weight}}}{\text{Volumen of solution in litre}}$$

$$= \frac{\dfrac{5}{40}}{\dfrac{100}{1000}} = \frac{5}{40} \times 10 = \frac{5}{4} = 1.25\text{ N}$$

The equivalent weight = Molecular weight of NaOH. So, normality is equal to molarity.

N = M = 1.25

Hence, Normality (N) = Molarity (M) = 1.25

17. 2071 Set C Q.No. 2 What mass of 90% pure $CaCO_3$ is required to neutralize 2 litre deci-normal solution of HCl? **[1+1]**

Given,

2 litre 0.1 N HCl = 0.2 litre 1 N HCl = 200 mL 1N HCl

Volume of HCl = 200 mL

Normality of HCl = 1 N

Equivalent weight of $CaCO_3 = \frac{100}{2} = 50$

Weight of $CaCO_3$ (W) = ?

We know that,

$$W = \frac{NEV}{1000} = \frac{1 \times 50 \times 200}{1000} = 10\text{ g}$$

Let, X g of 90 % = 10 g

Or, $X \frac{90}{100} = 10$

Or, $X = \frac{10 \times 100}{90} = 11.11$ g

Hence, 11.11 g of 90% pure $CaCO_3$ is required to neutralize 2 litre of deci normal solution of HCl.

18. 2071 Set D Q.No. 2 How many moles of H_2SO_4 are required to neutralize 4 litres of 2 N NaOH solution? **[1+1]**

Given,

4 litres of 2N NaOH = 8 litres of 1N NaOH

Volume of NaOH = 8 litre = 8000 mL

Normality of NaOH = 1 N

Equivalent weight of H_2SO_4 = 49

Weight required for H_2SO_4 (W) =?

We know that,

$$W = \frac{NEV}{1000} = \frac{1 \times 49 \times 8000}{1000} = 392\ g$$

Molecular weight of H_2SO_4 = 98 g

$$\text{So, no. of moles of } H_2SO_4 = \frac{\text{Given weight}}{\text{Molecular weight}} = \frac{392}{98} = 4\ \text{mol}$$

Hence, 4 mol of H_2SO_4 are required to neutralize 4 liters of 2N NaOH solution.

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19. **2070 Supp. Q.No. 2 Define the term**
    - **I. Semi normal solution**
    - **II. Alkalimetry** **[1+1]**

Semi normal solution: If half gram equivalent of solute is present in one litre of solution then it is called seminormal solution. It is denoted by $\frac{N}{2}$

Alkalimetry: The method of determining the strength of alkali by titrating it with the known volume of standard acid solution is called alkalimetry.

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20. **2070 Set C Q.No. 2 Define secondary standard solution with a suitable example.** **[1+1]**

The solution made from secondary standard substance is called secondary standard solution. Example: HCl solution.

---

21. **2067 Q.No. 17 Write an example of redox titration. Why is it called so?** **[1+1]**

Example of redox reaction is

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8H_2O$$

Here, $KMnO_4$ is reduced to $MnSO_4$ and $C_2H_2O_4$ is oxidized to CO_2 and H_2O. So, this reaction is called redox titration.

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22. **2066 Q. No. 17 What is the normality of 20 cc of 2 M phosphoric acid (H_3PO_4)?** **[2]**

Molarity of H_3PO_4 = 2M

Basicity of H_3PO_4 = 3

Normality of 20 cc of H_3PO_4 = ?

We know that,

Normality = Molarity × basicity of acid

= 2 × 3 = 6 N

So, the normality of 20 cc. of H_3PO_4 is 6N.

---

23. **2065 Q.No. 17 What is normality? How is it related with molarity?** **[2]**

Normality (N): If the equivalent weight of a substance is expressed in gram is called gram equivalent. It is defined as the number of gram equivalent of a solute present in one liter of it's solution .It is denoted by "N"

$$\text{Normality (N)} = \frac{\text{No. of gram equivalent weight of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Weight of solute in g}}{\text{Equivalent weight of solute}} \times \frac{1000}{\text{Volume of solution in mL}}$$

Normality is related with molarity as

Normality (N) = molarity (M) × basicity of acid or acidity of base

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24. **2054 Q.No. 3 What do you mean by equivalent weight of an element?** **[2]**

The equivalent weight of an element is that parts by weight of it which combines with or displace from a compound 1.008 part by weight of hydrogen or 8 part by weight of oxygen or 35.5 part by weight of chlorine.

25. **2063 Q.No. 3 What are the requisites for a substance to be a primary standard?** **[2]**

Following are the requisities for a substance to be primary standard.

a. They should have high molecular and equivalent weight.

b. They should be easily available and highly purity.

c. They should be non-volatile, non-toxic, non-hygroscopic in nature.

d. They should be highly soluble in water.

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26. **2052 Q.No. 3 Define decinormal solution.** **[2]**

A solution containing $\frac{1}{10}^{th}$ of gram equivalent of solute present in one litre of solution is known as decinormal solution.

SHORT ANSWER QUESTIONS [5 MARKS]

27. **2076 Set B Q.No. 23 Are all standard solutions, primary standard solutions or not? Give reason. 1 g of a divalent metal was dissolved in 25 mL of 2N H_2SO_4 (f = 1.01). The excess acid required 15.1mL of 1N NaOH (f = 0.8) for complete neutralization. Find the atomic weight of the metal.** **[1+4]**

Not, all satandard solutions are not primary standard solution. To be a primary standard, a substance must fulfill the following criteria:

i. The substance must be easy to obtain and purity.

ii. The substance should not be hygroscopic or efflorescent of deliquescent.

iii. The composition should not change during storage or weighing.

iv. The substance should be readily soluble under the employed condition.

v. The substance should have high molecular mass.

Numerical:

Given,

The weight of metal = 1g

The valency of metal = 2

For acid:

Volume of acid (H_2SO_4) = 25 mL

Normality of acid = 2N (f=1.01)

We know that

$$\text{The gram equivalent of } H_2SO_4 = \frac{\text{Volume} \times \text{Normality}}{1000} = \frac{25 \times 2 \times 1.01}{1000} = 0.0505$$

For base:

Volume of base (NaOH) = 15.1 mL

Normality of acid = 1N (f=0.8)

We know that

$$\text{The gram equivalent of NaOH} = \frac{\text{Volume} \times \text{Normality}}{1000} = \frac{15.1 \times 1 \times 0.8}{1000} = 0.01208$$

For Metal:

$$\text{The gram equivalent of metal} = \frac{\text{Weight of metal}}{\text{Equivalent weight of metal}} = \frac{1}{\text{Equivalent weight of metal}}$$

We know that

The gram equivalent of metal = The gram equivalent of H2SO4 - The gram equivalent of NaOH

$$\frac{1}{\text{Equivalent weight of metal}} = (0.0505 - 0.01208) = 0.03842$$

Or, Equivalent weight of metal = 26.02

Hence, the atomic weight of metal = Equivalent weight × Valency = 26.02 × 2 = 52.05 amu.

28. 2076 Set C Q.No. 23 **It is better to express concentration in molality rather than molarity, Why? x g a metal (equivalent weight = 12) was completely dissolved in 100 cc of $\frac{N}{2}$ HCl solution. The volum was then made upto 500 cc. It is found that 25 cc of the diluted acid solution required 17.5 cc of $\frac{N}{1}$ NaOH for complete neutralization. Find the value of x.** **[1+**

Molality is considered better for expressing the concentration as compared to molarit because the molarity changes with temperature because of expansion or contraction the liquid with temperature. But molality does not changes with temperature becaus the mass of the solvent does not change with change in temperature

Numerical: Given,

Equivalent weight of metal = 12

Weight of metal (x) = ?

Given, 100 cc of $\frac{N}{2}$ HCl = 50 cc of 1N HCl

Again,

25 cc of the diluted acid requires 17.5 cc of $\frac{N}{10}$ NaOH

or, 1 cc of the diluted acid requires $\frac{17.5}{25}$ cc of $\frac{N}{10}$ NaOH

or, 500 cc of the diluted acid requires $\frac{17.5 \times 500}{25 \times 10}$ of 1N NaOH

= 35 cc of 1N NaOH

So, 35 cc of 1N NaOH solution requires 35 cc of 1N HCl solution for complet neutralization.

For dilution of 500 cc

500 cc of diluted HCl solution contains 50 cc of 1N HCl solution.

Hence, the amount of 1N HCl consumed by x g of metal = (50 – 35) = 15 cc of HCl

We, know that,

1000 cc of 1N HCl = 12 g of metal i.e. equivalent of metal

15 cc of 1N HCl = $\frac{12 \times 15}{1000}$ = 0.18 g

The weight of metal required i.e. the value of x is 0.18 g.

---

29. 2075 GIE Q.No. 23 **Define deci-normal solution. 12 g of commercial zinc is made to react with excess dil. H_2SO_4. The total volume of H_2 gas was found to be 4.2 litres at 570 mmHg pressure and 279 K temperature. Determine the percentage purity of the zinc.** **[1+4**

Deci-normal solution: The solution in which one tenth gram equivalent of solute is dissolved to prepare one litre solution is said to deci-normal solution.

Numerical:

Given weight of zinc = 12 g

Volume of hydrogen (V) = 4.2 L

Pressure of H_2 gas (P) = 570 mm Hg = 0.75 atm

Temperature of H_2 gas (T) = 279 K

Universal gas constant (R) = 0.0821 L atm $K^{-1}mol^{-1}$

No. of mole of H_2 gas (n) = ?

We know that

PV = nRT

or, $n = \frac{PV}{RT} = \frac{0.75 \times 4.2}{0.0821 \times 279} = 0.1375$ mole

The balanced equation is

$$\underset{65\ g}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{1\ mole}{H_2}$$

Here

1 mole of hydrogen gas is produced from 65 g Zinc

0.1375 mole of hydrogen is produced from 65 × 0.1375 g Zinc

= 8.9375 g Zinc

The percentage purity of zinc = $\frac{8.9375 \times 100}{12}$ = 74.48 %

---

30. 2075 Set A Q.No. 23 **Define end point. 12 g of commercial zinc is made to react with excess dilute H_2SO_4. The total volume of H_2 gas liberated was found to be 4.2 litres at 570 mmHg pressure and 279 K. Determine the percentage purity of the zinc. (Atomic mass of Zn = 65)** **[1+4]**

End point: The point in a titration at which the reaction between two solutions is complete as shown by the indicator is known as end point.

Numerical: Please refer to 2075 GIE Q.No. 23

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31. 2075 Set B Q.No. 25 2072 Set D Q.No. 25 **What is meant by normality factor? How many mL of conc. HNO_3 of specific gravity 1.41 containing 69% by mass are required to prepare 500 mL of 0.5 N HNO_3?[1+4]**

Normality Factor:

The ratio of actual weight of substance taken to the theoretical weight of substance to be taken is called normality factor. It is denoted by 'f'.

Normality factor (f) = $\frac{\text{Weight taken}}{\text{Weight to be taken}}$

Numerical:

Given, specific gravity = 1.41

% by mass of HNO_3 i.e.% $\left(\frac{w}{W}\right)$ = 69%

Equivalent weight of HNO_3 = (1 + 14 + 3 × 16) = 63

We know that,

$$\text{Normality} = \frac{\%\frac{w}{W} \times \text{Specific gravity} \times 10}{\text{Equivalent weight}} = \frac{69 \times 1.41 \times 10}{63} = 15.44\ N$$

Now,

Volume of HNO_3 (V_1) = ? Volume of HNO_3 (V_2) = 500 mL

Normality of HNO_3 (N_1) = 15.44 N Normality (N_2) = 0.5 N

For Normality equation

$V_1N_1 = V_2N_2$

Or, $V_1 = \frac{V_2N_2}{N_1} = \frac{500 \times 0.5}{15.44} = 16.19$ mL

Hence, volume of HNO_3 is 16.19 mL.

---

32. 2074 Supp. Q.No. 24 **Define the terms:**

i. Titration error

ii. Unknown solution

What volume of 10 M HCl and 3M HCl should be mixed to obtain one litre of 6 M HCl solution? [1+1+3]

i. **Titration error:** The difference between the equivalence point and the measured end point is called the titration error. A visual end point is always slightly beyond the equivalence point because of the necessity of seeing the color change by eye.

ii. **Unknown solution:** The solution whose strength is unknown is called unknown solution.

Numerical:

Moles = Molarity × Liters

1 liter of 6 M HCl contains 6 moles of HCl. This is the total number of moles in the final solution. The final volume = 1 Liters.

Let V = volume of 10 M HCl
(1- V) = volume of 3 M HCl
10 × V = moles of HCl from 10 M HCl
3 × (1 - V) = moles of HCl from 3 M HCl
Thus,
or, 10 × V + 3 × (1 - V) = 6
or, 10 × V + 3 - 3 × V = 6
or, 7 × V = 3
Hence,

$V = \frac{3}{7}$ Liters of 10 M HCl = 0.42 L of 10 M HCl

$(1 - \frac{3}{7}) = \frac{4}{7}$ Liter of 3 M HCl = 0.57 L of 3 M HCl

---

33. 2074 Set A Q.No. 24 Define titration error. 0.012 g of a divalent metal is completely dissolved in 40 cc of $\frac{N}{10}$ HCl. The excess of acid required 15 cc of $\frac{N}{5}$ NaOH for neutralization. Find the atomic weight of the metal. **[1+4]**

Titration error: The difference between the equivalence point and the measured end point is called the titration error. A visual end point is always slightly beyond the equivalence point because of the necessity of seeing the color change by eye.

Numerical:

Weight of metal = 0.012 g
Valency of metal = 2
Volume of HCl of $\frac{N}{10}$ = 40 cc
Volume of HCl of 1N = 4 cc
Volume of NaOH of $\frac{N}{5}$ = 15 cc
Volume of NaOH of 1N = 3 cc
The volume of acid (HCl) comsumed = (4 - 3) cc = 1 cc of 1N HCl
Now,
1 cc of 1 N HCl reacts with 0.012 g metal.
1000 cc of 1 N HCl reacts with 0.012 × 1000 g metal = 12 g metal
Hence, equivalent weight of metal = 12
We know that,
Atomic mass = Valency × Equivalent weight = 2 × 12 = 24
Hence, atomic mass of metal = 24 a.m.u.

---

34. 2074 Set B Q.No. 24 Define the terms;

I. Titration error
II. Standard solution

Calculate the volume of 1M NaOH required to neutralize 200 cc of 2M HCl. What mass of sodium chloride are produced from the neutralization reaction? **[1+1+1+2]**

i. **Titration error:** The difference between the equivalence point and the measured end point is called the titration error. A visual end point is always slightly beyond the equivalence point because of the necessity of seeing the color change by eye.

ii. **Standard solution:** In analytical chemistry, a standard solution is a solution containing a precisely known concentration of an element or a substance.

Numerical:

For NaOH	For HCl
$V_1 = ?$	$V_2 = 200$ cc
$M_1 = 1M$	$M_2 = 2M$

[Acidity of base = Basicity of acid]

We know that,

$V_1M_1 = V_2M_2$

Or, $V_1 = \frac{V_2M_2}{M_1} = \frac{200 \times 2}{1} = 400$ cc.

Hence, the volume of NaOH required is 400 cc.

The balanced chemical equation is

$$\begin{array}{llll} NaOH + & HCl & \longrightarrow NaCl + & H_2O \\ 1\ \text{mole} & 1\ \text{mole} & 1\ \text{mole} & \\ & & 58.5\ \text{g} & \end{array}$$

1000 cm^3 of 2M of HCl solution contains 2 mole

200 cm^3 of 2M of HCl solution contains $\frac{2 \times 200}{1000}$ mole $= \frac{4}{10}$ mole = 0.4 mole

1 mole of HCl reacts with NaOH to give 58.5 g NaCl
0.4 mole of HCl reacts with NaOH to give 0.4 × 58.5 g NaCl = 23.5 g NaCl
Hence, the mass of sodium chloride produced is 23.5 g NaCl.

---

35. 2073 Supp Q.No. 24 2073 Set C Q.No. 24 What is meant by acidity of base? 500 cc of 2 N Na_2CO_3 are mixed with 400 cc of 3N H_2SO_4 and volume was diluted to one litre. Will the resulting solution acidic, basic or neutral? Also, calculate the molarity of the dilute solution. **[1+2+2]**

Acidity of base: The number of replaceable of OH^- ion present in the base is called acidity of base.

Numerical:

Given, 500 cc of 2 N Na_2CO_3 = 1000 cc of 1 N Na_2CO_3
And 400 cc of 3 N H_2SO_4 = 1200 cc of 1 N H_2SO_4
We know that,

Equal volume of acid neutralizes equal volume of base, if acid and base have the same normality. So, 1000 cc of 1 N Na_2CO_3 neutralizes 1000 cc of 1 N of H_2SO_4. Thus, 200 cc of 1 N H_2SO_4 acid is left unreacted and solution is acidic in nature.

Molarity of dilute solution:

Volume of acid left (V_1) = 200 cc
Normality of acid (N_1) = 1 N
Final volume of solution (V_2) = 1 L = 1000 cc
Normality of dilute solution (N_2) = ?
From normality equation,
$V_1N_1 = V_2N_2$

Or, $N_2 = \frac{V_1N_1}{V_2} = \frac{200 \times 1}{1000} = 0.2$ N H_2SO_4

The normality of acidic solution is 0.2 N.
We know that,

Molarity of dilute solution (M) $= \frac{\text{Normality}}{\text{Basicity of acid}} = \frac{0.2}{2} = 0.1M$

Hence, the molarity of acidic solution is 0.1 M.

36. **2072 Supp. Q.No. 25** **What is meant by acidimetry? A solution of conc. HCl contain 38% HCl by mas**
1.19 g/cc?

i. What is the molarity of this solution if the density of the solution is 1.19 g/cc?

ii. What volume of the conc. HCl is required to neutralize one liter of 0.1 M NaOH solution? [1+2+

Acidimetry: The method of determining the strength of acid by titrating it with th known volume of standard alkali solution is known as acidimetry.

Numerical:

i. Given,

Density i.e. specific gravity = 1.19 g/cc

% by weight of HCl i.e. % (w/W) = 38%

Molarity of solution (M) =?

Equivalent weight of HCl = (1 + 35.5)= 36.5

We know that,

$$\text{Molarity} = \frac{\%\left(\frac{w}{W}\right) \times \text{specific gravity} \times 10}{\text{Molecular weight}} = \frac{38 \times 1.19 \times 10}{36.5} = 12.38\text{ M}$$

Hence, the molarity of HCl solution is 12.38 M.

ii. Given,

Volume of HCl required to neutralize (V_1) = ?

Normality of HCl (N_1) = 12.38 N

Volume of NaOH (V_2) = 1 litre = 1000 mL

Normality of NaOH (N_2) = 0.1 M = 0.1 N

We know that,

$V_1N_1 = V_2N_2$

$$\text{or, } V_1 = \frac{V_2N_2}{N_1} = \frac{1000 \times 0.1}{12.38} = 8.077\text{ mL}$$

Hence, the volume of HCl to neutralize 1 litre of 0.1M NaOH solution is 8.077 mL.

---

37. **2072 Set C Q.No. 25** **What is meant by redox titration? 4 g of a divalent metal was dissolved in 100 c of 2 M H_2SO_4 (f = 1.01).The excess acid required 30 cc of 1 N NaOH for complete neutralization. Fin the atomic mass of the metal.** **[1+5**

Redox Titration: A titration which involves the oxidation and reduction reaction i called redox titration. Example:

$$2\,KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10\,CO_2 + 8H_2O$$

Numerical:

Given,

Weight of metal = 4 g

Valency of metal = 2

Volume of H_2SO_4 = 100 cc

Molarity of H_2SO_4= 2M (f = 1.01)

We know that,

Normality = Molarity × basicity of acid = 2M × 2 = 4N (f = 1.01) = 4.04 N

Volume of NaOH = 30 cc

Normality of NaOH = 1N

Atomic mass of metal = ?

100 cc of 4.04 N H_2SO_4 = 404 cc of 1N H_2SO_4

30 cc of 1 N NaOH ≅ 30 cc of 1N H_2SO_4

The volume of H_2SO_4 consumed by metal = (404 – 30) = 374 cc

---

Percentage Purity = % by weight

Now,

374 cc of H_2SO_4 of 1N reacts with 4 g metal

1 cc of H_2SO_4 of 1N reacts with $\frac{4}{374}$ g metal

1000 cc H_2SO_4 of 1N reacts with $\frac{4}{374} \times 1000$ g metal = 10.69 g of metal

Thus, the equivalent weight of metal = 10.69

We know that,

Atomic weight = Valency × Equivalent weight = 2 × 10.69 = 21.38 amu

Hence, atomic weight of metal is 21.38 amu.

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38. **2072 Set E Q.No. 26** **Define normality and molarity. Write their relationship. A commercial sample of sulphuric acid has specific gravity 1.8. 10 mL of this acid was diluted upto 1 litre with water. 10 mL of diluted acid required 30 mL of $\frac{N}{10}$ NaOH for complete neutralization. Calculate the percentage purity of H_2SO_4 in the commercial sample.** **[2+3]**

Concentrated

Normality: The number of gram equivalent of a solute is present in one litre of solution is called normality.

Molarity: The number of gram mole of a solute is present in one litre of solution is called molarity.

Relationship between normality and molarity: Please refer to 2065 Q.No. 17

Numerical:

Given, specific gravity of H_2SO_4 = 1.8

Percentage purity (%) = ?

Equivalent weight of H_2SO_4 = 49

For dilute solution

Volume of acid (V_1) = 10 mL

Normality of acid (N_1) = ?

Volume of NaOH (V_2) = 30 mL

Normality of NaOH(N_2) = $\frac{N}{10}$ = 0.1 N

We know that

$V_1N_1 = V_2N_2$

$$\text{Or, } N_1 = \frac{V_2N_2}{V_1} = \frac{30 \times 0.1}{10} = 0.3\text{ N}$$

Hence, the normality of dilute H_2SO_4 is 0.3 N

10 mL of conc. H_2SO_4 is diluted to 1 litre

Volume of conc. H_2SO_4 (V_1) = 10 mL

Normality of conc. H_2SO_4 (N_1) = ?

Volume of dilute H_2SO_4 (V_2) = 1000 mL

Normality of dilute H_2SO_4 (N_2) = 0.3N

From normality equation

$V_1N_1 = V_2N_2$

$$\text{Or, } N_1 = \frac{V_2N_2}{V_1} = \frac{1000 \times 0.3}{10} = 30\text{ N}$$

Hence, the normality of commercial sample of H_2SO_4 i.e. Conc. H_2SO_4 is 30 N.

We know that,

$$\text{Normality} = \frac{\%\text{ purity} \times \text{specific gravity} \times 10}{\text{Equivalent weight}}$$

$$\text{Or, } 30\ N = \frac{\%\ \text{purity} \times 1.8 \times 10}{49}$$

$$\text{Or, } \%\ \text{purity} = \frac{30 \times 49}{1.8 \times 10} = 81.66\ \%$$

Hence, % purity of commercial sample of H_2SO_4 i.e. conc. H_2SO_4 is 81.66%

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39. 2071 Supp. Q.No. 25 What is meant by normality factor? What volume of 95 % sulphuric acid (density = 1.85 g / cc) and what mass of water must be taken to prepare 100 cc of 15% solution o sulphuric acid. (density = 1.1 g / cc)? [1+4

Normality factor (f) : The ratio of actual weight of substance taken to the theoretica weight of substance to be taken is called normality factor. It is denoted by symbol 'f'.

$$\text{Normality factor (f)} = \frac{\text{Weight taken}}{\text{Weight to be taken}}$$

Numerical:

Given,

% purity of H_2SO_4 = 95%

Density or specific gravity = 1.85 g/cc

Equivalent weight of H_2SO_4 = 49

We know that,

$$\text{Normality (N)} = \frac{\%\text{purity} \times \text{Specific gravity} \times 10}{\text{Equivalent weight}} = \frac{95 \times 1.85 \times 10}{49} = 35.86\ N$$

Normality of H_2SO_4 (N_1) = 35.86 N

Volume of H_2SO_4 (V_1) = ?

Again,

Given,

% purity of H_2SO_4 = 15%

Density or specific gravity = 1.1 g/cc

Eqv. wt. of H_2SO_4 = 49

$$\text{Normality (N)} = \frac{\%\ \text{purity} \times \text{Specific gravity} \times 10}{\text{Equivalent weight}} = \frac{15 \times 1.1 \times 10}{49} = 3.36\ N$$

Normality of H_2SO_4 (N_2) = 3.36 N

Volume of H_2SO_4 (V_2) = 100 cc

We know that from normality equation

$$V_1N_1 = V_2N_2$$

$$\text{or, } V_1 = \frac{V_2N_2}{N_1}$$

$$\text{or, } V_1 = \frac{100 \times 3.36}{35.86}$$

$$\text{or, } V_1 = 9.36\ cc$$

Hence, the volume of H_2SO_4 required (V_1) = 9.36 cc.

The volume of water added to prepare 100 cc solution.

= (100 – 9.36) = 90.64 cc

We know that

Density of water = 1 g /cc

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Mass = Density × Volume

= 90.64 × 1

= 90.64 g

Hence, the mass of water added to prepare 100 cc solution is 90.64 g.

40. 2071 Set C Q.No. 25 Differentiate between primary standard and secondary standard solution. What volume of 12 M NaOH and 2 M NaOH should be mixed to get 2 litres of 9 M NaOH solution? [2+3]

Following are the different between primary and secondary standard solution:

Primary standard solution	Secondary standard solution
1. It is prepared by dissolving pure substance which is not affected in its composition for a long time.	1. It is prepared by neutralizing against the primary standard solution.
2. Example: Na_2CO_3, Oxalic acid, silver nitrate, KCl etc.	2. Example: NaOH, $CuSO_4$, HCl, H_2SO_4, HNO_3, $KMnO_4$ etc.

Numerical:

Given,

Volume mixture of NaOH solution (V_{mix}) = 2 litre

Molarity of mixture of NaOH solution (M_{mix}) = 9M

Let, volume of 12 M NaOH solution (V_1) = χ litre

∴ Volume of 2 M NaOH solution (V_2) = $(2 - \chi)$ litre

We know that,

$$M_1V_1 + M_2V_2 = V_{mix} \times M_{mix}$$

$$\text{or, } 12 \times \chi + 2 \times (2 - \chi) = 2 \times 9$$

$$\text{or, } 12\chi + 4 - 2\chi = 18$$

$$\text{or, } 10\chi = 18 - 4 = 14$$

$$\text{or, } \chi = \frac{14}{10} = 1.4 \text{ litre}$$

Hence, the volume of 12 M NaOH solution is 1.4 litre and volume of 2M NaOH solution is (2 - 1.4) = 0.6 litre.

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41. 2071 Set D Q.No. 25 Define acidimetry. A solution of conc. hydrochloric acid contain 38% HCl by mass

a. What is the molarity of this solution if the density of the solution is 1.19 g / cc?

b. What volume of the conc. HCl is required to neutralize 1 litre of 0.1 M NaOH solution? [1+4]

Please refer to 2072 Supp. Q.No. 25

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42. 2070 Supp. Q.No. 25 Define acidity of a base giving an example. 0.8 g of a divalent metal was dissolved in 100 cc of 1.28 N HCl and the solution was diluted to 200 cc 50 cc of this dilute solution required 54.6 cc of 0.22 N NaOH for neutralization: Calculate the atomic mass of the metal. [1+4]

Acidity of base: The number of replaceable OH^- ion present in the base is called acidity of base.

Numerical:

Given,

For HCl

Normality of HCl = 1.28 N

$$\text{Volume of HCl} = 100\ cc = \frac{100}{1000} \text{ litre}$$

Equivalent weight of HCl = 36.5

Molecular weight of HCl = ?

We know that,

$$\text{Normality} = \frac{\dfrac{\text{Weight in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 1.28 = \frac{\frac{\text{Weight in g}}{36.5}}{\frac{100}{1000}}$$

$$\text{or, Weight in g of HCl} = \frac{1.28 \times 100 \times 36.5}{1000} = 4.672 \text{ g}$$

Given,

Volume of NaOH(V_2) = 54.6 cc

Normality of NaOH(N_2) = 0.22 N

Volume of diluted acid (V_1) = 50 cc

Normality of diluted acid (N_1) = ?

We know that,

$V_1N_1 = V_2N_2$

$$\text{or, } N_1 = \frac{V_2N_2}{V_1} = \frac{54.6 \times 0.22}{50} = 0.24\text{N}$$

Since, 50 cc of solution is taken from the diluted solution. So, the normality of diluted is also 0.24 N. The mass of HCl in diluted solution is calculated as:

Volume of diluted solution = 200 cc

$$\text{Normality} = \frac{\frac{\text{Weight in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 0.24 = \frac{\frac{\text{Weight in g}}{36.5}}{\frac{200}{1000}}$$

$$\text{or, wt. in g of HCl} = \frac{0.24 \times 200 \times 36.5}{1000} = 1.752 \text{ g}$$

Hence, the mass of HCl which is consumed by 0.8 g of metal = (4.672 - 1.752) = 2.92 g

Now,

2.92 parts by weight of HCl is consumed by 0.8 parts by weight of metal.

1 part by weight of HCl is consumed by $\frac{0.8}{2.92}$ parts by weight of metal.

36.5 parts by weight of HCl is consumed by $\frac{0.8}{2.92} \times 36.5$ parts by weight of metal.

= 10 parts by weight of metal i.e. equivalent weight of metal

Valency of metal = 2

Therefore, atomic mass of metal is 2 × 10 = 20 a.m.u.

---

43. **2070 Set C Q.No. 23** ***0.8 g of a divalent metal was dissolved in 100 cc of 1.28 N HCl and the solution was diluted to 200 cc. Then 50 cc of this solution required 54.6cc of 0.22 N NaOH for neutralization. Find the atomic weight of the metal.*** **[5]**

➣ Please refer to 2070 Supp. Q.No 25

44. **2069 (Set A) Q.No. 26** **Define the terms:** **[1 × 5]**

i. End point	**ii. Equivalence point**
iii. Indicators	**iv. Basicity of acid**
v. Acidimetry	

➣

i. **End point:** The point in a titration at which the reaction between two solutions is complete as shown by the indicator. End point is also known as equivalent point or neutral point where an acid solution is just neutralized by a basic solution in titration.

ii. **Equivalence point:** The point at which one gram equivalent of a substance completely reacts with one gram equivalent of another substance is called equivalence point.

iii. **Indicator:** Indicator is a chemical substance which indicates the end point or neutral point of the reaction between two solutions by changing its colour with the change of the pH of a solution near the equivalent point.

iv. **Basicity of acid:** The number of replaceable hydrogen ion present in one molecule of acid is called basicity of acid.

v. **Acidimetry:** The process of determining the strength of acid by titrating it against the standard solution of base in the presence of indicator is called acidimetry.

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45. **2066 Q. No. 25** **What are Primary and Secondary standard solutions? Calculate the resulting normality of a solution prepared by mixing 20 mL of 0.8 M NaOH with 25 mL of 0.4 M H_2SO_4 solutions.** **[2+3]**

➣ **Primary standard solution:** The substances whose standard solution can be prepared directly by dissolving the known weight of substance in certain volume of solution is called primary standard substance and the solution made from primary standard substance is called primary standard solution. Example: solution of oxalic acid.

Secondary standard solution: The substance whose solution can be standardized with the help of primary standard solution is called secondary substance and the solution is called secondary standard solution. Example: NaOH solution.

Numerical:

20 mL of 0.8 M NaOH = 20 mL of 0.8 N NaOH [Acidity of NaOH = 1 so, N = M]

= 20 × 0.8 of 1 N NaOH

= 16 mL of 1 N NaOH

25 mL of 0.4 M H_2SO_4 = 25 mL of 0.4 × 2 = 0.8 N H_2SO_4 [Basicity of H_2SO_4 = 2]

= 25 mL of 0.8 N H_2SO_4

= (25 × 0.8) mL of 1 N H_2SO_4

= 20 mL of 1N H_2SO_4

We know that,

Equal volume of acid neutralizes the equal volume of base.

16 mL of 1N NaOH is neutralized by 16 mL of 1N H_2SO_4

The volume of acid left = (20 – 16) = 4 mL of 1N H_2SO_4

Here,

Volume of acid left (V_1) = 4 mL

Strength (N_1) = 1N

Final volume (V_2) = 20 + 25 = 45 mL

Strength (N_2) = ?

We know that,

$V_1N_1 = V_2N_2$

$$N_2 = \frac{V_1N_1}{V_2} = \frac{4 \times 1}{45} = 0.088\text{N}$$

Thus, the normality of the resulting solution = 0.088N.

LONG ANSWER QUESTIONS [10 MARKS]

46. **2064 Q.No. 30(i)** **Define the terms:**

a. **Gram equivalent weight**

b. **Equivalent point of reaction**

c. **End point of titration** **[5]**

➣

a. **Gram equivalent weight:** If equivalent weight of substance is expressed in gram is called gram equivalent weight.

$$\text{No. of gram equivalent} = \frac{\text{Weight in gram}}{\text{Equivalent weight}}$$

b. **Equivalence point:** The point at which one gram equivalent of a substance completely reacts with one gram equivalent of another substance is called equivalence point.

c. **End point of titration:** The point in a titration at which the reaction between two solutions is complete as shown by the indicator. End point is also known as equivalent point or neutral point where an acid solution is just neutralized by a basic solution in titration.

---

47. 2064 Q.No. 30(ii) Define indicator. Explain how are indicators selected in acid base titration? [5]

↘ We know that an indicator is a substance which change colour at different pH but this is not a sufficient condition for it to be used as indicator in a certain titration. The characteristics of a good indicator are:

i. The colour change should be sharp, i.e. the colour should change over a short range of pH value.

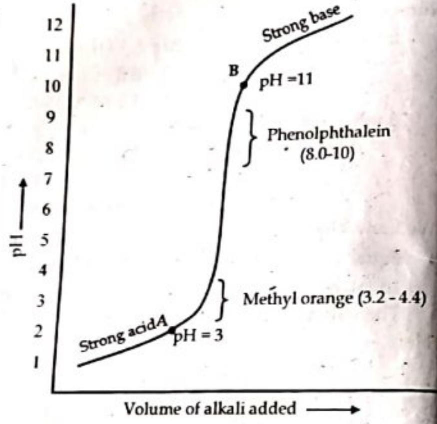
ii. The colour change should be stable and between contrasting colours.

iii. The colour change should be at the equivalence point or end point of the reaction. The suitability of indicators depends on the nature of the acid and base used in a particular titration.

a. **Titration of strong acid and strong base:** In the titration of strong acid such as HCl and strong base such as NaOH, the steep rise of curve occurs at pH 3 to 11. Any indicator capable of changing colour within this range is a suitable indicator.

$HCl + NaOH \longrightarrow NaCl + H_2O$

The colour changing pH range of methyl orange is 3.2 to 4.4 and that of phenolphthalein is 8 to 10. So either methyl orange or phenolphthalein can be used as indicator.

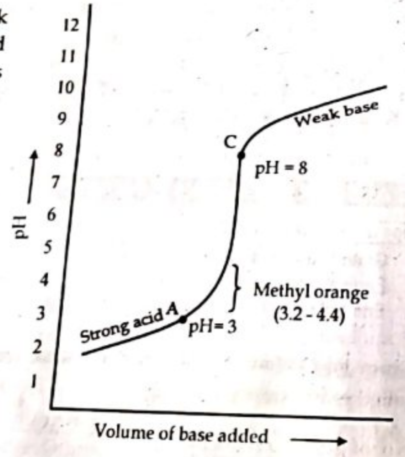


b. ***Titration of strong acid and weak base:*** *In the titration of strong acid such as HCl and weak base such as NH₄OH, the steep rise of curve occurs at pH 3 to 8.*

$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$

Any indicator capable of changing its colour within this pH range is a suitable indicator.

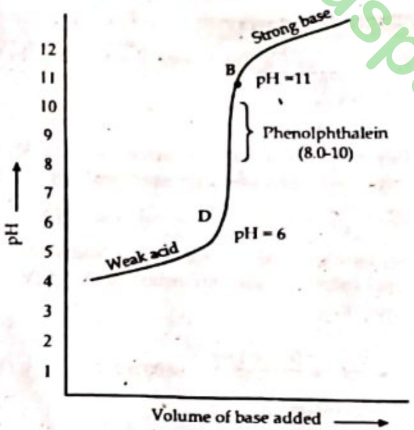
The colour changing pH range of methyl orange is 3.2 to 4.4. So methyl orange is a suitable indicator in the titration of strong acid and weak base.



c. **Titration of weak acid and strong base:** In the titration of weak acid such as CH_3COOH and strong base such as NaOH the steep rise of curve occurs at pH 6 to 11.

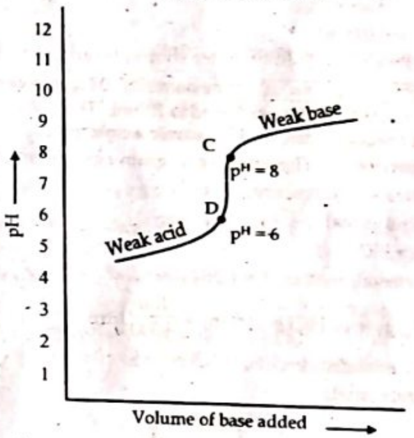
$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Any indicator capable of changing its colour within this pH range is a suitable indicator. The colour changing pH range of phenolphthalein is 8.0 to 10.0. So phenolphthalein is a suitable indicator in the titration of weak acid and strong base.



d. **Titration of weak acid and weak base:** In the titration of weak acid such as CH_3COOH and weak base such as NH_4OH there is no enough steep rises in the curve. . The tapering of curve takes place within pH value of 6 to 8.

$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$



The colour changing pH range of methyl orange is 3.2 to 4.4 and that of phenolphthalein is 8.0 to 10.0. Therefore, neither methyl orange nor phenolphthalein is suitable indicator. Hence end point of weak acid-weak base titration is not determined by acid-base titration which may be determined by other methods such as conductometric titration.

Acid	Base	Approx. p^H range near equivalence point	Indicator	Approximate pH transition of indicator
Strong	Strong	3 - 11	Methyl orange phenolphthalein	3.2 - 4.4 8 - 10
Strong	Weak	3 - 8	Methyl orange	3.2 - 4.4
Weak	Strong	6 to 11	phenolphthalein	8 - 10
Weak	Weak	about 6 to 8	None	----

48. 2062 Q.No. 30(b) Define indicator. How is a suitable indicator selected for a particular titration? [5]

↘ Please refer to 2064 Q.No. 30(ii)

NUMERICAL PROBLEMS

49. **2070 Set D Q.No. 2** **What volume of water should be added to 500 mL of 2 N (f = 0.98) Na_2CO_3 to mak it exactly $\frac{N}{10}$?** **[2**

Given,

Initial volume of sodium carbonate (V_1) = 500 mL

Initial normality of sodium carbonate (N_1) = 2N (f = 0.98) = (2 × 0.98) = 1.96 N

Final normality of sodium carbonate $(N_2) = \frac{N}{10} = 0.1N$

Suppose x mL of water should be added then,

Final volume of sodium carbonate $(V_2) = (V_1 + x)$ mL

We know that,

$V_1N_1 = V_2N_2$

$V_2 = \frac{V_1N_1}{N_2} = \frac{500 \times 1.96}{0.1} = 9800$ mL

or, 500 + x = 9800 mL

or, x = (9800 - 500)

or, x = 9300 mL

Hence, 9300 mL of water should be added to make exactly decinormal solution.

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50. **2070 Set D Q.No. 26** **Define normality, 0.8 g of divalent metal was dissolved in 100 mL of 1.28 N HC and the solution was diluted to 200 mL. Then, 50 mL of the solution required 54.6 mL of 0.22 N NaO for neutralization. Find the atomic weight metal.** **[1+4**

Normality: The number of gram equivalent of a solute is present in one litre of solutio is called normality.

Numerical:

For HCl

Normality of HCl = 1.28 N

Volume of HCl = 100 ml = $\frac{100}{1000}$ litre

Equivalent weight of HCl = 36.5

We know that,

$$\text{Normality} = \frac{\frac{\text{Weight in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 1.28 = \frac{\frac{\text{Weight in g}}{36.5}}{\frac{100}{1000}}$$

$$\text{or, Weight in g of HCl} = \frac{1.28 \times 100 \times 36.5}{1000} = 4.672 \text{ g}$$

Given,

Volume of NaOH(V_2) = 54.6 mL

Normality of NaOH(N_2) = 0.22 N

Volume of diluted acid (V_1) = 50 mL

Normality of diluted acid (N_1) = ?

We know that,

$V_1N_1=V_2N_2$

or, $N_1 = \frac{V_2N_2}{V_1} = \frac{54.6 \times 0.22}{50} = 0.24N$

Since, 50 mL of solution is taken from the diluted solution. So, the normality of diluted is also 0.24 N. the mass of HCl in diluted solution is calculated as:

Volume of diluted solution = 200 mL

$$\text{Normality} = \frac{\frac{\text{Weight in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 0.24 = \frac{\frac{\text{Weight in g}}{36.5}}{\frac{200}{1000}}$$

$$\text{or, Weight in g of HCl} = \frac{0.24 \times 200 \times 36.5}{1000} = 1.752 \text{ g}$$

Hence, the mass of HCl which is consumed by 0.8 g of metal = (4.672 – 1.752) = 2.92 g

Now,

2.92 parts by weight of HCl is consumed by 0.8 parts by weight of metal.

1 parts by weight of HCl is consumed by $\frac{0.8}{2.92}$ parts by weight of metal

36.5 parts by weight of HCl is consumed by $\frac{0.8}{2.92} \times 36.5$ parts by weight of metal

= 10 parts by weight of metal i.e. equivalent weight of metal

Valency of metal = 2

Therefore, atomic weight of metal is (2 × 10) = 20 amu.

---

51. **2073 Set D Q.No. 24** **Define redox titration. 10 g of NaOH was added to 200 cc of $\frac{N}{2}$ (f = 1.5) H_2SO_4. The volume was diluted to two litres. Predict whether the dilute solution is acidic, basic or neutral and also calculate the resulting molarity of the dilute solution.** **[1+2+2]**

Redox Titration: A titration which involves the oxidation and reduction reaction is called redox titration. Example:

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Numerical:

Given, weight of NaOH = 10 g

Volume of H_2SO_4 = 200 cc

Strength of $H_2SO_4 = \frac{N}{2}$ (f = 1.5) = 0.5 × 1.5 = 0.75 N

Equivalent of H_2SO_4 = 49

Weight of H_2SO_4 (w) = ?

We know that,

$$N = \frac{\text{Weight in g(w)} \times 1000}{\text{Equivalent weight} \times \text{Volume of solution in cc}} = \frac{w \times 1000}{49 \times 200}$$

$$\text{Or, } 0.75 = \frac{w \times 1000}{49 \times 200}$$

$$\text{Or, } w = \frac{49 \times 200 \times 0.75}{1000} = 7.35 \text{ g } H_2SO_4$$

The balanced chemical equation is

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

1 mol 2 mol

98 g 80 g

98 g of H_2SO_4 is neutralized by 80 g of NaOH

7.35 g of H_2SO_4 is neutralized by $\frac{80 \times 7.35}{98}$ of NaOH = 6 g of NaOH

The weight of NaOH left = (10 - 6) = 4 g. so, the resulting solution is basic in nature. The strength of basic solution in g/L = $\frac{4}{2}$ = 2 g/L (volume of solution = 2 L)

We know that,

$$\text{Molarity} = \frac{g/L}{\text{Molecular weight}} = \frac{2}{40} = 0.05\ \text{M (Molecular weight of NaOH = 40)}$$

Hence, the molarity of resulting solution is 0.05 M.

---

52. **2069 Supp. Set B Q.No. 2 What volume of 5 % NaOH are required to neutralize 2 litres of decinormal H_2SO_4?** **[2]**

Equivalent weight of NaOH (E) = 40
Volume of H_2SO_4 to neutralize (V) = 2 litre = 2000 mL
Normality of NaOH (N) = ?
5 % NaOH means 5 g of NaOH in 100 g of NaOH
So, weight of NaOH (W) = 5 g

We know that,

$$W = \frac{NEV}{1000}$$

or, $5 = \frac{N \times 40 \times 2000}{1000}$

or, $5 = N \times 80$

or, $N = \frac{5}{80}$

or, N = 0.0625 N

Thus, the normality of NaOH solution (N) = 0.0625 N

From question

H_2SO_4	NaOH
V_1 = 2 litre	V_2 =?
N_1 = 0.1N	N_2 = 0.0625N

From normality equation,

$V_1N_1 = V_2N_2$

$$V_2 = \frac{V_1N_1}{N_2} = \frac{2 \times 0.1}{0.0625} = 3.2\ \text{litre}$$

The volume of NaOH required is 3.2 litre of 5%

$\frac{3.2 \times 5}{100}$ = 0.16 litre

Thus, 0.16 litre of NaOH is required to neutralize 2 litre of decinormal H_2SO_4.

---

53. **2069 (Set A) Q.No. 2 X cc of 5 N HCl was diluted to one litre of normal solution. Calculate the value of X.** **[2]**

Given,
V_1 = X cc V_2 = 1 litre = 1000 cc
N_1 = 5N N_2 = 1N

We know that,

$V_1N_1 = V_2N_2$

X × 5 = 1000 × 1

or, $X = \frac{1000}{5}$ = 200 cc

Hence, the value of X is 200 cc

54. **2069 (Set B) Q.No. 2 What mass of Na_2CO_3 is required to make 50 cc of its seminormal solution?** **[2]**

Given,
Volume of solution (V) = 50 cc = 0.05 litre
Normality of Na_2CO_3 (N) = seminormal = $\frac{1}{2}$N = 0.5N
Weight of Na_2CO_3 (w) = ?
Equivalent weight of Na_2CO_3 = 53

We know that,

$$\text{Normality} = \frac{\text{Weight of solute in gram}}{\text{Equivalent weight of solute} \times \text{Volume of solution in liter}}$$

or, $0.5 = \frac{w}{53 \times 0.05}$

or, w = 0.5 × 53 × 0.05 = 1.325 g

Hence, mass of Na_2CO_3 required is 1.325 g to make 50 cc of seminormal solution.

---

55. **2068 Q.No. 17 Convert the followings:** **[1+1]**
 i. **2.5 M H_3PO_4 into Normality**
 ii. **4.9 M H_2SO_4 into gram / litre.**

i. **2.5 M H_3PO_4 into normality**
Basicity of H_3PO_4 = 3
We know that,
Normality = molarity × basicity = (2.5 × 3) = 7.5 N

ii. **4.9 M H_2SO_4 into g/L**
Molecular weight of H_2SO_4 = 98
We know that,
Gm/L = Molarity × Molecular weight = (4.9 × 98) = 480.2 g /L

---

56. **2068 Q.No. 30 Define the terms:** **[5 + 5]**
 i. **Primary standard solution**
 ii. **Normality factor**
 iii. **Acidity of a base**
 iv. **Alkalimetry**

What is meant by redox titration? Write an example of it. 4 g of NaOH was added to 20 cc of 2 N H_2SO_4 solution and the volume was diluted to one litre. Predict whether the dilute solution is acidic, basic or neutral and also calculate the resulting normality of the dilute solution in term of g / litre.

i. **Primary standard solution:** The substances whose standard solution can be prepared directly by dissolving the known weight of substance in certain volume of solution is called primary standard substance and the solution made from primary standard substance is called primary standard solution. Example: solution of oxalic acid.

ii. **Normality factor:** The ratio of actual weight of substance taken to the theoretical weight of substance to be taken is called normality factor.

iii. **Acidity of base:** The number of OH^- ion present of any base is known as acidity of base.

iv. **Alkalimetry:** The process of determining the strength of alkali by titrating it against the standard solution of acid in the presence of indicator is called alkalimetry.

Redox titration: A titration which involves the oxidation and reduction reaction is called redox titration.

Example of redox reaction is

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8H_2O$$

Here, $KMnO_4$ is reduced to $MnSO_4$ and $C_2H_2O_4$ is oxidized to CO_2 and H_2O. So, this reaction is called redox

Numerical

Given,

Weight of NaOH = 4 g
Volume of H_2SO_4 = 20 cc
Strength of H_2SO_4 = 2N
Equivalent wt. of H_2SO_4 = 49
Wt. of H_2SO_4 (w) = ?

We know that,

$$N = \frac{\text{Weight in g (w)}}{\text{Equivalent weight}} \times \frac{1000}{\text{Volume of solution in cc}}$$

$$\text{or, } 2 = \frac{w}{49} \times \frac{1000}{20}$$

or, 1000 w = 2 × 49 × 20

$$\text{or, } w = \frac{1960}{1000} = 1.96 \text{ g}$$

The balanced equation is

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

1 mole 2 mole
98g 2 × 40 = 80 g

98 g of H_2SO_4 is neutralized by 80 g of NaOH

1.96 g of H_2SO_4 is neutralized by $\frac{80 \times 1.96}{98}$ g of NaOH = 1.6 g NaOH

The weight of NaOH left = (4 – 1.6) = 2.4 g

So, the solution is basic in nature. The strength of dilute solution in g/liter = 2.4 g/litre.

We know that,

$$N = \frac{g/L}{\text{Equivalent weight}} = \frac{2.4}{40} = 0.06N$$

Hence, the resulting solution of NaOH is basic and normality is 0.06 N.

---

57. 2067 Q.No. 25 Define: i. Acidity of base ii. End point

What volumes of $\frac{N}{2}$ and $\frac{N}{10}$ HCl must be mixed to give 2 liters of $\frac{N}{5}$ HCl? [2+3=5]

i. **Acidity of base:** The number of OH^- ion present of any base is known as acidity of base.

ii. **End point:** The state at which the change in color of indicator indicates the completion of reaction during titration is known as end point.

Numerical:

Given,

Final volume (V_f) = 2 litre

Final strength (N_f) = $\frac{N}{5}$ = 0.2N

Type-1 Strength of HCl (N_1) = $\frac{N}{2}$ = 0.5N

Type-2 Strength of HCl (N_2) = $\frac{N}{10}$ = 0.1N

Suppose, volume of type -1 (V_1) = x
Volume of type – 2 (V_2) = (2 – x)

We know that,

$$V_1N_1 + V_2N_2 = V_fN_f$$

$$0.5 \times x + (2 - x)\, 0.1 = 0.2 \times 2$$

or, 0.5x + 0.2 – 0.1 x = 0.4
or, 0.4x = 0.4 – 0.2
or, 0.4 x =0.2

$$\text{or, } x = \frac{0.2}{0.4} = 0.5$$

So, V_1 = x =0.5 litre
And V_2 = (2 – x) = (2 – 0.5) = 1.5 litre

Hence, 0.5 lit of $\frac{N}{2}$ HCl and 1.5 litre of $\frac{N}{10}$ HCl must be mixed to form 2 litre of $\frac{N}{5}$ HCl.

---

58. 2065 Q.No. 25 Define decinormal solution. 3 g of a trivalent metal was completely dissolved with 750 mL of 1N HCl. The residual solution further required 1000 mL of $\frac{N}{2}$ NaOH for the complete neutralization. Find the atomic mass of the metal. [1+4]

Decinormal solution: A solution having normality 0.1 N is called decinormal solution.

Numerical:

Given,

Weight of metal = 3 g
Valency of metal = 3
Total volume of HCl (1N) = 750 mL

1000 mL of $\frac{N}{2}$ NaOH = 500 mL of 1N NaOH ≅ 500 mL of 1N HCl

The volume of HCl consumed by metal = (750 – 500) = 250 mL of 1N HCl

Now,

250 mL of 1N HCl reacts with 3 g of metal.

1 mL of 1N HCl reacts with $\frac{3}{250}$ g of metal.

1000 mL of 1N HCl reacts with $\frac{3}{250} \times 1000$ g of metal = 12 g of metal.

So, the equivalent weight of metal = 12

We know that,

Atomic mass = Valency × Equivalent weight = 3 × 12 = 36
So, the atomic mass of metal = 36 amu.

---

59. 2064 Q.No. 30(iii) 0.715 g of $Na_2CO_3 \cdot x H_2O$ required 20 mL of seminormal hydrochloric acid solution for complete reaction. Find the value of x. [3]

Given,

Weight of $Na_2CO_3.xH_2O$ = 0.715 g
Volume of HCl = 20 mL

Normality of HCl = $\frac{N}{2}$ (semi-normal) = 0.5 N

No. of water molecules i.e. water of crystallization (x) = ?

We know that,

1 g equivalent weight of HCl = 1 g equivalent weight of $Na_2CO_3.xH_2O$
1000 mL of 1N HCl = x g

$$20 \text{ mL of 1N HCl} = \frac{x}{1000} \times 20$$

$$20 \text{ mL of } \frac{N}{2} \text{ HCl} = \frac{x}{1000} \times 20 \times \frac{1}{2} = \frac{x}{100} \text{ g}$$

So, $\frac{x}{100}$ g = 0.715 g

or, x = 71.5 g

Hence, the equivalent weight of $Na_2CO_3.xH_2O$ = 71.5

The molecular weight of $Na_2CO_3.xH_2O$ = 71.5 × 2 (acidity of sodium carbonate is 2) = 143

$2 \times Na + C + 3 \times O + x(2H + O) = 143$

or, $2 \times 23 + 12 + 3 \times 16 + x(2 + 16) = 143$

or, $46 + 12 + 48 + x(18) = 143$

or, $106 + x(18) = 143$

or, $x(18) = 143 - 106 = 37$

or, $x = \frac{37}{18} = 2.05 \cong 2$

Therefore, the value of x i.e. water of crystallization = 2

---

60. 2063 Q.No. 18 0.315 g of a dibasic acid required 50 mL of decinormal sodium hydroxide solution for complete neutralisation. Find the molecular mass of the acid. **[2]**

Basicity of acid = 2
Weight of acid = 0.315 g
Molecular weight of acid = ?
Volume of NaOH = 50 mL
Normality of NaOH = 0.1 N

Given,

50 mL of 0.1 N NaOH requires 0.315 g acid for complete neutralization.

1 mL of 0.1 N NaOH requires $\frac{0.315}{50}$ g acid for complete neutralization.

1 mL of 1 N NaOH requires $\frac{0.315}{50 \times 0.1}$ g acid for complete neutralization.

1000 mL 1N N NaOH requires $\frac{0.315}{50 \times 0.1} \times 1000$ g acid for complete neutralization.

= 63 g acid for complete neutralization.

Equivalent weight of acid = 63

Molecular mass of dibasic acid = Equivalent weight × basicity = 63 × 2 = 126 amu.

Hence, the molecular mass of acid = 126 amu.

---

61. 2063 Q.No. 26 Define normality and molarity of a solution. Find their relationship for a given solution. 1 g of NaOH is added to 2 litres of x M H_2SO_4 solution, so that the pH of the resulting solution is 7. Find the value of x. **[1+1+1+2]**

Normality: *The number of gram equivalent of solute is present in per litre of solution.*

Molarity: *The number of moles of solute is present in per litre of solution.*

Relationship between normality and molarity:

Normality x Equivalent wt. = Molarity × Molecular weight

or, Normality = Molarity × $\frac{\text{Molecular weight}}{\text{Equivalent weight}}$

or, Normality = Molarity × basicity of acid = Molarity × acidity of base

Numerical:

Given,

pH of acid solution = 7
Weight of NaOH = 1 g
Volume of $H_2SO_4(V_1)$ *= 2 litre*
Molarity of H_2SO_4 *= x M*
Normality of $H_2SO_4(N_1)$ *= 2x N*
Volume of NaOH (V_2) *= ?*

Normality of NaOH (N_2) = ?
Equivalent weight of NaOH = 40

We know that,

$V_1N_1 = V_2N_2$

or, $2 \times 2x = \text{volume of NaOH in litre} \times \frac{\frac{\text{Weight of NaOH}}{\text{Equivalent weight of NaOH}}}{\text{Volume of NaOH in litre}}$

or, $4x = \frac{1}{40}$

or, $x = 0.00625 = 6.25 \times 10^{-3}$N or M

Hence, the molarity of $H_2SO_4 = 6.25 \times 10^{-3}$ M

---

62. 2062 Q.No. 13 Define normal solution. What is the normality of 500 mL solution of sodium hydroxide containing 30 g NaOH? **[2]**

Normal solution: A solution containing one gram equivalent of solute present in one litre of solution is called normal solution.

Numerical:

Volume of solution = 500 mL = 0.5 litre
Wt. of NaOH = 30 g

No. of gram equivalent of NaOH = $\frac{30}{40} = 0.75$

Normality = $\frac{\text{No. of gram Equivalent weight}}{\text{Volume of solution in liter}} = \frac{0.75}{0.5} = 1.5$ N

Hence, the normality of NaOH is 1.5 N.

---

63. 2061 Q.No. 30 (a) Provide a short definition of each of the following terms:

i. Equivalent weight
ii. Standard solution
iii. Neutralization point
iv. Primary standard
v. Indicator
[5]

i. **Equivalent weight:** Equivalent weight is defined as the number of gram or the number of parts by weight of that element which either combines or displaces 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

Example:

Hydrogen reacts with oxygen to form water.

$$\underset{4 \times 1.008}{2H_2} + \underset{4 \times 8}{O_2} \longrightarrow 2H_2O$$

Here, (4 × 1.008) parts by weight of hydrogen reacts with (4 × 8) parts by wt. of oxygen

1.008 parts by weight of hydrogen reacts with 8 parts by weight of oxygen

So, equivalent weight of oxygen is 8

ii. **Standard solution:** The solution whose concentration is known is called standard solution.

iii. **Neutralization point:** A point at which acid complete neutralizes base. is called neutralization point.

iv. **Primary standard solution:** The substances whose standard solution can be prepared directly by dissolving the known wt. of substance in certain volume of solution is called primary standard substance and the solution made from primary standard substance is called primary standard solution. Example: solution of oxalic acid.

v. **Indicator:** Indicator is a chemical substance which indicates the end point or neutral point of the reaction between two solutions by changing its colour with the change of the pH of a solution near the equivalent point.

64. **2061 Q.No. 30 (b)** **7.35 g of a dibasic acid was dissolved in water and diluted to 250 mL. 25 mL of th solution was neutralized by 15 mL of 1 N NaOH solution. What is equivalent weight and molecu weight of the acid?**

➢ Given,

Weight of the acid = 7.35 g

Given, 7.35 g of the acid is present in 250 cc of its solution.

Now,

Volume of diluted acid solution V_1 = 25 cc

Strengh of diluted acid solution S_1 = ?

Volume of NaOH consumed (V_2) = 15 mL

Strength of NaOH (S_2) = 1N

We know that,

$V_1S_1 = V_2S_2$

$25 \times S_1 = 15 \times 1N$

or, $S_1 = \frac{15}{25} = 0.6N$

So, the strength of 25 cc acid solution = 0.6N

Since, 25 cc of acid solution is taken from 250 cc acid solution which contains 7.35 g dibasic acid.

So, the strength of the whole acid solution i.e. 250 cc = 0.6 N

We know that,

$$\text{Normality} = \frac{\frac{\text{Weight in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 0.6 = \frac{\frac{7.35}{\text{Equivalent weight}}}{\frac{250}{1000}}$$

$$\text{or, } 0.6 = \frac{7.35 \times 1000}{250 \times \text{Equivalent weight}}$$

$$\text{or, Equivalent weight} = \frac{7.35 \times 1000}{250 \times 0.6} = 49$$

Basicity of acid = 2

So, molecular weight of acid = 2 × 49 = 98

Hence, the equivalent weight and molecular weight of acid is 49 and 98 respectively.

65. **2060 Q.No. 13** **5 g of a diacidic base is completely neutralized by 50 mL 2 N HCl. Find the molecular weight of the base.** **[2]**

➢ Weight of base = 5 g

Acidity = 2

Given,

50 mL of 2N HCl is completely neutralized by 5 g of a base.

i.e. 100 mL of 1N HCl is completely neutralized by 5 g of a base.

1 mL 1N HCl is completely neutralized by $\frac{5}{100}$ g of a base.

1000 mL 1 N HCl is completely neutralized by $\frac{5}{100} \times 1000$ g of a base = 50g of a base

Equivalent weight of base = 50

Molecular weight of the base = Equivalent weight × Acidity
= 50 × 2 = 100

Hence, molecular weight of base is 100 amu.

66. **2059 Q.No. 13** **What volume of decinormal solution of HCl is required to neutralize 25 mL NaOH solution containing 8 g NaOH in one litre solution?** **[2]**

➢ Given,

G/L of NaOH = 8 g/L

Equivalent weight of NaOH = 40

Normality of NaOH = ?

We know that,

$$\text{Normality (N)} = \frac{\frac{g}{L}}{\text{Equivalent weight}} = \frac{8}{40} = 0.2\text{ N}$$

Here,

Volume of NaOH (V_1) = 25 mL

Normality of NaOH (N_1) = 0.2 N

Volume of HCl (V_2) = ?

Normality of HCl (N_2) = 0.1 N (decinormal)

We know that,

$V_1N_1 = V_2N_2$

or, $V_2 = \frac{V_1N_1}{N_2} = \frac{25 \times 0.2}{0.1} = 50$ mL

Hence, 50 mL of decinormal solution of HCl is required to neutralize 25 mL of NaOH containing 8 g NaOH in one litre solution.

67. **2059 Q.No. 26** **x g of a metal (Equivalent weight = 12) was completely dissolved in 100 cc of $\frac{N}{2}$ HCl. The volume was then made up to 500 cc. 25 cc of this diluted acid required 17.5 cc $\frac{N}{10}$ NaOH for complete neutralization. Find the value of x.** **[5]**

➢ Please refer to **2076 Set C Q.No. 23**

68. **2058 Q.No. 13** **x g of $CaCO_3$ reacts completely with 20 mL of 1M HCl. Calculate the value of x.** **[2]**

➢ Given,

1M HCl = 1N HCl

So, 20 mL of 1M HCl = 20 mL of 1N HCl

Equivalent weight of $CaCO_3 = \frac{40 + 12 + 48}{2} = 50$

We know that,

1 g equivalent weight of acid = 1 g equivalent weight of base

or, 1000 mL of 1N HCl = 50 g equivalent weight of $CaCO_3$

or, 20 mL of 1N HCl = $\frac{50}{1000} \times 20 = 1$ g equivalent weight of $CaCO_3$

Therefore, the value of x = 1 g

69. **2057 Q.No. 13** **What volume of water must be added to 40 mL of 0.25 N acid solutions in order to make it exactly decinormal?** **[2]**

➢ **Initial condition**

Volume of acid (V_1) = 40 mL

Normality of acid (N_1) = 0.25 N

Let, x mL of water is added to 40 mL of 0.25 N acid to make decinormal i.e. 0.1 N

Final condition

Volume of acid solution (V_2) = (x + 40) mL

Normality of acid solution (N_2) = 0.1 N

We know from normality equation

$V_1N_1 = V_2N_2$

or, 40 x 0.25 = (x + 40) x 0.1

or, 10 = 0.1 x + 4

or, (10 – 4) = 0.1 x

or, 6 = 0.1 x

or, $x = \frac{6}{0.1} = 60$ mL

Hence, 60 mL of water is added to make decinormal solution.

70. **2057 Q.No. 30 (a) Define molar solution, end point and indicator. Calculate the molarity of 5% H_2SO_4 solution. [5]**

Molar solution: A solution containing one mole of solute present in one litre of solution is called molar solution.

End point: The point in a titration at which the reaction between two solutions is complete as shown by the indicator. End point is also known as equivalent point or neutral point where an acid solution is just neutralized by a basic solution in titration.

Indicator: Indicator is a chemical substance which indicates the end point or neutral point of the reaction between two solutions by changing its colour with the change of the pH of a solution near the equivalent point.

Numerical:

Given,

100 cc of H_2SO_4 solution contains 5 g H_2SO_4

1cc of H_2SO_4 solution contains $\frac{5}{100}$

1000 cc of H_2SO_4 solution contains $\frac{5}{100} \times 1000$

= 50 g of H_2SO_4

i.e. 50 g of H_2SO_4 is present in 1 litre.

So, g / L = 50

Now,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}} = \frac{50}{98} = 0.5 \text{ M}$$

Hence, molarity of 5% H_2SO_4 solution is 0.5 M.

71. **2057 Q.No. 30 (b) 7.5 g of a dibasic acid dissolved in water and the solution made up to 250 cc. 25 cc of this acid requires 16.3 cc 1 N NaOH for complete neutralisation. Calculate the molecular weight of the acid.**

Weight of the acid = 7.5 g

Given, 7.5 g of the acid is present in 250 cc of its solution.

Now,

Volume of diluted acid solution V_1 = 25 cc

Strength of diluted acid solution S_1 = ?

Volume of NaOH consumed (V_2) = 16.3 cc

Strength of NaOH (S_2) = 1N

We know that,

$V_1S_1 = V_2S_2$

$25 \times S_1 = 16.3 \times 1N$

or, $S_1 = \frac{16.3}{25} = 0.652N$

So, the strength of 25 cc acid solution = 0.652N

Since, 25 cc of acid solution is taken from 250 cc acid solution which contains 7.5 g dibasic acid.

So, the strength of the whole acid solution i.e. 250 cc = 0.652 N

We know that,

Normality = molarity × basicity

$$\text{Molarity} = \frac{\text{Normality}}{\text{Basicity}} = \frac{0.652}{2}$$

So, molarity = 0.326 M

Here,

250 cc acid solutions contain 7.5 g acid.

1000 cc acid solution contains $\frac{7.5}{250} \times 1000$ = 30g i.e. 30 g / L

So, g / litre = 30

We know that,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}}$$

$$\text{Molecular weight} = \frac{\frac{g}{L}}{\text{Molarity}} = \frac{30}{0.326} = 92.02$$

So, the molecular weight of the dibasic acid = 92.02 amu.

72. **2056 Q.No. 21 100 mL of 0.1 M HCl is mixed with 50 mL of 0.1 M KOH. Calculate the concentration of acid in terms of g / litre in the resulting solution. [5]**

For HCl

Volume of acid (V_a) = 100 mL

Molarity of acid (M_a) = 0.1 M

Basicity of HCl is 1

So, Normality of acid (N_a) = 0.1 N

For KOH

Volume of base (V_b) = 50 mL

Molarity of base (M_b) = 0.1 M

Acidity of KOH is 1

So, Normality of base (N_b) = 0.1 N

Final i.e. resulting volume of solution (V_f) = (100 + 50) = 150 mL

Final normality of resulting solution (N_f) = ?

The concentration of acid in terms of g/L of resulting solution = ?

We know that, equal volume of acid neutralize equal volume of base

$(V_a \times N_a) - (V_b \times N_b) = V_f \times N_f$

or, $(100 \times 0.1) - (50 \times 0.1) = 150 \times N_f$

or, $(10 - 5) = 150 \times N_f$

or, $5 = 150 \times N_f$

or, $N_f = \frac{5}{150} = 0.033$ N

Equivalent wt. of HCl = 36.5

And g/L = Normality × Equivalent weight = 0.033 × 36.5 = 1.2045 g/L.

Hence, the concentration of resulting acid solution in terms of g/L is 1.2045 g/L.

73. **2055 Q.No. 1 Find the equivalent weight of H_3PO_4 in the reaction**

$Ca(OH)_2 + H_3PO_4 \longrightarrow CaHPO_4 + 2H_2O$. [2]

Here, two H-atom is replaced by 2 OH⁻

$$\text{So, Equivalent weight of } H_2PO_4 = \frac{\text{Molecular weight of } H_3PO_4}{\text{No. of H-atom replaced}} = \frac{3 + 31 + 64}{2} = 49$$

Hence, equivalent weight of H_3PO_4 = 49

74. **2055 Q.No. 21** **20 mL of a sulphuric acid solution neutralizes 0.265 g of Na_2CO_3. Calculate the normality of the acid solution.** **[5]**

Given,

Volume of H_2SO_4 = 20 mL = 0.02 litre.

Normality of H_2SO_4 = ?

Wt. of Na_2CO_3 = 0.265 g

We know from normality equation,

Volume of H_2SO_4 × Normality of H_2SO_4 = Volume of Na_2CO_3 × Normality of Na_2CO_3

or, 0.02 litre × Normality of H_2SO_4 = Volume of Na_2CO_3 in litre × $\frac{\text{No. of gram - equivalent of } Na_2CO_3}{\text{Volume of } Na_2CO_3 \text{ in litre}}$

or, 0.02 litre × Normality of H_2SO_4 = No. of gram equivalent of Na_2CO_3

or, 0.02 litre × Normality of H_2SO_4 = $\frac{\text{Weight of } Na_2CO_3}{\text{Equivalent weight of } Na_2CO_3}$

or, 0.02 litre × Normality of H_2SO_4 = $\frac{0.265}{53}$

or, 0.02 litre × Normality of H_2SO_4 = 0.005

or, Normality of H_2SO_4 = $\frac{0.005}{0.02}$

or, Normality of H_2SO_4 = 0.25 N

Hence, the normality of H_2SO_4 solution is 0.25N.

75. **2054 Q.No. 27** **X g of magnesium (equivalent weight = 12) reacts with 20 mL of N (f = 0.95) acid. Calculate the weight of X.** **[5]**

Given,

Equivalent weight of Mg = 12

Volume of acid = 20 mL

Normality = 1N

Normality factor = 0.95

Actual normality of acid = normality × normality factor = 1N × 0.95 = 0.95N

We know that,

1000 mL of 1 N acid completely reacts with 12 g of magnesium

or, 20 mL of 1N acid completely reacts with $\frac{12}{1000} \times 20$ g of magnesium

or, 20 mL of 0.95N completely reacts with $\frac{12}{1000} \times 20 \times 0.95$ g of magnesium

= 0.228 g of Mg

Therefore, the value of X is 0.228 g.

76. **2053 Q.No. 19** **25 cc of an alkali solution is mixed with 8 cc of 0.75 N acid solution and for complete neutralization, it further requires 15 cc of 0.8 N acid solution. Find the strength of the given alkali solution.** **[2]**

Given,

Volume of alkali (V_b) = 25 cc

Normality of alkali (N_b) = ?

For 1st acid

Volume of acid (Va_1) = 8 cc

Normality of acid (Na_1) = 0.75 N

For 2nd acid

Volume of acid (Va_2) = 15 cc

Normality of acid (Na_2) = 0.8 N

We know from normality equation,

$V_b \times N_b = (Va_1 \times Na_1) + (Va_2 \times Na_2)$

or, $25 \times N_b = (8 \times 0.75) + (15 \times 0.8)$

or, $25 \times N_b = 6 + 12$

or, $N_b = \frac{18}{25} = 0.72$ N

Hence, the normality of alkali solution is 0.72 N.

77. **2052 Q.No. 19** **If 20 mL of 0.5 N NaOH is mixed with 30 mL of 0.3 N HCl, is the resulting solution acidic or basic? Calculate the normality with respect to the acidic or basic final solution.** **[2]**

Given,

20 mL of 0.5 N NaOH = (20 × 0.5) mL 1 N NaOH = 10 mL 1 N NaOH

And 30 mL of 0.3 N HCl = (30 × 0.3) mL 1 N HCl = 9 mL 1 N HCl

We know that,

Equal volume of acid neutralizes equal volume of base, if acid and base have the same normality. So, 9 mL of 1 N HCl neutralize 9 mL of 1 N NaOH. Thus, 1 mL of base is left unreacted and the solution is basic.

Normality of resulting solution;

Volume of acid left (V_1) = 1 mL

Normality of acid (N_1) = 1 N

Final volume of solution (V_2) = (20 + 30) = 50 mL

Normality of solution (N_2) = ?

From normality equation,

$V_1N_1 = V_2N_2$

or, $N_2 = \frac{V_1N_1}{V_2}$

or, $N_2 = \frac{1 \times 1}{50} = 0.02$ N

Hence, the normality of resulting basic solution is 0.02 N.

WRITE SHORT NOTES ON [5 MARKS]

78. **2069 Supp. Set B Q.No. 33 c** **2069 (Set B) Q.No. 33d** **Selection of indictors in acid base titration.** **[5]**

Please refer to **2064 Q.No. 30(ii)**

□□□

$$\frac{\left((0.599) \times 10^{-2}\right)^2 - \left(0.938 \times 10^{-2}\right)^2}{4 \times 10 \left(5890 \times 10^{-10}\right)}$$

Unit 3

Ionic Equilibrium

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 3 Find the pH of 1×10^{-5} N H_2SO_4.**

Given, normality of $H_2SO_4 = 1\times10^{-5}$ N

Basicity of $H_2SO_4 = 2$

We know that,

$$\text{Molarity (M)} = \frac{\text{Normality (N)}}{\text{Basicity of acid}} = \frac{1\times10^{-5}}{2} = 5\times10^{-6}\ \text{M}$$

H_2SO_4 ionises as

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

1 M 2 M

5×10^{-6} M 1×10^{-5} M

So, $[H^+] = 1\times10^{-5}$ M

We know that,

$pH = -\log[H^+] = -\log[1\times10^{-5}] = 5$

Hence, pH of 1×10^{-5} N H_2SO_4 is 5

2. **2076 Set C Q.No. 3 Write the conjugate acid and base of NH_3.**

The conjugate of acid of NH_3 is NH_4^+ ion which is shown by the reaction.

$$\underset{\text{Base}}{NH_3} + \underset{\text{acid}}{H_2O} \longrightarrow \underset{\text{conjugate acid}}{NH_4^+} + \underset{\text{conjugate base}}{OH^-}$$

Similarly, the conjugate base of NH_3 is NH_2^- which is shown by the reaction.

$$\underset{\text{Base}}{NH_3} + \underset{\text{acid}}{NH_3} \longrightarrow \underset{\text{conjugate acid}}{NH_4^+} + \underset{\text{conjugate base}}{NH_2^-}$$

3. **2075 GIE Q.No. 3 Is the solution acidic basic or neutral in which concentration of hydro 3.33×10^{-10} mol L^{-1}?**

The concentration of OH^- ion $= 3.33\times10^{-10}$ mol L^{-1}

pH = ?

We know that

$pOH = -\log[OH^-] = -\log[3.33\times10^{-10}] = 9.47$

$pH = 14 - 9.47 = 4.53$

The pH of aqueous solution is less than 7. So, the aqueous solution is acidic in nat

4. **2075 Set A Q.No. 3 Is the solution acidic, basic or neutral in which the hydrogen ion concen 3×10^{-5} molL^{-1}?**

Given,

The concentration of $H^+ = 3\times10^{-5}$ mol L^{-1}

pH = ?

We know that,

$pH = -\log[H^+] = -\log[3\times10^{-5}] = 4.52$

The pH of aqueous solution is less than 7. So, the aqueous solution is acidic in nature.

5. **2075 Set B Q.No. 3 Calculate the pH of the solution by dissolving 1 g of NaOH in 1 litre of its solution.** [2]

Given,

The concentration of NaOH = 1 g/L

Molecular weight of NaOH = (23 + 16 + 1) = 40

We know that,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}} = \frac{1}{40} = 0.025\ \text{M}$$

Now,

$NaOH \rightleftharpoons Na^+ + OH^-$

0.025 M 0.025 M 0.025 M

$p^{OH} = -\log[OH^-] = -\log[0.025] = 1.60$

We know that,

$p^H = 14 - p^{OH} = (14 - 1.6) = 12.4$

Hence, the pH of 1g/L NaOH solution is 12.4.

6. **2074 Supp. Q.No. 3 Is an aqueous solution containing hydroxyl ion concentration 3.33×10^{-10} mol L^{-1} acidic, basic or neutral?** [2]

Please refer to 2075 GIE Q No. 3

7. **2074 Set A Q.No. 3 Is an aqueous solution containing hydrogen ion concentration 3×10^{-5} mol L^{-1} acidic, basic or neutral?** [2]

Please refer to 2075 Set A Q No. 3

8. **2074 Set B Q.No. 3 Is an aqueous solution containing hydroxyl ion concentration 3.33×10^{-1} mol L^{-1} acidic, basic or neutral?** [2]

Given,

The concentration of $[OH^-] = 3.33\times10^{-1}$ mol L^{-1}

pH = ?

We know that,

$pOH = -\log[OH^-] = -\log[3.33\times10^{-1}] = 0.477$

$pH = 14 - 0.477 = 13.52$

The pH of aqueous solution is more than 7. So, the aqueous solution is basic in nature.

9. **2073 Supp Q.No. 3 Define** [1+1]

   i. **Ionic product of water**
   ii. **pH of solution**

i. **Ionic product of water:** The product of the concentration of hydronium ion and hydroxyl ion in pure water is constant at particular temperature which is known as ionic product of water. It is denoted by K_w.

$Kw = 1.008\times10^{-14} = [H_3O^+][OH^-]$ at 25°C.

ii. **pH of solution:** The magnitude of negative power to which 10 must be raised to express the hydronium ion concentration is called pH of solution.

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

10. **2073 Set C Q.No. 3 State Ostwald's dilution law and mention its limitation.** [1+1]

According to the theory of electrolytic dissociation of an electrolyte, when dissolved in water undergoes spontaneous dissociation into +vely and -vely charged ions and in the case of a weak electrolyte like CH_3COOH, NH_4OH, etc. there exists a definite equilibrium between the unionized molecules of electrolyte and the ions present in solution at a given temperature. It is, therefore, to be expected that the law of mass action can be applied to this equilibrium. This application was first carried out by Ostwald and the result is known as Ostwald dilution law.

$\alpha = \sqrt{K.V}$ Where, V = dilution.

Limitations: Weak electrolyte obeys Ostwald's dilution law fairly well, but in the case of strong electrolyte it fails completely. In the case of strong electrolytes, the value of K far from remaining constant rapidly falls with dilution. This is due to the fact strong electrolyte are completely ionized at all dilutions .i.e. α for strong electrolyte is equal to 1 and therefore, it is expected from the equation $\alpha = \frac{\lambda v}{\lambda \alpha}$ that $\lambda v = \lambda \alpha$, but in practice it is not so. It means that the equation $\alpha = \frac{\lambda v}{\lambda \alpha}$ does not hold good for strong electrolyte. It is observed that the value of λv is lower than $\lambda \alpha$ even though $\alpha = 1$.

11. **2073 Set D Q.No. 3 Define:** **[1+1]**
    - **i. Degree of Ionization**
    - **ii. Ostwald's dilution law**

↘

i. **Degree of ionization:** *It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by* α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

ii. **Ostwald dilution law:** According to the theory of electrolytic dissociation of an electrolyte, when dissolved in water undergoes spontaneous dissociation into +vely and -vely charged ions and in the case of a weak electrolyte like CH_3COOH, NH_4OH, etc. there exists a definite equilibrium between the unionized molecules of electrolyte and the ions present in solution at a given temperature. It is, therefore, to be expected that the law of mass action can be applied to this equilibrium. This application was first carried out by Ostwald and the result is known as Ostwald dilution law.

12. **2072 Supp. Q.No. 3 What are the limitation of Lewis acid and base?** **[1+1]**

↘ Following are the limitation of Lewis acid and base:

i. This concept cannot tell anything about the strength of acid and base.

ii. This concept is unable to explain the catalytic activity and amphoteric nature of several compounds.

iii. This concept does not consider about ionization process of acid and base.

iv. Relative strength of acid and base are not quantitatively estimated by this concept.

13. **2072 Set C Q.No. 3 Calculate the pH of 0.1 N H_2SO_4.** **[2]**

↘ Given, normality of $H_2SO_4 = 0.1N$

Basicity of $H_2SO_4 = 2$

We know that

Normality (N) = Molarity (M) × Basicity of acid

or, Molarity (M) = $\frac{\text{Normality (N)}}{\text{Basicity of acid}} = \frac{0.1}{2} = 0.05M$

H_2SO_4 ionizes as

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

1 M 2M

0.05M 0.1M

1 mole of H_2SO_4 produces 2 mole of H^+

0.05 mole of H_2SO_4 produces 0.1 mole of H^+

So, $[H^+] = 0.1$ M

We know that,

$$\begin{aligned} pH &= -\log[H^+] \\ &= -\log[0.1] \\ &= 1 \end{aligned}$$

Hence, pH of 0.1 N H_2SO_4 is 1.

14. **2072 Set D Q.No. 3 Define Lewis concept of base and point out its limitation.** **[1+1]**

↘ **Lewis Concept of Base:**

According to Lewis concept base is defined as the chemical species which donates a pair of electron to an acid.

Limitations:

a. This concept is unable to explain the catalytic activity and amphoteric nature of several compounds.

b. Relative strength of acid-base is not quantitatively estimated by this concept.

15. **2072 Set E Q.No. 3 Define Bronsted concept of acid and base with an example of each.** **[2]**

↘ **Bronsted acid:** An acid is a substance which can donate proton (H^+) to another substance. Example: HCl

Bronsted base: A base is a substance which can accept proton (H^+) from another substance. Example: NH_3

16. **2071 Supp. Q.No. 3 Give an example of each of the following**

i. Lewis acid	**ii. Lewis base**
iii. Acidic salt	**iv. Bronsted-Lowry acid**

[0.5×4]

↘ Example of i. Lewis acid = $AlCl_3$
ii. Lewis base = NH_3
iii. Acidic salt = $CuSO_4$
iv. Bronsted -Lowry acid = HCl

17. **2071 Set C Q.No. 3 Define the term:**
    - **a. Degree of ionization**
    - **b. Bronsted Lowry acid**

[2]

↘

a. **Degree of ionization:** It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

b. **Bronsted Lowry acid:** "Acid is a substance which has a tendency to donate proton while base is a substance which has a tendency to accept proton during chemical reactions." In other words we can say that 'an acid is a proton donor and a base is proton acceptor.'

18. **2071 Set D Q.No. 3 What happens when HCl gas is passed through a saturated solution of NaCl and why?** **[2]**

↘ When HCl gas is passed over a saturated solution of NaCl, the NaCl will precipitated out i.e. super saturated solution is formed. This is due to the increase in concentration of Cl^- by the ionization of HCl.

$$HCl \rightleftharpoons H^+ + Cl^-$$

We know that NaCl is also ionized

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

The ionic product of NaCl exceeds its solubility product due to common ion Cl^- which is formed form HCl that increase the concⁿ of Cl^- in the saturated solution.

K_{sp} of NaCl < ionic product of NaCl i.e. $[Na^+][Cl^-]$

19. **2070 Supp. Q.No. 3 State Ostwald's dilution law. What is its limitation?** [2]

Please refer to 2073 Set C Q.No. 3

20. **2070 Set D Q.No. 3 Define Lewis acid and Lewis base giving one example of each.** [2]

Lewis acid: The substance which has a capacity to accept an electron pair to form a co-ordinate bond is called Lewis acid. They are also called electrophiles i.e. electron loving.

Examples: $AlCl_3$, BF_3 etc.

Lewis base: The substance which has a capacity to donate an electron pair to form a co-ordinate bond is called Lewis base. They are also called nucleophiles i.e. nucleus loving.

Examples: NH_3, H_2O etc.

21. **2069 Supp. Q.No. 3 Define common ion effect.** [2]

If to a solution of an electrolyte (partially dissociated), another electrolyte (usually completely dissociated) consisting of an ion common is added, the dissociation of the former electrolyte is suppressed. This effect is called common ion effect.

22. **2069 (Set B) Q.No. 3 Write suitable examples to show water acts as Bronsted-Lowry acid and base.** [2]

According to Bronsted - Lowry concept acid is a proton donar and a base is a proton acceptor.

Water acts as both acid and base i.e. amphoteric is well shown by the following chemical reaction.

H_2O as base:

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

In this reaction H_2O acts as a base because it gains proton donated by acid.

H_2O as an acid:

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

In this reaction H_2O donates proton i.e. acts as an acid.

23. **2069 Supp. Set B Q.No. 3 Define pH of a solution and write the relation between pH and pOH.** [2]

pH is defined as the negative logarithm of the concentration of hydrogen ion.

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

pOH: Just like pH, pOH is used to indicate hydroxyl ion concentration of a solution.

It may be defined as the negative logarithm of hydroxyl ion concentration.

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

Relation between pH and pOH: $pH + pOH = 14$

24. **2067 Q.No. 14 Whether the aqueous solution of $CaCl_2$ is acidic basic or neutral? Given reason.** [2]

$CaCl_2$ is formed by the neutralization of strong acid HCl and weak base $Ca(OH)_2$. The strong acid HCl ionizes completely and weak base $Ca(OH)_2$ ionizes feebly.

$HCl \rightleftharpoons H^+ + Cl^-$

$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$

The concentration of H^+ in the solution is more than OH^-. So, the resulting solution is acidic in nature.

25. **2065 Q.No. 14 49 g of H_2SO_4 is present in 1000 mL of its solution. What is the pH of the solution?** [2]

Molecular weight of H_2SO_4 = 98

Weight of H_2SO_4 = 49 g

Volume of H_2SO_4 = 1000 mL = 1 litre

$$\text{Molarity} = \frac{g/L}{\text{Molecular weight}} = \frac{49}{98} = 0.5\ M$$

H_2SO_4 ionizes as

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

1 M   2M

0.5M   1M

1mole of H_2SO_4 produces 2 mole of H^+

0.5 mole of H_2SO_4 produces (2 × 0.5) = 1 mole

So, $[H^+]$ = 1M

We know that,

$pH = -\log[H^+] = -\log 1 = 0$

So, pH of solution = 0

26. **2064 Q.No. 15(i) Write the conjugate acid and conjugate base of NH_3.** [1]

Please refer to 2076 Set C Q.No. 3

27. **2064 Q.No. 15(ii) Predict whether the aqueous solution of $CuSO_4$ acidic, basic or neutral.** [1]

Aqueous solution of $CuSO_4$ is acidic in nature. This is due to the cationic hydrolysis and produce large concentration of H^+ ion in aqueous solution.

Molecular equation:

$CuSO_4 + 2H_2O \longrightarrow Cu(OH)_2 + H_2SO_4$

Ionic equation:

$Cu^{++} + SO_4^{--} + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + SO_4^{--}$

Net ionic equation:

$Cu^{++} + SO_4^{--} + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + SO_4^{--}$.

$Cu^{++} + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+$.

H_2SO_4 is strong acid ionizes completely and $Cu(OH)_2$ is weak base ionizes partially. So, the concentration of H^+ ion is more in solution and the resulting solution is acidic in nature.

28. **2062 Q.No. 18 Explain the fact that the aqueous solution of sodium carbonate is basic, while the aqueous solution of sodium chloride is neutral.** [2]

When strong base i.e. NaOH and weak acid i.e. H_2CO_3 is reacted then Na_2CO_3 is formed. Strong base NaOH ionizes completely but weak acid H_2CO_3 ionizes feebly.

$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$

$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{--}$

The concentration of OH^- in the solution is more than H^+. So, the resulting solution is basic in nature.

Aqueous solution of sodium chloride is neutral because it is formed by the neutralization of strong acid HCl and strong base NaOH.

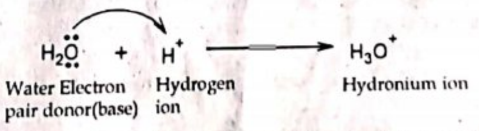
$NaOH + HCl \longrightarrow NaCl + H_2O$

The solution having same number of H^+ ion and OH^- ion hence the solution is neutral.

29. **2062 Q.No. 15 Water is a Lewis base as well as a Bronsted acid. Explain.** [2]

According to Lewis concept base is electron pair donor. Water behaves as base because it can donate electron pair present on O-atom to electron deficient centre or to an acid.

Example:



According to Bronsted concept, acid is proton donor while base is proton acceptor. Water acts as an acid because it donates a proton to the base.

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

Thus, water acts as both acid as well as base.

30. **2061 Q.No. 15** **Define Lewis acid and Lewis base. Give one example of each.** **[2]**

➘ **Lewis Acid**: Any species i.e. ion, group or molecules which is capable of accepting lone pair of electrons resulting in the formation of co-ordinate bond is known as Lewis acid. Example: $AlCl_3$, BF_3, SO_3 etc.

Lewis base: The species which is capable of donating a pair of electrons is known as Lewis base. Example: NH_3, RNH_2 etc.

31. **2060 Q.No. 14** **Calculate the pH of an aqueous solution containing 10^{-7} moles of NaOH per litre.** **[2]**

➘ Given, the molarity i.e. moles/L of NaOH = 10^{-7}M

NaOH ionizes as

$$NaOH \rightleftharpoons Na^+ + OH^-$$

10^{-7}M　　10^{-7}M　　10^{-7}M

The concentration of $[OH^-] = 10^{-7}$M

Water also ionizes as

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

Due to the auto ionization of H_2O, 10^{-7}M of H^+ ion and 10^{-7}M of OH^- ion are formed. The concentration of OH^- ion formed by the auto ionization of H_2O cannot be neglected.

Total concentration of $[OH^-] = (10^{-7}M + 10^{-7}M) = 2 \times 10^{-7}$M

We know that,

$pOH = -\log[OH^-] = -\log[2 \times 10^{-7}] = 6.698$

$pH = 14 - pOH = (14 - 6.698) = 7.302$

Therefore, the pH of aqueous solution of NaOH = 7.302

32. **2059 Q.No. 15** **Why is aqueous solution of $FeCl_3$ acidic?** **[2]**

➘ When $FeCl_3$ is dissolved in water, it gets dissociated into Fe^{+++} and Cl^- ions as follows:

$$FeCl_3 \rightleftharpoons Fe^{+++} + 3Cl^-$$

H_2O undergoes ionization as

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

Ferric ion i.e. Fe^{+++} combines with hydroxide ion to give ferric hydroxide.

$$Fe^{+++} + 3OH^- \longrightarrow Fe(OH)_3$$

Similarly, H^+ ion combines with Cl^- to give HCl which is highly ionizable.

$$H^+ + Cl^- \longrightarrow HCl$$

Thus the concentration of H^+ ion is more than the concentration of OH^- and the resulting solution is acidic in nature.

33. **2058 Q.No. 16** **Define Lewis acid and base giving one example from each.** **[2]**

➘ Please refer to to 2061 Q.No. 15

34. **2057 Q.No. 15** **What happens when dry HCl gas is passed through saturated solution of sodium chloride?** **[2]**

➘ Please refer to 2071 Set D Q.No. 3

35. **2057 Q.No. 16** **Why is aqueous Na_2CO_3 basic?** **[2]**

➘ When strong base i.e. NaOH and weak acid i.e. H_2CO_3 is reacted then Na_2CO_3 is formed. Strong base NaOH ionizes completely but weak acid H_2CO_3 ionizes feebly.

$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{--}$$

The concentration of OH^- in the solution is more than H^+. So, the resulting solution is basic in nature.

36. **2055 Q.No. 2** **10^{-2} mole of KOH is dissolved in 10 litres of water. What will be the pH of the solution?[2]**

➘ Given,

No. of moles of KOH = 10^{-2} moles

Volume of water = 10 litres

pH of KOH solution = ?

We know that,

$$\text{Molarity (M) of KOH} = \frac{\text{No. of moles}}{\text{Volume in litre}} = \frac{10^{-2}}{10} = 10^{-3}M$$

KOH ionizes as

$$KOH \rightleftharpoons K^+ + OH^-$$

10^{-3}M　　　　10^{-3}M

We know that,

$pOH = -\log[OH^-] = -\log[10^{-3}] = 3$

$pH = 14 - pOH = (14 - 3) = 11$

Therefore, the pH of aqueous solution of KOH = 11

37. **2055 Q.No. 4** **Explain why sodium chloride precipitates from a saturated salt solution when hydrogen chloride gas is passed into the solution.** **[2]**

➘ Please refer to 2071 Set D Q No. 3

38. **2054 Q.No. 2** **What will be the H^+ ion concentration of a solution having pH 5.5?** **[2]**

➘ Given,

pH of solution = 5.5

The concentration of $[H^+]$ = ?

We know that,

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

$[H^+] = \text{antilog}\,[-pH] = \text{antilog}\,[-5.5] = 3.16 \times 10^{-6}M$

Hence, the concentration of $[H^+] = 3.16 \times 10^{-6}M$

39. **2054 Q.No. 5** **What do you understand by equilibrium state in a reversible reaction?** **[2]**

➘ The condition in reversible reaction at which rate of forward reaction is equal to rate of backward reaction is called equilibrium state. At this state there is no change in concentration of reactant and-product with time.

40. **2054 Q.No. 8** **What will happen when HCl gas is passed over a saturated solution of NaCl, also explain the principle involved?** **[2]**

➘ Please refer to 2071 Set D Q.No. 3

SHORT ANSWER QUESTIONS [5 MARKS]

41. **2075 GIE Q.No. 25** **What is meant by Lewis acid and base? Point out it's limitations.** **[3+2]**

➘ **Bronsted and Lowry concepts:**

This theory of acids-bases is also known as "Proton-Transfer Theory". This theory was developed by J.N. Bronsted of Denmark and T.M. Lowry of England in 1923. According to this theory:

"Acid is a substance which has a tendency to donate proton while base is a substance which has a tendency to accept proton during chemical reactions." In other words we can say that 'an acid is a proton donor and a base is proton acceptor.'

Therefore, they may be represented through the following general equation.

$$\text{Acid} \rightleftharpoons \underset{\text{Proton}}{H^+} + \text{Base}$$

Bronsted acids: It may be molecules, cations or anions, which can donate proton in aqueous solution.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

Bronsted bases: Like Bronsted acids, it may be in form of molecules, cations and anion. They can accept proton in aqueous solution.

$NH_3 + H^+ \longrightarrow NH_4^+$

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

Merits: This concept explains the acid-basic nature of a large number of substance.

This concept is not dependent on the solvent.

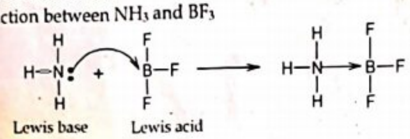
This concept is also applicable to non-aqueous solvent like liquid NH_3, liquid SO_2, HF etc.

Limitations: We know that this concept of acid-base is based on the principle of proton transfer. It is true that most of the acids are protonic but not all. This concept can not explain the acidic nature of non-protonic acids.

This concept fails to explain the acid-base reaction of non-protonic substance like CO_2, SO_2, BF_3, $AlCl_3$ etc.

Lewis Concept: In 1923, G.N. Lewis gave a broader definition of acids-bases. According to him"an acid is defined as a substance which can accept a pair of electrons where as a base is a substance which can donate a pair of electrons during chemical reactions." From the above definition, it is clear that there will be a co-ordinate bond between acid and base during neutralization.

For example: reaction between NH_3 and BF_3



Some example of Lewis acids:

$H^+, Ag^+, Cu^{++}, Fe^{3+}, Al^{3+}$, $AlCl_3, ZnCl_2, SnCl_4, PCl_5, SiCl_4$ etc.

Some example of Lewis bases:

$NH_3, H_2O, OH^-, X^-(Cl^-, Br^-, I^-), C_2H_5OH, CH_3NH_2$ etc.

Merits: Lewis concept of acid-base is as up-to-date concept of acid-base. It is more general than the Bronsted Lowry.

This concept explains the non-protic reactions which were not explained by Bronsted Lowry.

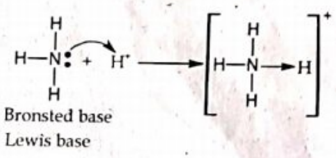
Acidic nature of non-metal oxide and basic nature of metal oxide can be explained by this concept.

Limitations: This concept is unable to explain the catalytic activity and amphoteric nature of several compounds.

Relative strength of acids-bases is not quantitatively estimated by this concept.

42. 2075 Set A Q.No. 25 All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids. Explain. If 80 mL of 0.01 M $AgNO_3$ are mixed with 20 mL of 0.001 M NaCl solution. Will any AgCl precipitate or not? [Ksp for AgCl = 1.5×10^{-10}] [1+4]

All Bronsted bases are also Lewis bases: According to Bronsted concept, the base is a substance which accepts a proton. According to Lewis concept, a base is a substance which can donate a pair of electrons. Any substance which can donate a pair of an electron can easily accept a proton.



All Bronsted acids are not Lewis acids: According to Bronsted concept, an acid is a substance that can donate a proton (H^+). According to Lewis concept an acid is any substance which can accept a pair of electrons from another substance to form a co-ordinate bond. Example: HCl, H_2SO_4 are Bronsted acids because they can donate protons but they cannot accept a pair of electrons to form a co-ordinate bond. Therefore, they are not Lewis acids. Thus, all Bronsted acids are not Lewis acids.

Numerical:

The reaction that would cause precipitation is

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

Now

The concentration of $[Ag^+] = 0.01 \times \frac{80}{80+20} = 0.008$ M

The concentration of $[Cl^-] = 0.001 \times \frac{20}{20+80} = 0.0002$ M

We have

$Q = [Ag^+][Cl^-] = [0.008][0.0002] = 0.0000016 = 1.6 \times 10^{-6}$

Ksp of AgCl = 1.5×10^{-10} (Given)

Q > Ksp So, precipitation will occur.

43. 2072 Set E Q.No. 27 Define the terms: [1+1+3]

i. Degree of ionization.

ii. Ostwald's dilution law.

Calculate the pH of a saturated solution of $Mg(OH)_2$, Ksp for $Mg(OH)_2$ is 8.9×10^{-12}.

i. **Degree of ionization:** It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

ii. **Ostwald dilution law:** According to the theory of electrolytic dissociation of an electrolyte, when dissolved in water undergoes spontaneous dissociation into +vely and -vely charged ions and in the case of a weak electrolyte like CH_3COOH, NH_4OH, etc. there exists a definite equilibrium between the unionized molecules of electrolyte and the ions present in solution at a given temperature. It is, therefore, to be expected that the law of mass action can be applied to this equilibrium. This application was first carried out by Ostwald and the result is known as Ostwald dilution law.

$\alpha = \sqrt{K.V}$ Where, V = dilution.

Numerical:

The solubility product of $Mg(OH)_2$ (Ksp) = 8.9×10^{-12}

The ionization of $Mg(OH)_2$ is

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

The concentration of $[Mg^{++}]$ and $[OH^-]$ is x $molL^{-1}$

We know that,

Solubility product (Ksp) of $Mg(OH)_2 = [Mg^{++}][OH^-]^2$

$8.9 \times 10^{-12} = x.x^2 = x^3$

Or, $x = \sqrt[3]{8.9 \times 10^{-12}} = 2.072 \times 10^{-4}$

Hence, the concentration of $[OH^-] = 2 \times 2.072 \times 10^{-4}\ molL^{-1}$

$= 4.144 \times 10^{-4}\ molL^{-1}$

We know that,

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

$= -\log[4.144 \times 10^{-4}] = 3.38$

Again, pH + pOH = 14

Or, pH = 14 - pOH = 14 - 3.38 = 10.62

Hence, pH of saturated $Mg(OH)_2$ is 10.62.

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44. **2070 Supp. Q.No. 24** **200 mL of an aqueous solution of HCl (pH = 2) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12). What will be the pH of resulting mixture solution?** **[5]**

For HCl,

Volume of HCl (V_A) = 200 mL

pH = 2

We know that,

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

$[H^+] = \text{antilog}[-pH]$

$[H^+] = \text{antilog}[-2] = 0.01M = M_A$

For NaOH,

Volume of NaOH (V_B) = 300 mL

pH = 12

We know that,

$pH + pOH = 14$

$pOH = 14 - 12 = 2$

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

$[OH^-] = \text{antilog}[-pOH] = \text{antilog}[-2] = 0.01\ M = M_B$

For mixture,

Volume of mixture (V_{mix}) = (200 + 300) = 500 mL

pH = ?

We know that,

$M_BV_B - M_AV_A = M_{mix}V_{mix}$

or, $(0.01 \times 200) - (0.01 \times 300) = M_{mix}\ 500$

or, $M_{mix} = \dfrac{(0.01 \times 300) - (0.01 \times 200)}{500} = \dfrac{3-2}{500} = \dfrac{1}{500} = 2 \times 10^{-3}\ M$

Hence, the molarity of NaOH in the mixture is 2×10^{-3} M

NaOH ionizes as

$$\begin{array}{lccc} NaOH & \longrightarrow Na^+ & + & OH^- \\ 2 \times 10^{-3}\ M & 2 \times 10^{-3}\ M & & 2 \times 10^{-3}\ M \end{array}$$

Concentration of $[OH^-] = 2 \times 10^{-3}$ M

We know that,

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

$[H^+] = \dfrac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}M$

We have,

$pH = -\log[H^+] = -\log[5 \times 10^{-12}M] = 11.30$

Hence, the pH of the resulting solution is 11.30.

---

45. **2069 (Set B) Q.No. 28** **Define degree of ionization. Calculate the pH of 1.0 M solution of acetic acid. To what volume one litre of this solution be diluted so that the pH of the solution that is formed will be twice of original value [Ka = 1.8×10^{-5}]?** **[5]**

Degree of ionization: It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

Numerical:

Given,

Molarity of acetic acid i.e. CH_3COOH = 1.0M = 1.0 N

Ionization constant of acetic acid (ka) = 1.8×10^{-5}

pH of acetic acid = ?

Volume of solution (V_1) = 1 litre = 1000 mL

Volume of solution (V_2) at which pH becomes double = ?

$[H^+]$ concentration of Acetic acid = ?

CH_3COOH ionizes as

$$\begin{array}{lccc} & CH_3COOH \rightleftharpoons & CH_3COO^- & + & H^+ \\ \text{Initially} & C & 0 & & 0 \\ & (C - C\alpha) & C\alpha & & C\alpha \end{array}$$

We know that,

From Ostwald's dilution law, $ka = \alpha^2C$

$\alpha = \sqrt{\dfrac{Ka}{C}} = \sqrt{\dfrac{1.8 \times 10^{-5}}{1.0}} = \sqrt{1.8 \times 10^{-5}} = 4.24 \times 10^{-3}$

Now, $[H^+] = C\alpha = 1.0 \times 4.24 \times 10^{-3} = 4.24 \times 10^{-3}\ M$

We know that,

$pH = -\log[H^+] = -\log[4.24 \times 10^{-3}\ M] = 2.37$

According to the questions, pH of solution becomes double then pH = 2 × 2.37 = 4.74

To calculate $[H^+]$ ion concentration,

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

$[H^+] = \text{antilog}[-pH] = \text{antilog}[-4.74] = 1.819 \times 10^{-5}M$

Hence, the molarity of acetic acid = $1.819 \times 10^{-5}M$

Acetic acid is monobasic acid. So, the molarity is equal to the normality of acid.

Normality of acetic acid = $1.819 \times 10^{-5}N$

Here,

$N_1 = 4.24 \times 10^{-3}N$ $\qquad N_2 = 1.819 \times 10^{-5}N$

$V_1 = 1000\ mL$ $\qquad V_2 = ?$

From normality equation,

$V_1N_1 = V_2N_2$

$V_2 = \dfrac{V_1N_1}{N_2} = \dfrac{1000 \times 4.24 \times 10^{-3}}{1.819 \times 10^{-5}} = 233095\ mL = 233.095\ litre$

Hence, the volume of solution is 233.095 litre.

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46. **2065 Q.No. 30 a** **Define the following terms and give one example of each:** **[5]**
   i. **Bronsted Lowry acid and base.**
   ii. **Lewis acid and base.**

i. **According to Bronsted Lowry concept:**

Acid: Acid is substance which has a tendency to donate proton during chemical reaction. It may be molecules, cations or anions, which can donate proton in aqueous solution.

Example: HCl

$HCl \longrightarrow \underset{\text{Proton}}{H^+} + Cl^-$

Base: Base is substance which has a tendency to accept proton during chemical reaction. It may be molecules, cations or anions, which can accept proton in aqueous solution.

Example: NH_3

$NH_3 + \underset{\text{Proton}}{H^+} \longrightarrow NH_4^+$

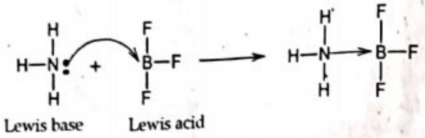
ii. According to Lewis concept:

Acid: Acid is a substance which can accept a pair of electrons during chemical reaction.

Example: BF_3

Base: Base is a substance which can donate a pair of electrons during chemical reaction.

Example: NH_3



47. **2062 Q.No. 26 Explain Bronsted and Lewis concepts of acid and base with suitable examples.** **[5]**

Please refer to 2075 GIE Q No. 25

48. **2062 Q.No. 30(a) Write a concise account of solubility product principle.** **[5]**

When a less soluble solute is added to a solvent, an equilibrium is established between the undissolved solute (solid phase) and its solute part which completely dissociates into ion.

$$AB\ (Solid) \xrightleftharpoons{Water} AB\ (Soluble\ part) \longrightarrow A^+ + B^-$$

The soluble part of AB makes the solution saturated at the temperature and pressure of experiment. Thus, the law of mass action can be applied in this case.

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

Now, since very little quality of solid AB has dissolved, the concentration of undissolved AB remains constant.

$\therefore$ $[A^+][B^-] = K[AB] = S$ (constant) or Ksp

Where, Ksp is called solubility product of AB. Thus, solubility product of a substance can be defined as follows:

The product of the ionic concentration of the ions present in saturated solution of an electrolyte at a given temperature is called solubility product of the electrolyte at that temperature.

Thus, in general, for an electrolyte A_xB_y dissociating to the following:

$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$

The solubility product of $A_xB_y = [A^{y+}]^x[B^{x-}]^y$

Since, solubility product of an electrolyte is constant a particular temperature and is equal to its ionic product in its saturated solution it can also be concluded that.

If ionic product < solubility product. The solution will remain unsaturated.

If ionic product = solubility product. The solution will remain saturated.

If ionic product > solubility product. The precipitation of the electrolyte will occur.

LONG ANSWER QUESTIONS [10 MARKS]

49. **2076 Set C Q.No. 32 State Ostwald's dilution law. What is the limitation of this law? Define the terms**

i. Ionic product of water **ii. Common ion effect**
iii. Degree of ionization **iv. pH value**

What will be the resultant pH when 200 mL of aqueous solution of HCl (pH = 2) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12)? **[1+1+1+1+1+1+4]**

Ostwald's dilution law: "Degree of ionization of an electrolyte is directly proportional to the square root of dilution."

Limitation: Ostwald's dilution law is only applicable for weak electrolyte. For strong electrolyte 1-α cannot be approximated as 1. This means, this law is not applicable for the strong electrolyte.

Define:

i. **Ionic product of water:** The product of the concentration of hydronium ion and hydroxyl ion in pure water is constant at particular temperature known as ionic product of water. It is denoted by K_w.

$K_w = 1.008 \times 10^{-14} = [H_3O^+][OH^-]$ at 25°C.

ii. **Common ion effect:** The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one ion common with the weak electrolyte is known as common ion effect.

iii. **Degree of dissociation:** It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α.

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

iv. **pH value of solution:** p^H of solution is defined as the magnitude of negative power to which 10 must be raised to express the hydronium ion concentration.

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

Numerical: Please refer to 2070 Supp. Q.No. 24

50. **2075 Set B Q.No. 30 How is a strong electrolyte differed from a weak electrolyte? Derive the mathematical equation for Ostwald's dilution law. Point out its limitation. Calculate pH of the solution obtained by mixing 150 mL of 0.2N HCl and 150 mL of 0.1 N NaOH solution.** **[2+3+1+4]**

Strong electrolyte ionizes almost completely in solution whereas weak electrolyte ionizes only to a small extent in solution. Strong electrolyte is completely dissociated at moderate concentration whereas weak electrolyte is not completely dissociated at moderate concentration. In the strong electrolyte, there are strong interionic attraction at moderate concentration but in weak electrolyte, there are not strong interionic attraction at higher concentration.

Derivation of Ostwald's dilution law:

Let us consider the ionization of a binary electrolyte AB in the solution of concentration C mol L^{-1}. Suppose the degree of ionization of electrolyte is α.

	$AB \rightleftharpoons$	A^+	+	B^-
Initial concⁿ	C	0		0
Change in concⁿ	- Cα	+Cα		+Cα
Concⁿ at Equilibrium	(C - Cα)	Cα		Cα

Applying the law of mass action at equilibrium state, the equilibrium constant of the electrolyte is given as:

$$K = \frac{[A^+][B^-]}{[AB]} \quad \text{... (i)}$$

Where, K = ionization constant of electrolyte

Substituting their concentration, we get

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

$$K = \frac{\alpha^2 C}{(1-\alpha)} \quad \text{... (ii)}$$

Equation (ii) is the mathematical equation for Ostwald's dilution law. For weak electrolyte, the degree of ionization is very small. Since, 1 - α ~1. Now equation (ii) becomes

$$K = \alpha^2 C \quad \text{... (iii)}$$

or, $\alpha^2 = \frac{K}{C}$

or, $\alpha = \sqrt{\frac{K}{C}}$ .... (iv)

We know that

Molar concentration (C) = $\frac{\text{No. of mole of solute (n)}}{\text{Volume of solution in litre (V)}}$

If one mole of solute is used to prepare V litre of solution then, $C = \frac{1}{V}$

Then, the equation (iii) becomes

$K = \frac{\alpha^2}{V(1-\alpha)}$ ... (v)

Taking $1 - \alpha = 1$, the equation (v) becomes

$K = \frac{\alpha^2}{V}$ ... (vi)

or, $\alpha = \sqrt{KV}$ ... (vii)

Equation (vii) reveals that the degree of ionization is directly proportional to the squa root of dilution.

Therefore, according to Ostwald's dilution law 'Degree of ionization of an electrolyte directly proportional to the square root of dilution'

Limitations:

Ostwald's dilution law is only applicable for weak electrolytes. Strong electrolyte ioniz almost completely. For strong electrolyte $1 - \alpha$ cannot be taken as 1. So, the equation as given above becomes $K = \frac{\alpha^2 C}{0}$ =Undetermined. This means, Ostwald's dilution law not applicable for strong electrolyte.

Numerical:

For HCl	For NaOH
$V_1 = 150$ mL	$V_2 = 150$ mL
$N_1 = 0.2$ N	$N_2 = 0.1$ N

Total volume of mixture $(V_m) = V_1 + V_2 = 150 + 150 = 300$ mL

Normality of resulting solution (N_m) = ?

We know that

$V_mN_m = V_1 \times N_1 - V_2 \times N_2$

or, $N_m = \frac{V_1 \times N_1 - V_2 \times N_2}{V_m} = \frac{150 \times 0.2 - 150 \times 0.1}{300} = 0.05$ N

In the question, 150 mL of 0.2 N HCl i.e. 300 mL of 0.1N HCl neutralizes 150 mL of 0.1 N NaOH solutions. 150 ml of 0.1 N HCl will remain in the solution. So, the solution is acidic.

Molarity of acidic solution = $\frac{\text{Normality}}{\text{Basicity}} = \frac{0.05}{1} = 0.05$ M

HCl ionizes as

$$\underset{0.05\ M}{HCl} \rightleftharpoons \underset{0.05\ M}{H^+} + Cl^-$$

We know that

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

$pH = -\log[0.05] = 1.30$

Hence, the pH of the resulting solution is 1.30.

51. 2073 Supp Q.No. 32 **State solubility product principle and common ion effect. What are its main applications? If the volume of 25 cm^3 of 0.05 M $Ba(NO_3)_2$ are mixed with 25 cm^3 of 0.02 M NaF. Will any BaF_2 precipitate? (Ksp of $BaF_2 = 1.7\times10^{-4}$ at 298K)** [2+4+4]

Solubility product principle: When a less soluble solute is added to a solvent, an equilibrium is established between the undissolved solute (solid phase) and its solute part which completely dissociates into ion.

$$AB\ (Solid) \xrightleftharpoons{Water} AB\ (Soluble\ part) \longrightarrow A^+ + B^-$$

The soluble part of AB makes the solution saturated at the temperature and pressure of experiment. Thus, the law of mass action can be applied in this case.

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

Now, since very little quality of solid AB has dissolved, the concentration of undissolved AB remains constant.

$\therefore [A^+][B^-] = K[AB] = S$ (constant) or Ksp

Where, Ksp is called solubility product of AB. Thus, solubility product of a substance can be defined as follows:

Common ion effect: The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one ion common with the weak electrolyte is known as common ion effect.

Application of solubility product principle and common ion effect:

Following are the some important application:

In the purification of NaCl: When HCl gas is passed in a saturated solution of impure NaCl, pure NaCl crystals precipitate out. This happens because $[Na^+]$ and $[Cl^-]$ are maximum in the saturated solution of NaCl. On bubbling HCl into it the concentration of Cl^- ion increases due to dissolution of HCl in solution. Hence, $[Na^+]$ $[Cl^-]$ becomes larger than the solubility product of NaCl. Hence, NaCl precipitates out. It must be noted that a substance precipitates from its solution when its ionic product exceeds its solubility product.

Precipitation of soap: When excess of NaCl is added to a solution of a soap which is RCOONa, the concentration of the common Na^+ ion increase too much so that $[RCOO^-]$ $[Na^+]$ becomes greater than solubility product of RCOONa (soap). Hence, soap precipitates out.

Precipitation of sulphides of group (II) in salt analysis: When H_2S gas is passed in an acidified solution of cupric salt, lead salt, Cd-salt, Bi-salt, Hg(ic) salt, stannous salt, As-salt and Sb-salt, their sulphides are precipitated because the product of the concentration of these metal ions and S^{--} ions exceeds the solubility product of CuS, PbS, CdS, Bi_2S_3, HgS, SnS, As_2S_3 and Sb_2S_3 respectively.

Precipitation of hydroxides of group (IIIA) in salt analysis: When NH_4Cl and NH_4OH solution are added to solution of a salt mixture containing Fe^{3+}, Cr^{3+}, Al^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} ions, only $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$ are precipitated in Group (IIIA) but those of Mg^{2+},Ni^{2+},Zn^{2+},Co^{2+},Mn^{2+} are not precipitated. This is because of the fact that ionic products exceed the solubility products of $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$, but ionic products do not exceed solubility product of $M(OH)_2$ Where, M = Ni,Co, Mn,Zn, Mg.

Numerical:

Volume before mixing = 25 cm^3

Volume after mixing = 50cm^3

The concentration of Ba^{2+} after mixing = $0.05 \times \frac{25}{50} = 2.5 \times 10^{-2}$ M

The concentration of F− after mixing = $0.02 \times \frac{25}{50} = 1.0 \times 10^{-2}$ M

The balanced equation is

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$$

Ionic product = $[Ba^{2+}][F^-]^2$

Ionic product = $2.5 \times 10^{-2} \times (1.0 \times 10^{-2})^2 = 2.5 \times 10^{-6}$

Ksp = 1.7×10^{-8} at 298 K. Since, ionic product is more than Ksp, precipitation will occur.

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52. **2073 Set C Q.No. 32 What is the common-ion effect? Explain its main applications. The solubi product constant (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 mL of saturated solution of $Ca(OH)_2$ mixed with an equal volume of 0.4 M NaOH. What mass of $Ca(OH)_2$ is precipitated out? [2+4**

Common ion effect: The suppression of degree of ionization of weak electrolyte by th addition of strong electrolyte having one ion common with the weak electrolyte known as common ion effect.

Application of common ion effect: Please refer to 2073 Supp Q.No. 32

Numerical:

The ionization of $Ca(OH)_2$ is represented as

$$\underset{S}{Ca(OH)_2} \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

$$\begin{aligned}\text{Ksp of } Ca(OH)_2 &= [Ca^{2+}][OH^-]^2\\ &= S \times [2S]^2\\ &= 4S^3\end{aligned}$$

$$\text{or, } S = \sqrt[3]{\frac{Ksp}{4}} = \sqrt[3]{\frac{4.42 \times 10^{-5}}{4}} = 2.227 \times 10^{-2}M$$

No. of moles of Ca^{2+} ions in 500 mL of the solution = $\frac{2.227 \times 10^{-2}}{2} = 0.011135M$

When 500 mL of saturated solution is mixed with 500 mL of 0.4M NaOH, the resultant volume is 1000 mL. The molarity of OH^- ions in the resultant solution becomes 0.2M.

Now, $[Ca^{2+}] = \frac{Ksp}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{0.2 \times 0.2} = 0.001105M$

No. of moles of Ca^{2+} ions or $Ca(OH)_2$ precipitated

$$\begin{aligned}&= \text{Initial conc}^n \text{ of } Ca^{2+} - \text{Final conc}^n \text{ of } Ca^{2+}\\ &= 0.011135 - 0.001105\\ &= 0.010245M\end{aligned}$$

Thus, the mass of $Ca(OH)_2$ precipitated = $0.010245 \times 74 = 0.75813$ g

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53. **2073 Set D Q.No. 32 State solubility product constant. What is the proper condition of precipitation of salt from its solution? Explain application of the solubility product principle and common ion effect. What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K? (given, solubility product (Ksp) for $CaSO_4 = 9.1 \times 10^{-6}$] [1+1+4+4]**

Solubility Product Constant

Solubility product constant is defined as the product of ionic concentration in saturated solution at constant temperature. It is denoted by K_{sp}.

Proper condition of precipitation of salt from its solution: If ionic product (Q) of salt > solubility product (Ksp) of that salt at a given temperature, then precipitation occurs. This solution is supersaturated solution.

Application of solubility product principle and common ion effect:

Please refer to 2073 Supp Q.No. 32

Numerical:

Given, Weight of calcium sulphate = 1 g

Solubility product of $CaSO_4$ (Ksp) = 9.1×10^{-6}

Volume of water required (V) = ?

$CaSO_4$ dissociates as

$$\begin{array}{llll} CaSO_4 & \rightleftharpoons & Ca^{++} + & SO_4^{--}\\ 1\text{ mol} & & 1\text{ mol} & 1\text{ mol}\\ S & & S & S\end{array}$$

We know that,

Solubility product constant (Ksp) = $[Ca^{++}][SO_4^{--}]$

Or, Ksp = $[S][S] = [S]^2$

Or, $[S] = \sqrt{Ksp} = \sqrt{9.1 \times 10^{-6}} = 3.0 \times 10^{-3}$ M

The molarity of $CaSO_4$ solution = 3.0×10^{-3} M

We know that,

g/L = Molarity × Molecular weight

or, g/L = $3.0 \times 10^{-3} \times 136$ [Molecular weight of $CaSO_4$ = 136]

or, g/L = 0.408 g/L

Thus,

0.408 g of $CaSO_4$ is dissolved in 1 L = 1000 mL water

1 g of $CaSO_4$ is dissolved in $\frac{1000}{0.408}$ mL water = 2.450×10^3 mL water

Hence, the volume of water is required to dissolve 1 g $CaSO_4$ = 2.450×10^3 mL

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54. **2072 Supp. Q.No. 32 State Ostwald's dilution law. What is the limitation of this law? Define the terms (i) ionic product of water (ii) common ion effect (iii) degree of ionisation (iv) pH value. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12)? [1+1+1+1+1+1+4]**

Ostwald's dilution law: According to the theory of electrolytic dissociation of an electrolyte, when dissolved in water undergoes spontaneous dissociation into +vely and -vely charged ions and in the case of a weak electrolyte like CH_3COOH, NH_4OH etc. there exists a definite equilibrium between the unionized molecules of electrolyte and the ions present in solution at a given temperature It is, therefore, to be expected that the law of mass action can be applied to this equilibrium. This application was first carried out by Ostwald and the result is known as Ostwald dilution law.

$\alpha = \sqrt{K.V}$ Where, V = dilution.

Limitations: Weak electrolyte obeys Ostwald's dilution law fairly well, but in the case of strong electrolyte it fails completely. In the case of strong electrolytes, the value of K far from remaining constant rapidly falls with dilution. This is due to the fact strong electrolyte are completely ionized at all dilutions .i.e. α for strong electrolyte is equal to 1 and therefore, it is expected from the equation $\alpha = \frac{\lambda v}{\lambda \alpha}$ that $\lambda v = \lambda \alpha$, but in practice it is not so. It means that the equation $\alpha = \frac{\lambda v}{\lambda \alpha}$ does not hold good for strong electrolyte. It is observed that the value of λv is lower than $\lambda \alpha$ even though $\alpha = 1$.

Define the terms:

i. **Ionic product of water:** The product of the concentration of hydronium ion and hydroxyl ion in pure water is constant at particular temperature known as ionic product of water. It is denoted by K_w.

$K_w = 1.008 \times 10^{-14} = [H_3O^+][OH^-]$ at 25°C.

ii. **Common ion effect:** The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one ion common with the weak electrolyte is known as common ion effect.

ii. **Degree of ionization:** It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

iv. **pH value:** p^H of solution is defined as the magnitude of negative power to which 10 must be raised to express the hydronium ion concentration.

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

Numerical: Please refer to 2070 Supp. Q.No. 24

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55. **2072 Set D Q.No. 30 What is meant by the terms:** **[2+4+2+2]**
   - i. **Common ion effect**
   - ii. **Solubility product constant (K_{sp})**

Explain the common ion effect and solubility product principle in qualitative salt analysis. What will be the resulting pH of a solution prepared by mixing 200 mL of aquous solution of HCl (pH = 2) with 300 mL of an aquous solution of NaOH (pH = 12).

i. **Common ion effect:** The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one ion common with the weak electrolyte is known as common ion effect.

ii. **Solubility Product Constant:** Solubility product constant is defined as the product of ionic concentration in saturated solution at constant temperature. It is denoted by K_{sp}.

Common ion effect: When a weak electrolyte is dissolved in water, there exists equilibrium between the unionized molecules and ions and so the law of mass action can be applied to it.

Consider a binary electrolyte (AB), which ionizes as,

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

Applying the law of mass action,

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

Now if an electrolyte is added to this solution which produces either of the ions A^+ or B^- then the concentration of that ion is increased and the equilibrium is distributed. But K is a constant and in order to keep it so, the concentration [AB] must evidently increase. It means that the degree of dissociation of electrolyte is suppressed by the addition of another electrolyte cantaining a common ion. It is known as common ion effect.

For example, ionization of NH_4OH is suppressed by the addition of NH_4Cl which produces the common NH_4^+ ion and that of CH_3COOH is suppressed by the addition of CH_3COONa producing the common acetate ion.

The presence of a common ion, affects the solubility of a salt and this effect can easily be calculated.

Let AB be a sparingly soluble salt in solution and A'B be added to it. Let S and S' be the solubility of the salt AB before and after the addition of the electrolyte A'B. Let C be the concentration of AB.

Considering the solution containing AB alone, we have

$$[A^+][B^-] = Ksp = S^2 \qquad \text{... (i)}$$

But after addition of A'B the solubility of AB changes while its solubility produce being constant remains the same. Therefore,

$$[A^+][B^-] = Ksp = S'[S' + C] \qquad \text{... (ii)}$$

From (i) and (ii) we have,

$$S^2 = [S'][S' + C]$$

Solubility product principle in qualitative analysis: Please refer to 2073 Supp Q.No. 32

Numerical: Please refer to 2070 Supp. Q.No. 24

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56. **2071 Supp. Q.No. 32 Write short note on solubility product and its application in analytical chemistry. The solubility product (K_{sp}) of $Ca(OH_2)$ at 25°C is 4.42×10^{-5}. A 500 mL of a saturated solution of $Ca(OH_2)$ is mixed with an equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ is precipited?** **[5+5]**

Solubility product: Please refer to 2062 Q.No. 30 (a)

Application of solubility product principle and common ion effect: Please refer to 2073 Set D Q No. 32

Numerical: Please refer to 2073 Set C Q.No. 32

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57. **2071 Set C Q.No. 30 2071 Set D Q.No. 32 State the following terms:**

a. **Ostwald's Dilution Law**	b. **Degree of dissociation**
c. **Ionic product of water**	d. **Common ion effect**
e. **pH value of a solution**	

Why is Ostwald's dilution law not applicable to strong electrolyte? What mass of KOH should be dissolved in one litre of solution to prepare a solution having pH is 12 at 25°C? (Atomic Weight of K = 39) **[10]**

a. **Ostwald's Dillution Law:** Please refer to 2072 Supp. Q.No. 32

b. **Degree of dissociation:** It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α.

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

c. **Ionic product of water:** Please refer to 2072 Supp. Q.No. 32

d. **Common ion effect:** Please refer to 2072 Supp. Q.No. 32

e. **pH value of solution:** Please refer to 2072 Supp. Q.No. 32

Numerical:

Given,

Volume of solution = 1 litre

Molecular mass of KOH = (30 + 16 + 1) = 56

pH = 12

We know that,

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

$$[H^+] = \text{antilog}[-pH]$$

$$[H^+] = \text{antilog}[-12] = 1 \times 10^{-12} M$$

We have,

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

$$[OH^-] = \frac{10^{-14}}{1 \times 10^{-12}} = 0.01M$$

KOH ionizes as

$$\underset{0.01M}{KOH} \rightleftharpoons K^+ + \underset{0.01M}{OH^-}$$

Molarity of KOH = 0.01 M

We have,

$$\text{Molarity} = \frac{\dfrac{\text{Weight of KOH}}{\text{Molecular weight}}}{\text{Volume of solution in litre}}$$

$$\text{or, } 0.01 = \frac{\frac{\text{Weight of KOH}}{56}}{1}$$

or, Weight of KOH = (56 × 0.01) = 0.56 g

Hence, the mass of KOH is 0.56 g.

NUMERICAL PROBLEMS

58. **2070 Set C Q.No. 3** **Calculate the pH of 1 g / litre NaOH solution.**

Given,

The concentration of NaOH = 1 g/L

Molecular weight of NaOH = (23 + 16 + 1) = 40

We know that,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}} = \frac{1}{40} = 0.025\ \text{M}$$

Now,

$$NaOH \rightleftharpoons Na^+ + OH^-$$

0.025 M 0.025 M 0.025 M

$p^{OH} = -\log[OH^-] = -\log[0.025] = 1.60$

We know that,

$p^H = 14 - p^{OH} = (14 - 1.6) = 12.4$

Hence, the pH of 1g/L NaOH solution is 12.4.

59. **2070 Set D Q.No. 27** **What is meant by degree of ionization? 0.41 g of NaOH is placed in 100 mL of 0.1N H_2SO_4. Find the pH of the resulting solution.** [5]

Degree of ionization: It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α.

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

Numerical:

Given,

Mass of NaOH = 0.41 g

Volume of H_2SO_4 = 100 mL = 0.1 litre

Normality of H_2SO_4 = 0.1N

Equivalent weight of H_2SO_4 = 49

Mass of H_2SO_4 =?

We know that,

$$\text{Normality} = \frac{\frac{\text{Wieght in g}}{\text{Equivalent weight}}}{\text{Volume in litre}}$$

$$\text{or, } 0.1\ \text{N} = \frac{\frac{\text{Weight in g}}{49}}{0.1}$$

or, Weight in g of H_2SO_4 = (0.1 × 0.1 × 49) = 0.49 g

According to the law of equivalence,

49 g of H_2SO_4 is completely reacted with 40 g of NaOH

1 g of H_2SO_4 is completely reacted with $= \frac{40}{49}$ g of NaOH

0.49 g of H_2SO_4 is completely reacted with $= \frac{40}{49} \times 0.49$ g of NaOH

= 0.40 g of NaOH

Now, the weight of unreacted NaOH = (0.41 – 0.40) = 0.01 g

Molecular weight of NaOH = 40

Volume of NaOH = 100 mL = 0.1 litre

Molarity of NaOH = ?

We know that,

$$\text{Molarity} = \frac{\frac{\text{Weight in g}}{\text{Molecular weight}}}{\text{Volume in litre}} = \frac{\frac{0.01}{40}}{0.1} = \frac{0.01}{40 \times 0.1} = \frac{0.01}{4} = 2.5 \times 10^{-3}\text{M}$$

NaOH ionizes as

$$NaOH \rightleftharpoons Na^+ + OH^-$$

2.5×10^{-3}M 2.5×10^{-3}M

We know that,

$pOH = -\log[OH^-] = -\log[2.5 \times 10^{-3}\text{M}] = 2.6$

$pH = 14 - pOH = (14 - 2.6) = 11.4$

Therefore, the pH of aqueous solution of NaOH = 11.4

60. **2069 (Set A) Q.No. 3** **What is pH of solution of NaOH whose concentration is 0.4 g / liter?** [2]

Given,

The concentration of NaOH = 0.4 g/L

Molecular weight of NaOH = (23 + 16 + 1) = 40

We know that,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}} = \frac{0.4}{40} = 0.01\text{M}$$

Now,

$$NaOH \rightleftharpoons Na^+ + OH^-$$

0.01 M 0.01 M 0.01 M

We know that,

$pOH = -\log[OH^-] = -\log[0.01] = 2$

We know that,

$pH = 14 - pOH = (14 - 2) = 12$

Hence, the pH of 1 g/L NaOH solution is 12.

61. **2069 Supp. Set B Q.No. 27** **What are the limitations of Lewis concept of acid and base? A 500 mL of a saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. What mass of $Ca(OH)_2$ is precipitated. K_{sp} of $Ca(OH)_2$ is 4.42×10^{-5}.** [5]

Limitations of Lewis concept of acid and base: Please refer to **2075 GIE Q.No. 25**

Numericals: Please refer to **2073 Set C Q.No. 32**

62. **2068 Q.No. 13** **Calculate the strength in g / litre of NaOH whose pH values is 11.** [2]

Given,

pH = 11

So, pOH = (14 – 11) = 3

g/L of NaOH = ?

We know that,

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

$[OH^-] = \text{antilog}(-pOH) = \text{antilog}(-3) = 0.001$ mol/L

NaOH ionizes as

$$NaOH \rightleftharpoons Na^{+} + OH^{-}$$

1mole 1 mole 1 mole

0.001 M 0.001 M

Molecular weight of NaOH = 40

g/L = molarity × molecular weight

= 0.001 × 40 = 0.04 g/L

Hence, the strength in g/L of NaOH is 0.04 g/L.

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63. **2068 Q.No. 26 Define solubility product principle. 0.00143 g of AgCl dissolve in one litre of water 25°C to form a saturated solution. What is the solubility product of the salt? (Ag = 108, Cl = 35.5).**

⤳ **Solubility product principle:** Please refer to 2073 Supp Q.No. 32

Numerical:

Concentration of AgCl $= 0.00143 \text{ g L}^{-1}$

$= \frac{0.00143}{143.5} \text{ mol L}^{-1}$

$= 9.96 \times 10^{-6} \text{ mol L}^{-1}$

AgCl can ionize as

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

1mole 1 mole 1 mole

9.96×10^{-6} 9.96×10^{-6} 9.96×10^{-6}

$Ksp = [Ag^{+}][Cl^{-}] = 9.96 \times 10^{-6} \times 9.96 \times 10^{-6} = 9.92 \times 10^{-11} \text{ mol}^2\text{L}^{-2}$

So, the solubility product of AgCl is $9.92 \times 10^{-11} \text{ mol}^2\text{L}^{-2}$.

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64. **2067 Q.No. 29 Define the terms**

i. Common ion effect **ii. pH of a solution**

iii. Lewis base **iv. Degree of ionization**

v. Ionic product of water **vi. Ostwald's dilution law**

A sample of AgCl is treated with 5 mL of 2 M Na_2CO_3 solution to produce Ag_2CO_3. The remaining solution contained 0.003 g of Cl^{-} per litre. Calculate solubility product of AgCl. (Ksp of Ag_2CO_3 = 8.2×10^{-12}).

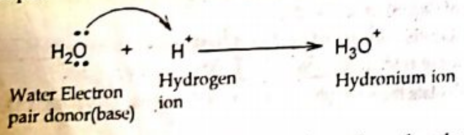
⤳

i. **Common ion effect:** The suppression of degree of ionization of weak electrolyte by the addition of strong electrolyte having one ion common with the weak electrolyte known as common ion effect.

ii. **p^H of solution:** p^H of solution is defined as the magnitude of negative power to which 10 must be raised to express the hydronium ion concentration.

$p^{H} = -\log [H^{+}]$

iii. **Lewis base:** According to Lewis concept base is electron pair donor. Water behaves a base because it can donate electron pair present on O-atom to electron deficient centre o to an acid. Example:



iv. ***Degree of ionization:*** *It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α*

$$\alpha = \frac{\text{No. of molecules split inot ions}}{\text{Total no. of molecules of the electrolyte}}$$

v. ***Ionic product of water:*** *The product of the concentration of hydronium ion and hydroxyl ion in pure water is constant at particular temperature known as ionic product of water. It is denoted by K_w.*

$K_w = 1.008 \times 10^{-14} = [H_3O^{+}][OH^{-}]$ at 25°C.

vi. **Ostwald dilution law :** According to the theory of electrolytic dissociation of an electrolyte, when dissolved in water undergoes spontaneous dissociation into +vely and -vely charged ions and in the case of a weak electrolyte like CH_3COOH, NH_4OH etc. there exists a definite equilibrium between the unionized molecules of electrolyte and the ions present in solution at a given temperature. It is, therefore, to be expected that the law of mass action can be applied to this equilibrium. This application was first carried out by Ostwald and the result is known as Ostwald dilution law.

$\alpha = \sqrt{K.V}$ Where, V = dilution.

Numerical

Concentration of chloride ion $[Cl^{-}] = 0.003 \text{ g L}^{-1}$

$= \frac{0.003}{35.5} \text{ mol L}^{-1} = 8.45 \times 10^{-5} \text{ mol L}^{-1}$

Concentration of Na_2CO_3 = 2M

The reaction that takes place according to question is

$$2AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaCl$$

or, $2AgCl + CO_3^{--} \longrightarrow Ag_2CO_3 + 2Cl^{-}$

Let, S be the solubility of Ag_2CO_3 in 2M Na_2CO_3

Ksp of $Ag_2CO_3 = 8.2 \times 10^{-12}$

Ksp of AgCl = ?

Ag_2CO_3 dissociates as

$$Ag_2CO_3 \rightleftharpoons 2Ag^{+} + CO_3^{--}$$

1 mole 2 mole 1mole

S 2S S + 2M

Now,

$Ksp = [Ag^{+}]^2 [CO_3^{--}]$

or, $8.2 \times 10^{-12} = (2S)^2 (S + 2)$

or, $8.2 \times 10^{-12} = 4S^2 \times 2$ $[\because S + 2 \simeq 2]$

or, $8.2 \times 10^{-12} = 8S^2$

or, $S = \sqrt{\frac{8.2 \times 10^{-12}}{8}} = 1.0124 \times 10^{-6}$

$\therefore [Ag^{+}] = 2S = 2 \times 1.0124 \times 10^{-6} = 2.0248 \times 10^{-6}\text{M}$

To calculate the solubility product of AgCl

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

We have

$Ksp = [Ag^{+}][Cl^{-}]$

$Ksp = 2.0248 \times 10^{-6} \times 8.45 \times 10^{-5}$

$= 1.71 \times 10^{-10}$

Hence, Ksp of AgCl = 1.71×10^{-10}

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65. **2066 Q. No. 14 The pH of a solution of KOH is 10. Calculate the hydroxyl ion concentration.** [2]

⤳ pH of KOH = 10

We know that,

pH + pOH = 14

pOH = 14 - pH

pOH = 14 - 10 = 4

we know that,

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

or, $[OH^{-}] = \text{antilog}[-pOH] = \text{antilog}[-4] = 1 \times 10^{-4}$ M

Hence, the concentration of hydroxide ion is 1×10^{-4} M.

66. **2065 Q.No. 30 b** **What is ionic product of water? The pH of 0.1 M HCN solution is 5.2. What is va ionization constant (Ka) for the acid?**

Ionic product of water: The product of the concentration of hydronium ion hydroxyl ion in pure water is constant at particular temperature known as ionic pro of water. It is denoted by K_w.

$K_w = 1.008 \times 10^{-14} = [H_3O^+][OH^-]$ at 25°C.

Numerical:

Given, pH of HCN = 5.2
Molarity of HCN = 0.1M
Ionization constant (Ka) of HCN = ?
Concentration of $[H^+]$ = ?.

We know that,

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

$[H^+] = \text{antilog}\,[-pH] = \text{antilog}\,[-5.2] = 6.30 \times 10^{-6}$ M

HCl ionizes as

$$\begin{array}{lccccc} & HCN & \rightleftharpoons & H^+ & + & Cl^- \\ \text{Initially} & C & & 0 & & 0 \\ & (C - C\alpha) & & C\alpha & & C\alpha \end{array}$$

We know that,

From Oswald's dilution law, $Ka = \alpha^2C$

$$\alpha = \sqrt{\frac{ka}{C}}$$

$$[H^+] = C\alpha = C \times \sqrt{\frac{Ka}{C}}$$

or, $[H^+]^2 = C \times Ka$

or, $Ka = \dfrac{[H^+]^2}{C}$

or, $Ka = \dfrac{[6.30 \times 10^{-6}]^2}{0.1}$

or, $Ka = 3.969 \times 10^{-10}$

Hence, the ionization constant (Ka) of HCN solution is 3.969×10^{-10}.

---

67. **2064 Q.No. 16** **Define pH. Calculate the pH of 0.1 M H_2SO_4.**

pH of solution is defined as the magnitude of negative power to which 10 must be raise to express the hydronium ion concentration.

If in a solution,

$[H_3O^+] = 10^{-x}$ ... (i)

$p^H = x$

Taking logarithm of both side of equation (i) we get,

$\log[H_3O^+] = \log 10^{-x} = -x \log 10 \ [\log 10 = 1] = -x$

or, $x = -\log[H_3O^+]$

or, $pH = -\log[H_3O^+] = -\log[H^+]$

Numerical

$[H_2SO_4] = 0.1M$

p^H of H_2SO_4 = ?

Ionization of H_2SO_4 is

$$\begin{array}{lcl} H_2SO_4 & \longrightarrow & 2H^+ + SO_4^{--} \\ 1M & & 2M \\ 0.1M & & 0.2M \end{array}$$

So, $[H^+] = 0.2M$

We know that,

$pH = -\log[H^+] = -\log[0.2] = 0.699$

Hence, pH of 0.1 M H_2SO_4 is 0.699

---

68. **2064 Q.No. 26** **What is meant by solubility product of sparingly soluble electrolyte? The solubility of AgCl in water at 298 K is 1.43×10^{-3} g L^{-1}, calculate its solubility in 0.5 M KCl solution.** [5]

The solubility product of a sparingly soluble electrolyte is product of ionic concentration in its saturated solution at a given temperature Suppose, sparingly soluble electrolyte AB is dissolved in water then it ionizes partially and the ions remains in equilibrium with unionized molecule.

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

According to the law of mass action:

$K = \dfrac{[A^+][B^-]}{[AB]}$ Where, K = equilibrium constant.

or, $K[AB] = [A^+][B^-]$

If the electrolyte is feebly ionized, the concentration of AB remains constant. So, K[AB] is represented by another constant K_{sp} called solubility product constant.

$K_{eq} = [A^+][B^-]$

Numerical:

Given, solubility of AgCl = 1.43×10^{-3} g/L
Molecular weight of AgCl = (108 + 35.5) = 143.5
Solubility product constant (Ksp) = ?
Molarity of HCl = 0.5 M

We know that,

$$\text{Solubility of AgCl in mole/L} = \frac{g/L}{\text{Molecualr weight}} = \frac{1.43 \times 10^{-3}}{143.5}$$
$$= 9.965 \times 10^{-6}\ \text{mole/L}$$

AgCl ionizes as

$$\begin{array}{ccccc} AgCl & \rightleftharpoons & Ag^+ & + & Cl^- \\ 9.965 \times 10^{-6} & & 9.965 \times 10^{-6} & & 9.965 \times 10^{-6} \end{array}$$

We know that,

$$\text{Solubility product constant (Ksp)} = [Ag^+][Cl^-]$$
$$= [9.965 \times 10^{-6}]\,[9.965 \times 10^{-6}]$$
$$= [9.965 \times 10^{-6}]^2\ mol^2L^{-2}$$

When KCl is added to the solution, the concentration of Cl^- is increased and the solubility is calculated with refrence to Ag^+ ions.

KCl ionizes as

$$\begin{array}{ccccc} KCl & \rightleftharpoons & K^+ & + & Cl^- \\ 0.5M & & 0.5M & & 0.5M \end{array}$$

Total concentration of $[Cl^-] = [9.965 \times 10^{-6} + 0.5]$

We know that,

Solubility product constant (Ksp) = $[Ag^+][Cl^-]$

$[9.965 \times 10^{-6}]^2 = [Ag^+][9.965 \times 10^{-6} + 0.5]$

or, $[Ag^+] = \dfrac{[9.965 \times 10^{-6}]^2}{[9.965 \times 10^{-6} + 0.5} = 1.985 \times 10^{-10}$ mol/L

Hence, the solubility of AgCl in 0.5 M KCl is 1.985×10^{-10} mol/L.

---

69. **2063 Q.No. 13** **Calculate the hydroxide ion concentration of a solution having pH 10.5** [2]

pH = 10.5

$[OH^-]$ = ?

We know that,

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

or, $10.5 = -\log[H^+]$

or, $\log[H^+] = -10.5$

or, $[H^+] = \text{antilog} - 10.5$

or, $[H^+] = 3.16 \times 10^{-11}$

We know that,

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

$1.0 \times 10^{-14} = [3.16 \times 10^{-11}][OH^-]$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{3.16 \times 10^{-11}} = 3.16 \times 10^{-4}$$

So, the concentration of $[OH^-] = 3.16 \times 10^{-4}M$

---

70. **2063 Q.No. 25 What are ionization constant and degree of ionization of a weak electroyte? How do they vary with temperature? Calculate the pH of 0.1 M acetic acid solution having Ka 1.8 × 10⁻⁵.**

Ionization constant: The equilibrium constant between ionized and unionized form of an electrolyte in a solution is known as ionization constant. When an electrolyte AB is dissolved in water, it ionizes to form A^+ and B^- and the equilibrium is between ionized and unionized form of an electrolyte is expressed as.

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

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

Where, K = Equilibrium constant called ionization constant.

Degree of ionization of weak electrolyte: It is the fraction of the total number of molecules of electrolyte present as free ions in the solution. It is represented by α

$$\alpha = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules of the electrolyte}}$$

Variation of degree of ionization with temperature: Degree of ionization increase with increase in temperature and therefore the value of ionization constant also increase with the increase in temperature.

Numerical:

CH_3COOH ionizes as

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

Applying law of mass action

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

Here, $[H^+] = [CH_3COO^-]$

$[CH_3COOH] = 0.1M$

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

Putting the value in the equation (i) we get

$$1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

or, $1.8 \times 10^{-5} = \frac{[H^+][H^+]}{0.1}$

or, $1.8 \times 10^{-5} \times 0.1 = [H^+]^2$

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

or, $[H^+] = 1.34 \times 10^{-3}$

We know that,

$pH = -\log[H^+] = -\log[1.34 \times 10^{-3}] = 2.87$

So, the pH of 0.1 M CH_3COOH is 2.87.

---

71. **2061 Q.No. 13 The solubility of CaF₂ in water at 18°C is 2.05 × 10⁻⁴ mole per litre. Calculate its solubility product.** [2]

Given,

Solubility of $CaF_2 = 2.05 \times 10^{-4}\ molL^{-1}$

Solubility product (Ksp) = ?

CaF_2 ionizes as

$$\underset{2.05 \times 10^{-4}}{CaF_2} \rightleftharpoons \underset{2.05 \times 10^{-4}}{Ca^{++}} + \underset{2 \times 2.05 \times 10^{-4}}{2F^-}$$

We know that,

Solubility product of CaF_2 (Ksp) $= [Ca^{++}][F^-]^2$

$= [2.05 \times 10^{-4}][2 \times 2.05 \times 10^{-4}]^2$

$= 3.446 \times 10^{-11}\ mol^2L^{-2}$

Hence, the solubility product of $CaF_2(Ksp) = 3.446 \times 10^{-11}\ mol^2L^{-2}$

---

72. **2060 Q.No. 15 The solubility product constant of BaSO₄ in water at 25°C is 1×10⁻¹⁰ mol²L⁻². Calculate the solubility of BaSO₄ in g / L. [Ba = 137]** [2]

Given,

The solubility constant of $BaSO_4$ (Ksp) $= 1 \times 10^{-10} mol^2L^{-2}$

The ionization of $BaSO_4$ is

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

Suppose the solubility of $BaSO_4$ is x mole/L. So, the concentration of $[Ba^{++}]$ and $[SO_4^{--}]$ will be x mole/L

We know that,

Solubility product (Ksp) of $BaSO_4 = [Ba^{++}][SO_4^{--}]$

$1 \times 10^{-10} mol^2L^{-2} = x.x = x^2$

$x = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5}$ mole/L

We know that,

$$\text{Molarity} = \frac{\frac{g}{L}}{\text{Molecular weight}}$$

Molecular weight of $BaSO_4 = (137 + 32 + 64) = 233$

g / L = Molarity × molecular weight $= 1 \times 10^{-5} \times 233$

g / L $= 2.33 \times 10^{-3}$

Hence, the solubility of $BaSO_4$ in g/L is 2.33×10^{-3}

---

73. **2060 Q.No. 26 Define ionic product of water. Why does Kw of water increases with temperature? 10 cc $\frac{N}{2}$ HCl, 30 cc $\frac{N}{10}$ HNO₃ and 60 cc $\frac{N}{5}$ H₂SO₄ are mixed together. Find the pH of the mixture.** [5]

Ionic product of water: The product of the concentration of hydronium ion and hydroxyl ion in pure water is constant at particular temperature known as ionic product of water. It is denoted by K_w.

$K_w = 1.008 \times 10^{-14} = [H_3O^+][OH^-]$ at 25°C.

Consider, the ionization of weak electrolyte water is as

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

The ionization constant (K) of water is given as

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K[H_2O] = [H^+][OH^-] \quad \dots (i)$$

Water ionizes to very less extent and the dissociation of water is so small that its concentration remains constant i.e. $K[H_2O]$ = constant at constant temperature and it is denoted by K_w.

From equation

$K_w = [H^+][OH^-]$ ... (ii)

Where, K_w is called ionic product of water. It is defined as the product of the concentration of hydrogen ion and hydroxyl ion during ionization of water.

Effect of Temperature on ionic product of water: Ionization of water is exothermic process. So, ionization of water is increased with increasing the temperature i.e. formation of H^+ and OH^- ion is increased. At higher temperature, the equilibrium concentration of H^+ and OH^- would be higher and K_w of water is increased with increasing temperature.

Numerical:

Given,

10 cc of $\frac{N}{2}$ HCl = 5 cc of 1N HCl

30 cc of $\frac{N}{10}$ HNO_3 = 3 cc of 1N HNO_3

60 cc of $\frac{N}{5}$ H_2SO_4 = 12 cc of 1N H_2SO_4

Total volume of mixture of acid = (10 + 30 + 60) = 100 cc

Total volume of 1N acid mixture = (5 + 3 + 12) = 20 cc

Now, $V_1 = 20$ cc $N_1 = 1N$

$V_2 = 100$ cc $N_2 = ?$

We know that,

$V_1N_1 = V_2N_2$

or, $N_2 = \frac{V_1N_2}{V_2} = \frac{20 \times 1}{100} = \frac{1}{5}$ N H_2SO_4 = 0.2 N H_2SO_4

Mixture of acid contains dibasic acid. So, normality = molarity i.e. 0.2 N = 0.2 M. Because normality of acid mixture is due to H^+ ion concentration.

Therefore, $[H^+] = 0.2$ M

pH = - log $[H^+]$ = - log [0.2] = -[-0.698] = 0.698

So, the pH of the acid mixture is 0.698.

---

74. **2060 Q.No. 14** **Calculate the pH of an aqueous solution containing 10^{-7} moles of NaOH per litre.**

Given,

The molarity i.e. moles/L of NaOH = 10^{-7}M

NaOH ionizes as

$$\underset{10^{-7}M}{NaOH} \rightleftharpoons \underset{10^{-7}M}{Na^+} + \underset{10^{-7}M}{OH^-}$$

The concentration of $[OH^-] = 10^{-7}$M

Water also ionizes as

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

Due to the auto ionization of H_2O, 10^{-7}M of H^+ ion and 10^{-7}M of OH^- ion are formed. The concentration of OH^- ion formed by the auto ionization of H_2O cannot be neglected.

Total concentration of $[OH^-] = (10^{-7}M + 10^{-7}M) = 2 \times 10^{-7}$M

We know that,

$p^{OH} = -\log[OH^-] = -\log [2 \times 10^{-7}] = 6.698$

$p^H = 14 - p^{OH} = 14 - 6.698 = 7.302$

Therefore, the pH of aqueous solution of NaOH = 7.302

75 **2059 Q.No. 16** **Calculate the pH value of 0.04 N HNO_3 solution, assuming HNO_3 to be completely ionized.** **[2]**

Nitric acid i.e. HNO_3 is monobasic acid. So, the normality is equal to the molarity.

The concentration of HNO_3 = 0.04 N = 0.04M

HNO_3 ionizeas as

$$\underset{0.04M}{HNO_3} \rightleftharpoons \underset{0.04M}{H^+} + NO_3^-$$

The concentration of $[H^+]$ = 0.04M

We know that,

$p^H = -\log[H^+] = -\log [0.04] = 1.39$

Hence, the pH of HNO_3 is 1.39.

---

76 **2059 Q.No. 30** **Explain Bronsted Lowry concept of acids and bases. Calculate the degree of ionization of HCN having concentration 0.01 M (K_a of HCN = 4.8×10^{-10}). Also calculate H^+ ion concentration and pH.** **[10]**

According to Bronsted Lowry concept:

Acid: Acid is substance which has a tendency to donate proton during chemical reaction. It may be molecules, cations or anions, which can donate proton in aqueous solution.

Example: HCl

$$HCl \longrightarrow \underset{\text{Proton}}{H^+} + Cl^-$$

Base: Base is substance which has a tendency to accept proton during chemical reaction. It may be molecules, cations or anions, which can accept proton in aqueous solution.

Example: NH_3

$$NH_3 + \underset{\text{Proton}}{H^+} \longrightarrow NH_4^+$$

Numerical:

Given, the concentration of HCN = 0.01 M

Ionization constant of HCN (Ka) = 4.8×10^{-10}

$[H^+]$ ion concentration = ?

pH = ?

Degree of ionization of HCN (α) = ?

HCN ionizes as

	HCN	$\rightleftharpoons$	H^+	+	CN^-
Initially	C		0		0
	(C - Cα)		Cα		Cα

We know that,

From Ostwald's dilution law, Ka = α^2C

$$\alpha = \sqrt{\frac{Ka}{C}} = \sqrt{\frac{4.8 \times 10^{-10}}{0.01}} = 2.2 \times 10^{-4}$$

The concentration of $[H^+] = C\alpha = 0.01 \times 2.2 \times 10^{-4} = 2.2 \times 10^{-6}$

We know that,

$pH = -\log[H^+] = -\log [2.2 \times 10^{-6}] = 5.65$

Hence, the pH of solution is 5.65.

---

77. **2058 Q.No. 15** **Calculate the hydrogen ion concentration of a solution whose pH is 9.5.** **[2]**

Given,

pH = 9.5

The concentration of $[H^+]$ = ?

We know that,

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

$[H^+]$ = antilog [-pH] = antilog [-9.5] = 3.16×10^{-10}M

Hence, the concentration of $[H^+] = 3.16 \times 10^{-10}$M

78. **2057 Q.No. 25** **Define solubility product. The solubility of CaF_2 in water at 18°C is 2.05×10^{-4} mo** **Calculate its solubility product.** [5]

Solubility product: Please refer to 2073 Supp Q.No. 32

Numerical: Please refer to 2061 Q.No. 13

79. **2056 Q.No. 5** **The pH of HCl solution is 3. Calculate the strength of HCl in terms of molarity.** [5]

Given,

pH of HCl = 3

Strength of HCl in terms of molarity (M) = ?

We know that,

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

$[H^+]$ = antilog [–pH] = antilog [–3] = 1×10^{-3}M

1 M of HCl gives 1M of H^+ ion. So, the strength of HCl is 1×10^{-3}M.

80. **2056 Q.No. 22** **The solubility product of CuS is 8.0×10^{-45} at a certain temperature. Find its solubi** **at this temperature.** [5]

Given,

The solubility product (Ksp) = 8.0×10^{-45}

Solubility of CuS = ?

The ionization of CuS is

$CuS \rightleftharpoons Cu^{++} + S^{--}$

Suppose the solubility of CuS is x mole/L. So, the concentration of $[Cu^{++}]$ and $[S^{--}]$ will be x mole/L

We know that,

Solubility product (Ksp) of CuS = $[Cu^{++}][S^{--}]$

$8.0 \times 10^{-45} = x.x = x^2$

$x = \sqrt{8.0 \times 10^{-45}} = 8.94 \times 10^{-23}$ mole/L

Hence, the solubility of CuS is 8.94×10^{-23} mole/L

81. **2055 Q.No. 22** **The solubility product of chalk is 9.3×10^{-8}. Calculate its solubility in gm per litre.** [5]

Given,

The solubility product of Chalk $CaCO_3$ (Ksp) = 9.3×10^{-8}

The ionization of $CaCO_3$ is

$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{--}$

Suppose the solubility of $CaCO_3$ is x mole/L. So, the concentration of $[Ca^{++}]$ and $[CO_3^{--}]$ will be x mole/L

We know that,

Solubility product (Ksp) of $CaCO_3$ = $[Ca^{++}][CO_3^{--}]$

$9.3 \times 10^{-8} = x.x = x^2$

$x = \sqrt{9.3 \times 10^{-8}} = 3.049 \times 10^{-4}$ mole/L

Hence, molarity of $CaCO_3$ = 3.049×10^{-4} M

We know that,

$$\text{Molarity} = \frac{g/L}{\text{Molecular weight}}$$

Molecular wt. of $CaCO_3$ = (40 + 12 + 48) = 100

g/L = Molarity × molecular weight = $3.049 \times 10^{-4} \times 100$

g/L = 3.49×10^{-2}

Hence, the solubility of $CaCO_3$ in g/L is 3.49×10^{-2}

82. **2054 Q.No. 22** **The solubility of CaF_2 in water at 18°C is 2.05×10^{-4} mole per litre. Calculate its solubility product.** [5]

Please refer to 2061 Q.No. 13

WRITE SHORT NOTES ON

83. **2076 Set B Q.No. 33iv** **2076 Set C Q.No. 33iii** **2060 Q.No. 31(i)** **Lewis concept of acid and base.** [5]

84. **2074 Supp. Q.No. 33(ii)** **2066 Q. No. 31 iv** **Solubility product principle and its application** [5]

Please refer to 2073 Supp. Q.No. 32

85. **2074 Set A Q.No. 33d** **2074 Set B Q.No. 33c** **2072 Set C Q.No. 33c** **2070 Set C Q.No. 33 c** **Application of common ion effect and solubility product principle in qualitative salt analysis.** [5]

Please refer to 2073 Supp Q No 32

86. **2069 (Set A) Q.No. 33 c** **Solubility product** [5]

Please refer to 2062 Supp Q No 30a

87. **2061 Q.No. 31(iii)** **pH and pH scale.** [5]

pH: the concentration of H^+ or H_3O^+ and OH^- in most solution are in the range of 10^{-1} to 10^{-14}. A convenient way of expressing such small concentration was suggested by Sorensen who introduced the pH scale. It is after the French expression puissance de-hydrogen meaning the strength or concentration of hydrogen.

pH is defined as the negative logarithm of the concentration of hydrogen ion.

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

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

For pure water or neutral solution

$[H^+] = 1 \times 10^{-7}$

∴ $pH = -\log[H^+] = -\log[1 \times 10^{-7}] = 7$ at 25°C

In acidic solution $[H^+]$ 10^{-7}, hence, pH will be less than 7. For alkaline solution $[H^+] < 10^{-7}$. Hence, pH will be greater than 7.

For, 1N HCl solution, $[H^+] = 1$

∴ $pH = -\log[H^+] = -\log[1] = 0$

For, 1N NaOH solution, $[H^+] = 10^{-14}$

∴ $pH = -\log[H^+] = -\log[10^{-14}] = 14$

pOH: Just like pH,pOH is used to indicate hydroxyl ion concentration of a solution.

It may be defined as the negative logarithm of hydroxyl ion concentration.

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

Like, pH and pOH, ionic product of water K_w may be express as

We know that,

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

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

or, $pK_w = pH + pOH$

This relationship is applicable for water as well as any aqueous solution. Now we can say that,

pOH = 7 for neutral solution

pOH < 7 for basic solution

pOH > 7 for acidic solution

88. **2059 Q.No. 31(b)** **2058 Q.No. 31(a)** **Solubility product principle** [5]

Please refer to 2062 Supp. Q No 30a

89. **2057 Q.No. 31(a)** **Common Ion effect** [5]

Please refer to 2072 Set D Q No 30

90. **2056 Q.No. 31(a)** **Law of mass action** [5]

Norwegian chemist Guldberg and Waage suggested a quantitative relationship between the rate of reaction and concentration of reactant, which is known as law of mass action.

Statement: "The rate at which a substance reacts is directly proportional to its active mass and the rate of a chemical reaction is directly proportional to the products of active masses of the reactants".

The term 'active mass'of any species is equivalents to the molar concentration of th species. It is expressed in square brackets [ ].For example, the active mass of th substance 'A' is expressed by [A] or C_A.

The term 'molar concentration i.e. molarity' of a substance means the no. of gram mo of the substance dissolved per unit volume of its solution.

$$\text{Molar Concentration} = \frac{\text{No. of gram moles of solute}}{\text{Volume of solutino in litre}}$$

$$= \frac{\text{Weight of solution in gram}}{\text{Molar mass of solute} \times \text{volume of soluiton in litre}}$$

Let us consider a reaction: $A \longrightarrow B$

According to law of mass action

Rate of reaction $\propto [A]$

Let us consider a reversible reaction,

$A + B \rightleftharpoons C + D$

According to law of mass action,

Rate of forward reaction $\propto [A][B]$

or, Rate of forward reaction $= k_f[A][B]$

Similarly, rate of backward reaction $\propto [C][D]$

or, Rate of backward reaction $= k_b[C][D]$

Where, k_f and k_b are the proportionality constants, called velocity constant for forward and backward reaction respectively.

At equilibrium, rate of forward reaction= rate of backward reaction.

$\therefore\ k_f[A][B] = k_b[C][D]$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][D]}$$

or $K = \dfrac{[C][D]}{[A][B]}$ Where, K is a constant called equilibrium constant.

Let us take a reaction, $2A \rightleftharpoons B$

The reaction can also be written as $A + A \rightleftharpoons B$.

The equilibrium constant can be expressed as

$$K = \frac{[B]}{[A][A]}$$

or, $K = \dfrac{[B]}{[A]^2}$

Here, the concentration of A raises to the power its stoichiometric coefficient i.e., 2

If we consider a reaction, $aA + bB \rightleftharpoons cC + dD$ Then, equilibrium constant can b expressed as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Expression for equilibrium constant for some reactions

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $K = \dfrac{[CaO][CO_2]}{[CaCO_3]}$. Since, CaO(s) and $CaCO_3$(s) are pur solids, their concentration are said to be constant then taken as unity. Then,

$$K = \frac{1 \times [CO_2]}{1}$$

$\therefore\ Kc = [CO_2]$

◆◆◆

Unit 4

Electrochemistry

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 4 How many coulombs are required to produce** **[1+1]**
   - i. **27 g of silver from $AgNO_3$?**
   - ii. **50 g of Aluminum from Al_2O_3?**

(Atomic weight of Ag = 108, Atomic weight of Al = 27)

i. $AgNO_3$ ionizes as

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

$Ag^+ + 1e^- \longrightarrow Ag$

1 mole of silver ion requires 1 mole of electron

108 g silver requires 1 mole of electron

27g silver requires $\dfrac{1 \times 27}{108}$ mole of electron

$= 0.25$ mole

We know that

1 mole of electron having charge 96500 coulomb

0.25 mole of electron having charge 96500 × 0.25 coulomb

$= 24125$ C

ii. Al_2O_3 ionizes as

$Al_2O_3 \longrightarrow 2Al^{+++} + 3O^{--}$

$Al^{+++} + 3e^- \longrightarrow Al$

1 mole of aluminium ion requires 3 mole of electron

27 g aluminium requires 3 mole of electron

50g aluminium requires $\dfrac{3 \times 50}{27}$ mole of electron

$= 5.55$ mole

We know that

1 mole of electron having charge 96500 coulomb

5.55 mole of electron having charge 96500 × 5.55 coulomb

$= 536111$ C

2. **2076 Set C Q.No. 4 How many coulombs are required to produce** **[1+1]**
   - i. **80 g of calcium from molten $CaCl_2$?**
   - ii. **50 g of Aluminum from molten Al_2O_3?**

i. $AgNO_3$ ionizes as

$CaCl_2 \longrightarrow Ca^{++} + 2Cl^-$

$Ca^{++} + 2e \longrightarrow Ca$

1 mole of calcium ion requires 2 mole of electron

40 g calcium requires 2 mole of electron

80g calcium requires $\frac{2 \times 80}{40}$ mole of electron

$= 4$ mole

We know that

1 mole of electron having charge 96500 coulomb

4 mole of electron having charge 96500 × 4 coulomb

$= 386000$ C

ii. Al_2O_3 ionizes as

$Al_2O_3 \longrightarrow 2Al^{+++} + 3O^{--}$

$Al^{+++} + 3e \longrightarrow Al$

1 mole of aluminium ion requires 3 mole of electron

27 g aluminium requires 3 mole of electron

50g aluminium requires $\frac{3 \times 50}{27}$ mole of electron

$= 5.55$ mole

We know that

1 mole of electron having charge 96500 coulomb

5.55 mole of electron having charge 96500 × 5.55 coulomb

$= 536111$ C

---

3. **2075 GIE Q.No. 4 Can $CuSO_4$ solution be stored in a Zinc Vessel?** **[2]**

$\frac{E^0\ Cu^{2+}}{Cu} = 0.34\ V$ $\frac{E^0\ Zn^{2+}}{Zn} = -0.76\ V$

Given,

$E^oCu^{+2}/Cu = 0.34V$ and $E^oZn^{+2}/Zn = -0.76\ V$

From given data the reduction potential of Cu is higher than Zn. It means $CuSO_4$ and Zn comes in contact. Zn gets oxidized and passes into the solution. So, $CuSO_4$ can't store in a Zn vessel.

---

4. **2075 Set A Q.No. 4 Why does silver nitrate solution become bluish when copper rod is dipped into it? [Given $E^\circ\ Cu^{2+}/Cu = 0.34V$ and $E^\circ\ Ag^+/Ag = 0.80\ V$]** **[2]**

The standard reduction potential of copper is lower than silver.

$E^\circ\ Cu^{2+}/Cu = 0.34\ V$

$E^\circ\ Ag^+/Ag = 0.80\ V$

The copper is oxidized when dipped into $AgNO_3$ solution and becomes bluish.

$$2AgNO_3 + Cu \longrightarrow \underset{\text{Bluish}}{Cu(NO_3)_2} + 2Ag$$

---

5. **2075 Set B Q.No. 4 A solution contains 1 g of NaCl in 200 cm^3 and its specific conductance is found to be $2.55 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$. Calculate its molar conductance.** **[2]**

Given, Weight of NaCl = 1g

Volume of NaCl solution = 200 cm^3

Molecular mass of NaCl = 58.5

$$\text{Molarity} = \frac{W}{\text{Molecular mass}} \times \frac{1000}{V} = \frac{1}{58.5} \times \frac{1000}{200} = 0.085\ M$$

Hence, the molarity of NaCl (M) = 0.085 M

Specific conduntance (K) = $2.55 \times 10^{-2}\ ohm^{-1}cm^{-1}$

Molar conductance ($\wedge_m$) = ?

We know that

$$\wedge_m = \frac{1000K}{\text{Molarity}} = \frac{1000 \times 2.55 \times 10^{-2}}{0.085} = 300\ S\ cm^2\ mol^{-1}$$

Hence, the molar conductance ($\wedge_m$) = 300 S cm^2 mol^{-1}

---

6. **2074 Supp. Q.No. 5 How many coulombs are required to produce 50 g of Al when electrode reaction is $Al^{+++} + 3e^- \longrightarrow Al$ (Atomic mass of Al = 27)?** **[2]**

The given reaction is

$Al^{+++} + 3e^- \longrightarrow Al$

1mole 3mole

Here,

1 mole of aluminium ion requires 3 mole of electron i.e.

27 g of aluminium requires 3 mole of electron

1g of aluminium requires $\frac{3}{27}$ mole of electron

50 g of aluminium requires $\frac{3}{27} \times 50$ mole of electron = 5.55 mole of electron

Hence, 50 g of aluminium requires 5.55 mole of electron

We know that,

1 mole of electron having charge 96500 coulomb

So, 5.55 mole of electron having charge 96500 × 5.55 coulomb = 535575 C

Therefore, 535575 coulomb charges are required to deposit 50 g of Al^{+3} into Al.

---

7. **2074 Set A Q.No. 5 How many coulombs are required to deposit 126 gram of Cu from $CuSO_4$ solution? (Atomic mass of Cu = 63.5)** **[2]**

$CuSO_4$ ionizes as

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

Reduction of Cu^{++} as

$$Cu^{++} + 2e^- \longrightarrow Cu$$

63.5 g 2 mole

63.5 g of Cu^{++} requires 2 mole of electron.

1 g of Ca^{++} requires $\frac{2}{63.5}$ mole of electron.

126 g of Ca^{++} requires $\frac{2}{63.5} \times 126$ mole of electron = 3.96 mole of electron.

We know that,

1 mole of electron carries 96500 coulomb charges.

3.96 mole of electron carries 96500 × 3.96 = 382140 coulomb charges.

---

8. **2074 Set B Q.No. 5 How many coloumbs of electricity are required to deposit 33 g of Ca from molten $CaCl_2$?** **[2]**

$CaCl_2$ ionizes as

$CaCl_2 \longrightarrow Ca^{++} + Cl^-$

Reduction of Ca^{++} is

$Ca^{++} + 2e^- \longrightarrow Ca$

40g 2 mole

40 g of Ca^{++} requires 2 mole of electron.

1 g of Ca^{++} requires $\frac{2}{40}$ mole of electron.

33 g of Ca^{++} requires $\frac{2}{40} \times 33$ mole of electron = 1.65 mole of electron.

We know that,
1 mole of electron carries 96500 coulomb charges.
1.65 mole of electron carries 96500 × 1.65 = 159225 coulomb charges.

---

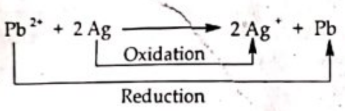
9. **2073 Supp Q.No. 4 Two metallic element X and Y have the following standard electrode potential.**
X = + 0.40V
Y = –0.80V
What would you expect to occur if X is added to an aqueous solution of salt of Y? Give reason. **[2]**

Standard electrode potential of X is + 0.40 V and standard electrode potential of Y is –0.80 V. The electrode potential of X is hither than Y. When X is added to an aqueous solution of salt of Y, X metal cannot displace Y metal from its salt solution. The metal X has more tendency to get oxidized.

---

10. **2073 Set C Q.No. 4 Predict whether the following reaction will occur spontaneously or not. Why?[1+1]**
$Pb^{2+} + 2Ag \longrightarrow 2Ag^{+} + Pb$
given,
$E^{0}_{Ag^{+}/Ag} = +0.80\ V$
$E^{0}_{Pb^{+2}/Pb} = -0.13\ V$

The given reaction is



The cell notation is
$Ag / Ag^{+} // Pb^{2+} / Pb$
Left Right
$E^{o}_{Cell} = E^{o}_{R} - E^{o}_{L} = -0.13 - (+0.80) = -0.13 - 0.80 = -0.93\ V$
Since, the E^{o}_{Cell} is negative, the reaction is non-spontaneously.

---

11. **2073 Set D Q.No. 4 Predict whether the following reaction will occur spontaneously or not. Why?[1+1]**
$Pb^{2+} + 2Ag \longrightarrow 2Ag^{+} + Pb$
given,
$E^{0}_{Ag^{+}/Ag} = +0.80\ V$
$E^{0}_{Pb^{2+}/Pb} = -0.13\ V$

Please refer to 2073 Set C Q No. 4

---

12. **2072 Supp. Q.No. 4 What is meant by single electrode potential? How is it measured?** **[1+1]**

Single electrode potential: When a metal is dipped in a solution containing its own ion, a potential is developed between them. This is called single electrode potential. It is measured by the separation of charges between the metal electrode and its solution. Example, when zinc metal rod is immersed into the zinc sulphate solution, zinc metal lose electron and zinc ion is formed. The zinc ions pass into the solution leaving behind the electrons in the metal surface.

---

13. **2072 Set C Q.No. 4 Calculate the number of coulombs required to deposit 40 g of aluminium from molten Al_2O_3.** **[2]**

Al_2O_3 ionizes as

$Al_2O_3 \longrightarrow 2Al^{+++} + 3O^{--}$

Reduction of Al^{+++} is
$Al^{+++} + 3e^{-} \longrightarrow Al$
1 mole 3 mole
27 g

27 g of Al^{+++} requires 3 mole of e^{-}

1 g of Al^{+++} requires $\frac{3}{27}$ mole of e^{-}

40 g of Al^{+++} requires $\frac{3}{27} \times 40$ mole of e^{-} = 4.44 mole of e^{-}

We know that,
1 mole of electron carries 96500 coulomb charge
4.44 mole of electron carry 4.44 × 96500 coulomb charge = 428460 coulomb charge

---

14. **2072 Set D Q.No. 4 Why does $AgNO_3$ solution become bluish when copper rod is dipped in it? (The standard reduction potential of Cu and Ag are +0.3V and +0.8V respectively).** **[1+1]**

The reduction potential of Cu is lower than Ag.
Cu = +0.3 V
Ag = + 0.8 V
The copper is oxidized when dipped in $AgNO_3$ solution and becomes bluish
$2AgNO_3 + Cu \longrightarrow \underset{\text{Bluish}}{Cu(NO_3)_2} + 2Ag$

---

15. **2072 Set E Q.No. 4 What is meant by standard hydrogen electrode? Write an important use of it. [1+1]**

Standard hydrogen electrode: A hydrogen electrode in which the pressure of hydrogen gas is maintained as 1 atm and the concentration of H^{+} ion in the solution is 1 M is called standard hydrogen electrode. It is used as primary reference electrode for measuring the EMF of other electrodes.

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16. **2071 Supp. Q.No. 4 How many coulombs of electric charge are required to deposit?**
i. 4.6 g of sodium **ii. 3 mole of aluminium** **[1+1]**

i. $Na^{+} + e^{-} \longrightarrow Na$
1 mole 1 mole 1 mole
1 mole of Na requires 1 mole of e^{-}
23 g of Na requires 1 mole of e^{-}

4.6 g of Na requires $\frac{1}{23} \times 4.6 = 0.2$ mole of e^{-}

We know that,
1 mole of e^{-} deposits 96,500 C
0.2 mole of e^{-} deposits 96,500 × 0.2 C = 19,300 C

ii. $Al^{+++} + 3e^{-} \longrightarrow Al$
1 mole 3 mole 1 mole
1 mole Al = 3 mole e^{-}
3 mole Al = 9 mole e^{-}

We know that,
1 mole e^{-} = 96,500 C
9 mole e^{-} = 9 × 96,500 C = 868,500 C

---

17. **2071 Set C Q.No. 4 What is meant by single electrode potential? Name any two factors that affect the magnitude of single electrode potential.** **[2]**

Single electrode potential: When a metal (M) is dipped in a solution containing its own ion (M^{++}), a potential is developed between them. This is called the single electrode potential. It is denoted by E. The two factors that affect the magnitude of single electrod potential are temperature and concentration of solution.

18. **2071 Set D Q.No. 4 How would you justify that value of one Faraday is 96500 coulumbs?** [2]

One Faraday is the charge required to deposit 1 g equivalent of the substance.

Let us suppose three different electronic reactions-

$Na^{+} + e^{-} \longrightarrow Na$

1 mole 1 mole 1 mole

Equivalent Weight = Valency

Equivalent Weight = 1 = 1g Equivalent Weight

$Cu^{++} + 2e^{-} \longrightarrow Cu$

2 mole 2 mole 1 mole

Equivalent Weight = Valency

Equivalent Weight = 2 = 2g Equivalent Weight

$Co^{+++} + 3e^{-} \longrightarrow Co$

3 mole 3 mole 1 mole

Equivalent Weight = Valency

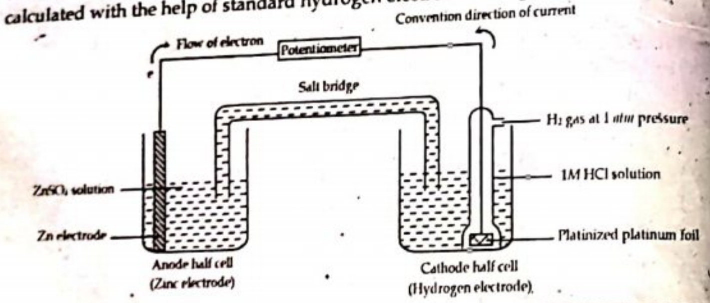
Equivalent Weight = 3 = 3g Equivalent Weight

From these three reactions we can conclude that to deposite 1 g equivalent weight of the substance we need one mole of the electron. Therefore, 1 faraday charge is numerically equal to charge on one mole of the electron which is equal to 96500 C

$1\ Faraday = 1.6 \times 10^{-19}\ C \times 6.02 \times 10^{23} = 96500$ Coulomb

19. **2070 Supp. Q.No. 4 2070 Set C Q.No. 4 Mention important application of standard hydrogen electrode giving example.** [2]

Standard hydrogen electrode is used as a primary reference electrode for measuring the emf of all other electrodes. Example: Standard electrode potential of zinc electrode is calculated with the help of standard hydrogen electrode through salt bridge.



20. **2069 (Set A) Q.No. 4 What do you mean by electrolytic conduction?** [2]

Electrolytic conduction: The flow of current through electrolytic conductor is called electrolytic conduction. The passage of current through electrolytic conductors results in transfer of ions. Example: fused salts, aqueous solution of acid, base and salts etc.

21. **2069 Supp. Set B Q.No. 4 Standard hydrogen electrode acts as both an anode and cathode. Give reason.** [2]

Standard hydrogen electrode (SHE) i.e. normal hydrogen electrode: The electrode potential of SHE is assumed to be zero and can act as both anode and cathode while determining the potential of other electrode. If the electrode acts as a positive pole in the cell, it is assigned as positive sign. On the other hand, if the electrode acts as a negative pole in the cell, the electrode potential is assigned negative value.

22. **2068 Q.No. 14 Define the term:**
    - i. **Electrochemical equivalent**
    - ii. **Equivalent conductance** [2]

i. **Electrochemical equivalent:** Faraday is the quantity of charge which will deposit one gram equivalent of the substance. i.e. 1 Faraday of charge deposit 1 gram equivalent or 96500 coulombs of charge deposit 1 g equivalent substance

1 coulomb of charge deposit $\frac{E\ g}{96500}$ equivalent substance

As, Electrochemical equivalent is the mass deposited by passing 1 C charge therefore,

$$Z = \frac{E\ g}{96500}$$

$$Z = \frac{E}{F}$$

This equation is used to calculate electrochemical equivalent from chemical equivalent or vice-versa.

ii. **Equivalent conductance:** It is defined as the conductance given by certain volume of electrolytic solution which is prepared by dissolving 1 g eqv. Electrolyte and placed between two parallel electrode of 1 cm apart and sufficiently large enough to contain whole solution. It is represented by λ.

Let us suppose V cc of the electrolytic solution is prepared by dissolving 1 g eqv. electrolyte. As know conductance due to 1 cc electrolytic solution i.e. K then Conductance due to V cc of electrolytic solution is KV

$\lambda = KV$

To prepare N normal solution N g equivalent should be dissolved in 1000 cc

To prepare N normal solution 1 g equivalent should be dissolved in $\frac{1000}{N}$.

$$\lambda = KV = K\frac{1000}{N}$$

Unit: $\frac{\text{Siemen cm}^{-1}}{\text{No. of g eqv.} \times \text{cm}^{-3}} = \text{Siemen cm}^{2}\ \text{g eqv.}^{-1}$

23. **2067 Q.No. 13 Can a solution of 1 M $ZnSO_4$ be stored in a vessel made up of Nickel? If not why?** [2]

Given

$E^0_{Ni^{++}/Ni} = -0.25\ V$

$E^0_{Zn^{2+}/Zn} = -0.76\ V$

Given,

$E^o_{Ni^{++}/Ni} = -0.25\ V$

$E^o_{Zn^{++}/Zn} = -0.76\ V$

From given data the reduction potential of Zn is lower than Ni. It means $ZnSO_4$ and Ni comes in contact. Ni gets reduced. So, $ZnSO_4$ can safely store in a Ni vessel.

24. **2066 Q. No. 13 Will the reaction occur: $Zn^{++} + 2Fe^{++} \longrightarrow Zn + 2Fe^{+++}$**

Given standard reduction potentials are: [2]

$E^{\circ}_{Zn^{++}/Zn} = -0.76V,$

$E^{\circ}_{Fe^{3+}/Fe} = +0.80\ V.$

Given reason.

Given reaction is

$Zn^{++} + 2Fe^{++} \longrightarrow Zn + 2Fe^{+++}$

Oxidation:

$2Fe^{++} \longrightarrow 2\ Fe^{+++} + 2e^{-}$

Reduction:

$Zn^{++} + 2e^- \longrightarrow 2Zn$

So, Fe^{++} / Fe^{+++} acts as anode

And Zn^{++} / Zn acts as cathode

∴ Emf of the cell = $E_{cathode} - E_{anode}$ = $(-0.76 - 0.8) = -1.56$ V

If the emf of cell is + ve then, the reaction is feasible. So, the given reaction is not feasible.

---

25. **2065 Q.No. 13 Can a solution of 1 M $CuSO_4$ be stored in a vessel made of nickel metal? If not, why?**

Given: $E^\circ_{Ni^{++}/Ni} = -0.25$ V; $E^\circ_{Cu^{++}/Cu} = 0.34$ V **[2]**

➢ Given, $E^\circ_{Ni^{++}/Ni} = -0.25$ V

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

From given data the reduction potential of Cu is higher than Ni. It means if $CuSO_4$ and Ni comes in contact. Ni gets oxidized and passes into the solution. So, $CuSO_4$ can't store in a Ni vessel.

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26. **2064 Q.No. 13 How is single electrode potential originated?** **[2]**

➢ The single electrode potential is originated by the separation of charges between the metal electrode and its solution. When a metal is dipped into a solution of its own ions, the metal atom ionizes and the ions pass into the solution leaving behind the electrons in the metal surface. This process results in the separation of charges. Similarly, if the metal ions have relatively greater tendency to take electrons from the electrode, the process is reversed which result in the separation of charges. This causes the origin of single electrode potential.

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27. **2063 Q.No. 15 What is meant by:**
    - **i. One ampere current is passing through a solution.**
    - **ii. The standard reduction potential of Cu^{++}/Cu is 0.34 V.** **[2]**

➢

i. The flow of charge at the rate of 1 coulomb per second is known as one ampere.

ii. Absolute electrode potential of a single electrode cannot be determined. A reference electrode hydrogen is used which is known as standard hydrogen electrode. The electrode potential for the standard hydrogen electrode is taken as zero. When Cu^{2+}/Cu electrode is connected with standard hydrogen electrode, observed emf of the cell is 0.34V which is standard reduction potential.

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28. **2060 Q.No. 18 Define the terms**

i. Cell constant and **ii. Molar conductivity.** **[2]**

➢

i. ***Cell constant:*** *The conductivity of cell is designed in such a way that the ratio between length of the two electrodes and their cross-sectional area is made constant which is constant for every conductivity cell.*

Mathematically, cell constant $= \frac{l}{a}$

Numerically, cell constant $= \frac{\text{Specific conductance}}{\text{Observed conductance}}$

Unit $= \frac{l}{a} = \frac{cm}{cm^2} = cm^{-1}$

ii. Molar conductance or molar conductivity

It is defined as the conductance due to certain volume of electrolytic solution prepared by dissolving 1 mole of electrolyte and kept between two parallel electrode 1 cm apart and sufficiently large enough to contain whole solution. It is represented by μ

If V cc of the electrolytic solution is prepared by dissolving 1 mole electrolyte then,

Conductance due to 1 cc of electrolytic solution is K

Conductance due to V cc of electrolytic solution is KV

Again,

To prepare M molar solution M no. of moles should be dissolved in 1000 cc

To prepare M molar solution 1 mole should be dissolved in $\frac{1000}{M}$ cc

So, $\mu = \frac{K \times 1000}{M}$ Unit = Siemen $cm^2 mol^{-1}$

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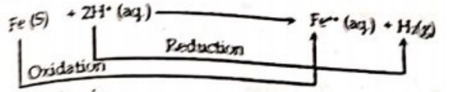
29. **2058 Q.No. 14 Construct a galvanic cell in which the cell reaction is:** **[2]**

$Fe(s) + H_2SO_4(aq.) \longrightarrow FeSO_4(aq.) + H_2(g)$

➢ The given cell reaction is

$Fe(s) + H_2SO_4(aq.) \longrightarrow FeSO_4(aq.) + H_2(g)$, Pt



Cell notation is

$Fe(s) / Fe^{++}(aq.)$ // $H^+(aq.) / H_2(g)$

Anode Salt bridge Cathode

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30. **2057 Q.No. 14 Define standard electrode potential.** **[2]**

➢ **Standard electrode potential:** The potential of an electrode measured against normal hydrogen electrode under standard condition i.e. T = 298K, concentration = 1M, pressure = 1 atm is called standard electrode potential.

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31. **2056 Q.No. 8 How does specific conductance decreases and equivalent conductance increases with dilution?** **[2]**

➢ **Effect of dilution on specific conductance:**

With increase in dilution, the specific conductance will decrease. It is due to decrease in number of ions per cm³. The decrease in specific conductance will be sharp or abrupt for strong electrolyte but will be gradual for weak electrolyte. With increase in dilution, degree of dissociation will also increase which is not possible in case of strong electrolyte.

Effect of dilution on equivalent conductance (λ): With increase in dilution, the equivalent Conductance will increase. The increase in equivalent conductance with increase in dilution will be sharp for weak electrolyte and will be slow for strong electrolyte. The value of conductance depends on (i) number of ions (ii) speed of ions.

In case of strong electrolyte the increase in equivalent conductance is only due to increase in speed of the ions because with increase in dilution force of attraction between ions will decrease.

In case of weak electrolyte, the increase in equivalent conductance with increase in dilution is sharp. It is because of number of ions will also increase.

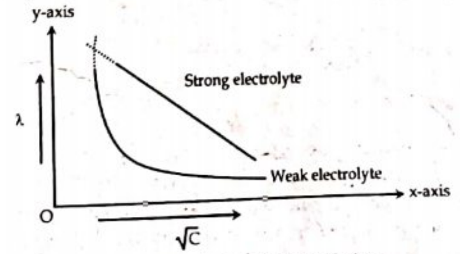


Fig: Variation of eqivalent conductance (λ) with dilution

32. 2055 Q.No. 3 **State Faraday's Second Law.** [2]

- Statement: If the same quantity of electricity is allowed to pass through the solutions of different electrolytes, then the amount of different substance or ions deposited or liberated at respective electrode are proportional to their chemical equivalent or equivalent weight.

  Mathematically,

  $W \propto E$

  or, $W = KE$

  or, $\frac{W}{E} = K$ (where, K = constant)

33. 2054 Q.No. 4 **Define the term electrochemical equivalent.** [2]

- The amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second. i.e. 1 coulombs charge is called electrochemical equivalent. It is denoted by symbol Z.

34. 2053 Q.No. 4 2052 Q.No. 4 **What is E.C.E. (Electro-chemical Equivalent)?** [2]

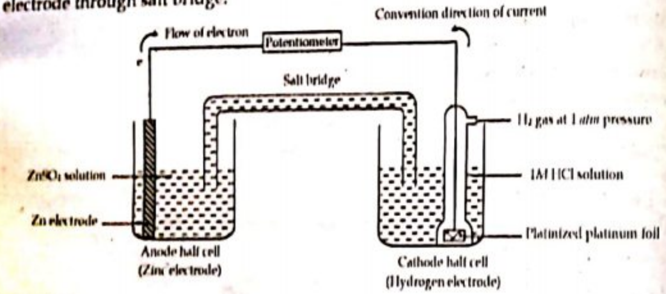
- Please refer to 2054 Q No 4

SHORT ANSWER QUESTIONS [5 MARKS]

35. 2076 Set B Q.No. 24 2076 Set C Q.No. 24 **Mention the important applications of standard hydrogen electrode. The standard electrode potential for Fe^{+3}/Fe^{+2} and I_2/I^- are + 0.77 V and +0.54 V respectively.**

    i. Draw the standard cell notation.
    ii. Identify the anode and cathode as the current drawn from it.
    iii. Write the cell reaction taking place at the electrodes.
    iv. Calculate standard cell potential. [1+1+1+1+1]

- **Standard hydrogen electrode:** Standard hydrogen electrode is used as a primary reference electrode for measuring the emf of all other electrodes. Example: Standard electrode potential of zinc electrode is calculated with the help of standard hydrogen electrode through salt bridge.



Numerical:

Given, The standard electrode potential for $Fe^{+3}/Fe^{+2} = +0.77$ V

The standard electrode potential for $I_2/I^- = +0.54$ V

i. The standard cell notation is given as

$I^-(aq) / I_2(aq)$ // $Fe^{++}(aq) / Fe^{++}(aq)$

Anode Cathode

+0.54 V +0.77 V

ii. $I_2/I^- = +0.54$ V < $Fe^{+3}/Fe^{+2} = +0.77$ V

Iodine (I_2) acts as anode which undergoes oxidation whereas Iron (Fe) acts as cathode which undergoes reduction.

$2I^- \longrightarrow I_2 + 2e^-$

$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{+2}$

iii. Net cell reaction: $2I^- + 2Fe^{+++} \longrightarrow I_2 + 2Fe^{++}$

iv. $E^\circ Cell$: $E^\circ Cathode - E^\circ Anode = (+0.77 - 0.54) = +0.23$ V

Hence, the standard cell potential is +0.23 V.

36. 2075 GIE Q.No. 24 **State and explain Faraday's 1st law of electrolysis. An electrolytic cell contains a solution of $CuSO_4$ and anode of impose copper. How many Kg of copper will be deposited at cathode by 150 ampere passing for 12 hours?** [2+3]

Faraday's 1st law of electrolysis

- **Statement:** "The amount of substance deposited or liberated at electrode during electrolysis is directly proportional to the quantity of electricity passed through the solution"

  If W be the weight of substance deposited by the passage of Q coulombs of charge then,

  $W \propto Q$ where, Q is the quantity of charge.

  $W = Zct$ where, Z is the proportionality constant called Electrochemical Equivalent.

  If 'c' be the current in ampere and 't' be the time in second then $c = \frac{Q}{t}$

  or, $Q = ct$

  When c = 1 ampere and t = 1 sec. then,

  $W = Z$

  Therefore, the electrochemical equivalent of a substance is defined as the amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second i.e. 1 coulombs charge.

  Numerical:

  Given,

  Current (I) = 150A

  Time (t) = 12 hr = 12 × 60 × 60 = 43200 sec

  Equivalent weight of copper (E) = 31.75

  Weight of copper deposited (W) = ?

  We know that,

  $W = ZIt$

  or, $W = \frac{E}{9650} It$

  or, $W = \frac{31.75}{96500} \times 150 \times 43200$

  or, $W = 2131.92$ g

  ∴ $W = 2.13192$ Kg

  Hence, the weight of copper deposited is 2.13192 Kg.

37) 2075 Set A Q.No. 24 **What is meant by (i) molar conductivity and (ii) Electro-chemical equivalent? How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal of surface area 80 cm² with 0.005 mm thick layer (Density of Ag = 10.5 g/cm²)** [2+3]

- i. **Molar conductivity:** The conductance offered by solution prepared by dissolving 1 mole of solute when the whole solution is placed between two parallel electrodes at 1 cm apart with area of cross-section of each electrode 1 cm² is called molar conductivity.

  ii. **Electro-chemical equivalent:** The amount of in gram deposited at either of the electrode during electrolysis due to flow of one ampere current for one second is called electro-chemical equivalent.

Numerical:

Given,

Current (I) = 3 A

Area of metal (A) = 80 cm^2

Thickness of silver = 0.005 mm = 0.0005 cm

Density of silver (d) = 10.5 g/cm^2

Equivalent of silver (E) = 108

Time (t) = ?

We know that

Volume = Area × thickness

Volume = 80 × 0.0005 = 0.04 cm^3

We know that

W = Density × Volume

W = 10.5 × 0.04 = 0.42 g

We know that

W = ZIt

or, $W = \frac{E}{96500} It$

or, $0.42 = \frac{108}{96500} \times 3 \times t$

or, t = 125 second

Hence, time required to deposit silver on metal surface = 125 second.

---

38. **2075 Set B Q.No. 23** **What is meant by standard hydrogen electrode? Write its important application. The standard electrode potentials are given as**

$E^\circ Zn/Zn^{+2} = -0.76V$

$E^\circ Fe^{+3}/Fe^{+2} = +0.77V$

- **i. Construct a cell notation for a galvanic cell indicating anode and cathode.**
- **ii. Calculate the e.m.f. at 1M solution of ions.**
- **iii. Will the reaction $Zn^{2+} + 2Fe^{2+} \longrightarrow Zn + 2Fe^{3+}$ Occur?** **[2+3]**

Standard hydrogen electrode: A standard hydrogen electrode is a reference electrode which is used on all half cell potential reactions. Its value is zero

Numerical:

Given,

$E^\circ Zn/Zn^{+2} = -0.76V$

$E^\circ Fe^{+3}/Fe^{+2} = +0.77 V$

*i. **Cell notation is***

$Zn/Zn^{+2} // Fe^{+3}/Fe^{+2}$

Anode Cathode

–ve charged +ve charged

Here,

$E^\circ Fe^{+3}/Fe^{+2} > E^\circ Zn/Zn^{+2}$

∴ Zn acts as anode which undergoes oxidation and Fe acts as cathode where reduction takes place.

*ii. **Emf of cell***

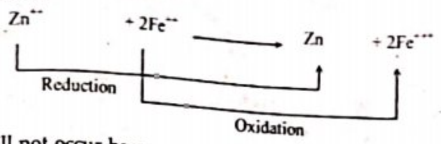
E° cell = E° red (cathode) – E° red (anode)

= + 0.77 – (–0.76)

= + 0.77 + 0.76

= + 1.53 V

iii. The given reaction is



This reaction will not occur because standard electrode potential of Fe^{+3}/Fe^{+2} is greater than Zn/Zn^{+2}

---

39. **2074 Supp. Q.No. 23** **What is meant by hydrogen electrode? Mention it's an important use. The standard electrode potentials are given as:**

$E^\circ Mg^{++}/Mg = -2.37$ V, $E^\circ Cu^{++}/Cu = +0.34V$

- **i. Construct a cell notation for an electrochemical cell.**
- **ii. Write the reactions taking place at anode and cathode.**
- **iii. Calculate the emf of the cell.** **[2+3]**

Hydrogen electrode: The Standard hydrogen electrode (abbreviated SHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. It is an example of of primary reference electrode.

Numerical:

The standard electrodes potential are

$E^\circ Mg^{++}/Mg = -2.37$ V,

$E^\circ Cu^{++}/Cu = +0.34V$

i. The cell notation is as

$Mg(s)/Mg^{++}(1M)//Cu^{++}(1M)/Cu(s)$

Anode Cathode

-2.37 V +0.34V

ii. Mg acts as anode which undergoes oxidation and Cu acts as cathode where reduction takes place.

$Mg \longrightarrow Mg^{++} + 2e^-$ (Oxidation)

$Cu^{++} + 2e^- \longrightarrow Cu$ (Reduction)

ii. Emf of cell

E° cell = E° red(cathode) – E° red(anode)

= +0.34 – (-2.37)

= +0.34 + 2.37

= + 2.71 V

Hence, the emf of 1M solution is +2.71V.

---

40. **2074 Set A Q.No. 23** **What is meant by primary reference electrode? Mention its one important use. The standard electrode potential of copper and silver are;**

[$E^\circ Cu^{++}/Cu = +0.34$ V and $E^\circ Ag^+/Ag = +0.80$ V]

- **I. Construct cell notation for an electrochemical cell.**
- **ii. Calculate the emf at 1M solution of its ions.**
- **iii. Will the reaction occur?**
  $Cu + 2 Ag^+ \longrightarrow Cu^{++} + 2 Ag$? Give reason. **[2+3]**

A primary reference electrode is an electrode which has a stable and well-known electrode potential. Standard Hydrogen Electrode is an example of primary reference electrode. A Standard Hydrogen Electrode (SHE) is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations.

Numerical:

Given,

$E^\circ Cu^{++}/Cu = +0.34$ V

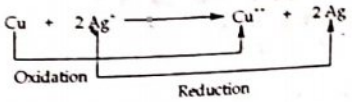
$E^\circ Ag^+/Ag = +0.80V$

i. Cell notation is given as:

Cu/Cu^{++} // Ag^+/Ag
Anode Cathode
Oxidation Reduction
+0.34V +0.80V

ii. Emf of cell $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = +0.80 - (+0.34) = +0.80 - 0.34 = +0.46V$

iii. The cell reaction is given as:



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

The oxidation occurs at anode and reduction occurs at cathode. The value of emf is +ve. Hence, reaction occurs spontaneously.

---

41. 2074 Set B Q.No. 23 Name a primary reference electrode and mention its one important use. For a cell;

$Mg(s)/Mg^{++}(1M)//Cu^{++}(1M)/Cu(s)$ **[2+3]**

$E^\circ Mg^{++}/Mg = -2.37$ V and $E^\circ Cu^{++}/Cu = +0.34$ V

i. Indicate cathode and anode.

ii. Write the reaction taking place at electrode.

iii. Calculate the emf at 1M solution of its ions.

A primary reference electrode is an electrode which has a stable and well-known electrode potential. Standard Hydrogen Electrode is an example of primary reference electrode. A Standard Hydrogen Electrode (SHE) is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations.

Numerical:

The given cell notation is as:

$Mg(s)/Mg^{++}(1M)//Cu^{++}(1M)/Cu(s)$
Anode Cathode
-2.37 V +0.34V

i. $Mg(s)/Mg^{++}$ is anode and $Cu^{++}/Cu(s)$ is cathode.
$E^\circ Cu^{++}/Cu = +0.34 V > E^\circ Mg^{++}/Mg = -2.37 V$

ii. Mg acts as anode which undergoes oxidation and Cu acts as cathode where reduction takes place.

$$Mg \longrightarrow Mg^{++} + 2e^- \text{ (Oxidation)}$$

$$Cu^{++} + 2e^- \longrightarrow Cu \text{ (Reduction)}$$

iii. Emf of cell
$E^\circ cell = E^\circ red(cathode) - E^\circ red(anode) = +0.34 - (-2.37) = +0.34 + 2.37 = + 2.71 V$
Hence, the emf of 1M solution is +2.71V.

---

42. 2073 Supp Q.No. 23 How do molar and equivalent conductivity vary with concentration for weak electrolyte? A solution contains 2 g of anhydrous $BaCl_2$ in 400cm³. It's conductivity is found to be 5.8 × 10^{-3} cm^{-1}. Calculate the molar conductivity of $BaCl_2$. (Atomic weight of Ba = 137) **[3+2]**

Variation of electrolytic conductances with concentration: With increase in dilution, the specific conductance will decrease. It is due to decrease in number of ions per cm³. The decrease in specific conductance will be sharp or abrupt for strong electrolyte but will be gradual for weak electrolyte. With increase in dilution, degree of dissociation will also increase which is not possible in case of strong electrolyte.

Effect of dilution on equivalent conductance (λ): With increase in dilution, the equivalent Conductance will increase. The increase in equivalent conductance with increase in dilution will be sharp for weak electrolyte and will be slow for strong electrolyte. The value of conductance depends on (i) number of ions (ii) speed of ions.

In case of strong electrolyte the increase in equivalent conductance is only due to increase in speed of the ions because with increase in dilution force of attraction between ions will decrease.

In case of weak electrolyte, the increase in equivalent conductance with increase in dilution is sharp. It is because of number of ions will also increase.

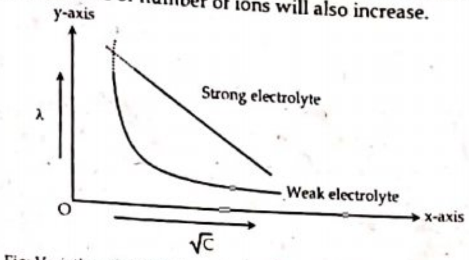


Fig: Variation of eqivalent conductance (λ) with dilution

Effect of dilution on molar conductance (μ): With increase in dilution, the molar Conductance will increase. The increase in molar conductance with increase in dilution will be sharp for weak electrolyte and will be slow for strong electrolyte. The value of conductance depends on (i) number of ions (ii) speed of ions.

In case of strong electrolyte the increase in molar conductance is only due to increase in speed of the ions because with increase in dilution force of attraction between ions will decrease.

In case of weak electrolyte, the increase in molar conductance with increase in dilution is sharp. It is because of number of ions will also increase.

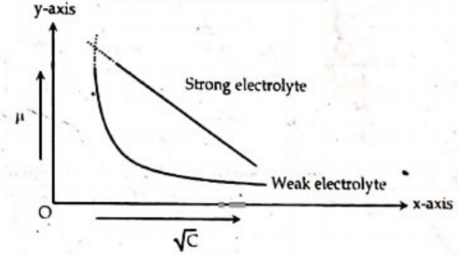


Fig: Variation of molar conductance (μ) with dilution

Numerical:

Given, weight of $BaCl_2$ = 2 g

Conductivity or specific conductance (κ) = 5.8 × 10^{-3} S cm^{-1}

Molar conductivity (μ) = ?

Molecular mass of $BaCl_2$ = (137 + 2 × 35.5) = 208

$$\text{No. of mole of } BaCl_2 \text{ (n)} = \frac{\text{Given weight}}{\text{Molecular weight}} = \frac{2}{208} = 9.6 \times 10^{-3} \text{ mol}$$

$$\text{Volume of } BaCl_2 \text{ solution} = 400 \text{ cm}^3 = \frac{400}{1000} = 0.4 \text{ L}$$

$$\text{Molarity of } BaCl_2 \text{ (M)} = \frac{\text{No. of mole}}{\text{Volume of solution in L}} = \frac{9.6 \times 10^{-3}}{0.4} = 0.024 \text{ M}$$

i. **Electrochemical equivalent:** The amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second. i.e. 1 coulombs charge is called electrochemical equivalent. It is denoted by symbol Z.

ii. **Standard electrode potential:** The potential of an electrode measured against normal hydrogen electrode under standard condition i.e. T = 298K, concentration = 1M, pressure = 1 atm is called standard electrode potential.

Numerical:

i. 80 g of aluminium from molten Al_2O_3

Given,

Wt. of Al = 80 g

No. of Coulombs = ?

Al_2O_3 ionizes as

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{--}$$

Reduction of Al^{3+} as

$$\underset{\substack{1\text{ mole}\\27\text{ g}}}{Al^{3+}} + \underset{3\text{ mole}}{3e^-} \longrightarrow \underset{1\text{ mole}}{Al}$$

27 g of Al^{3+} requires 3 mole electron for reduction

1 g of Al^{3+} requires $\frac{3}{27}$ mole electron for reduction

80 g of Al^{3+} requires $\frac{3}{27} \times 80$ mole electron for reduction

= 8.88 mole electron

We know that

1 mole electron carry 96500 coulomb charge

8.88 mole electron carry 96500 × 8.88 coulomb charge

= 856920 coulomb charge

Hence, 80 g of aluminum requires 856920 coulomb charge

ii. 24 g of magnesium from $MgCl_2$

Given,

Wt. of Mg = 24 g

No. of coulomb = ?

$MgCl_2$ ionizes as

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

Reduction of Mg^{+2} as

$$\underset{\substack{1\text{ mole}\\24\text{ g}}}{Mg^{+2}} + \underset{2\text{ mole}}{2e^-} \longrightarrow \underset{1\text{ mole}}{Mg}$$

24 g magnesium requires 2 mole electron for reduction.

We know that

1 mole of electron carries 96500 coulomb charge.

2 mole of electron carry 2 × 96500 coulomb charge

= 193000 coulomb charge

Hence, 24 g of magnesium requires 19300 coulomb charges.

---

47. 2072 Set E Q.No. 28 State Faraday's laws of electrolysis? Silver is electrodeposited on a metal plate of surface area 800 cm² by passing 0.2 ampere of current for 3 hours. Calculate the thickness of Ag deposited. (Given specific gravity of Ag = 10.47 and atomic mass = 108) [2+3]

Faraday's First law of electrolysis:

Statement: "The amount of substance deposited or liberated at electrode during electrolysis is directly proportional to the quantity of electricity passed through the solution"

If W be the weight of substance deposited by the passage of Q coulombs of charge then,

$W \propto Q$ where, Q is the quantity of charge.

$W = Zct$ where, Z is the proportionality constant called Electrochemical Equivalent.

If 'c' be the current in ampere and 't' be the time in second then $c = \frac{Q}{t}$

or, $Q = ct$

When c = 1 ampere and t = 1 sec. then,

$W = Z$

Therefore, the electrochemical equivalent of a substance is defined as the amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second i.e. 1 coulombs charge.

Faraday's second law of electrolysis:

Statement: If the same quantity of electricity is allowed to pass through the solutions of different electrolytes, then the amount of different substance or ions deposited or liberated at respective electrode are proportional to their chemical equivalent or equivalent weight.

Mathematically, $W \propto E$

or, $W = KE$

or, $\frac{W}{E} = K$ (Where, K = constant)

Let us suppose two different electrolytic solutions i.e. $AgNO_3$ and $CuSO_4$ through which same quantity of electricity is passed then,

$W_{Ag} \propto E_{Ag}$ ... (i)

$W_{Cu} \propto E_{Cu}$ ... (ii)

From equation (i) and (ii)

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{Cu}}{E_{Cu}}$$

$$\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}}$$

This equation can be used to determine the equivalent weight of substance.

Numerical:

Given, surface area of metal plate (A) = 800 cm²

Current (I) = 0.2 A

Time (t) = 3 hours = 3 × 60 × 60 = 10800 second

Thickness of silver deposited (l) = ?

Specific gravity or density silver (d) = 10.47

Atomic mass of silver = 108

Valency of silver = 1

Equivalent weight of silver = 108

We know that,

$W = ZIt$

Or, $W = \frac{E}{F} It$

Or, $W = \frac{108 \times 0.2 \times 10800}{96500} = 2.41$ g

Mass of silver (W) = 2.41 g

Volume of silver (V) = ?

We know that,

$$D = \frac{W}{V}$$

$$\text{Or, } V = \frac{W}{D}$$

$$\text{Or, } V = \frac{2.41}{10.47} = 0.23\ \text{cm}^3$$

Again,

Volume = Area × Thickness

$$\text{Or, Thickness} = \frac{\text{Volume}}{\text{Area}} = \frac{0.23}{800} = 2.875 \times 10^{-4}\ \text{cm}$$

Hence, the thickness of silver deposited is 2.875×10^{-4} cm.

---

48. 2071 Supp. Q.No. 23 What is meant by electrochemical cell? Design a Galvanic cell in which the reaction
$Zn(s) + 2Ag^+ (aq.) \longrightarrow Zn^{2+}(aq.) + 2Ag(s)$, takes place. Further predict. **[1+2+1+1+1]**

i. Which of the electrode is negatively charged?
ii. The carriers of the current in the cell.
iii. Individual reaction at each electrode.

Electrochemical cell: A system consisting of two electrodes dipping in the same or different electrolytic solutions for electrical communication is called electrochemical cell.

Given reaction is

$Zn\ (s) + 2\ Ag^+\ (aq.) \longrightarrow Zn^{2+}\ (aq.) + 2\ Ag\ (s)$

i. The cell notation is

$(-)\ Zn/Zn^{++}\ (1M)\ //\ 1M\ 2Ag^+\ /\ 2Ag\ (+)$

Oxidation / Negative pole/ Anode

$Zn \longrightarrow Zn^{++} + 2e^-$

Reduction / positive pole / cathode

$2\ Ag^+ + 2e^- \longrightarrow 2\ Ag$

ii. If two electrodes are connected through ammeter, a current will flow from silver to zinc, electrode through an external circuit as indicated by the deflection in ammeter.

$Zn \longrightarrow Zn^{++} + 2e^-$

The electron liberated by oxidation of zinc will flow through the external circuit via ammeter to silver electrode and silver ion will be reduced to metallic silver.

$2Ag^+ + 2e^- \longrightarrow 2Ag$

iii. At anode oxidation take place by loosing electron

$Zn \longrightarrow Zn^{++} + 2e^-$

At cathode reduction takes place by gaining electron

$2Ag^+ + 2e^- \longrightarrow 2Ag$

---

49. 2071 Set D Q.No. 23 What is meant by electrochemical cell? Design a Galvanic cell in which the reaction *$Zn(s) + 2Ag^+ (aq.) \longrightarrow Zn^{2+} (aq.) + 2\ Ag\ (s)$* takes place. Further predict:

a. Which of the electrode is negatively charged
b. The carriers of the current in the cell
c. Individual reaction at each electrode **[5]**

Electrochemical cell: *It is an arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by salt bridge.*

There are two type of electrochemical cell:

Electrolytic cell*: In this cell electricity produces chemical energy.*

Galvanic cell*: In this cell, electricity is produced by chemical reaction.*

Numerical:

Given reaction is

$Zn(s) + 2Ag^+(aq.) \longrightarrow Zn^{+2}(aq.) + 2Ag(s)$

Oxidation half cell reaction

$Zn(s) \longrightarrow Zn^{++}(aq.) + 2e^-$

Anode $\longrightarrow$ -vely charged.

Reduction half cell reaction

$2Ag^+(aq.) + 2e^- \longrightarrow 2Ag(s)$

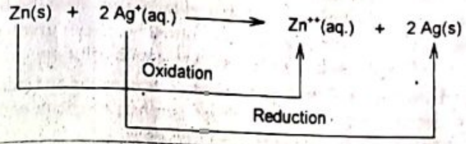
Cathode $\longrightarrow$ +vely charged.

The flow of electron occurs from anode to cathode Zn - Ag galvanic cell is represented as:

$Zn(s)\ /\ Zn^{++}(aq.)\quad //\quad Ag^+(aq.)\ /\ Ag(s)$

Anode　Salt bridge　Cathode

-ve charge　+ve charge



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50. **2070 Supp. Q.No. 23 State Faraday's IInd law of electrolysis. Equal amount current was passed through an aqueous solution of tri-valent metallic salt and dil. H_2SO_4. The volume of H_2 liberated was 96.5 mL at 27°C and 765 mm Hg pressure. The weight of the metal deposited was 0.74 g. Calculate the atomic weight of the metal.** **[5]**

Faraday's Second law of electrolysis: Please refer to 2072 Set E Q.No. 28

Numerical:

Given,

Valency of metal = 3

Volume of hydrogen (V) = 96.5 mL = 0.0965 litre

Temperature (T) = 27°C = (27 + 273) = 300 K

Pressure (P) = 765 mm Hg = 1.0065 atm

Weight of metal deposited (w) = 0.74 g

Atomic weight of metal = ?

Weight of H_2 (w) =?

Molecular weight of H_2 (M) = 2.016

We know that,

$$PV = nRT$$

$$PV = \frac{W}{M} RT$$

$$\text{or, } w = \frac{PV\,M}{RT}$$

$$\text{or, } w = \frac{1.0065 \times 0.0965 \times 2.016}{0.0821 \times 300}$$

$$\text{or, } w = 7.95 \times 10^{-3}\ \text{g}$$

We have,

Faraday 2nd law of electrolysis

$$\frac{\text{Weight of metal deposited}}{\text{Equivalent Weight of metal}} = \frac{\text{Weight of } H_2 \text{ liberated}}{\text{Equivalent Weight of } H_2}$$

$$\text{or, } \frac{0.74}{E} = \frac{7.95 \times 10^{-3}}{1.008}$$

Or, $E = \frac{0.74 \times 1.008}{7.95 \times 10^{-3}} = 93.82$

Equivalent weight of metal = 93.82

Atomic weight of metal = Equivalent Weight of metal × valency = (93.82×3)=281.47 amu.

Hence, the atomic weight of metal is 281.47 amu.

51. **2070 Set D Q.No. 28 Represent graphically the variation of equivalent conductivity of strong electrolyte and weak electrolyte with concentration. Why do equivalent conductivity of strong electrolyte and weak electrolyte vary differently with dilution?** [5]

First part: Please refer to 2073 Supp Q.No 23

Second part:

Strong electrolyte ionizes very fast with small dilution and the movement of ions is very fast due to this equivalent conductivity increase. But in the case of weak electrolyte, it ionizes slowly and movement of ions is very slowly. In such case the numbers of ions as well as their speed increase with increase in dilution. So, the equivalent conductivity of strong electrolyte and weak electrolyte vary different with dilution.

52. **2069 (Set B) Q.No. 27 Give any two differences between electrochemical and electrolytic cell. You are given zinc rod, copper rod, zinc sulphate and copper sulphate solutions and standard electrode potential of zinc and copper are –0.76 V and +0.34 V respectively.**

a. Represent an electrochemical cell indicating anode and cathode

b. Write net cell reactions

c. What will be the emf of the cell? [5]

Differentiate between electrochemical and electrolytic cell:

Electrochemical Cell(Voltaic cell)	Electrolytic Cell
1. It is the apparatus in which a chemical redox reaction produces electricity.	1. It is the apparatus in which chemical decomposition reaction is carried out by electricity.
2. It converts chemical energy into electrical energy.	2. It converts electrical energy into chemical energy.

Numerical:

Given,

$E^o_{Cu^{+2}/Cu} = +0.34\ V > E^o_{Zn/Zn^{+2}} = -0.76\ V$

So, zinc acts as anode and copper acts as cathode.

Galvanic cell can be constructed by using these two electrodes as:

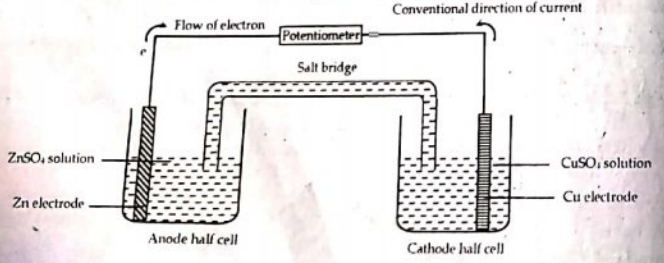


Fig: Galvanic or Voltaic Cell

Cell notation is

Zn / Zn^{+2} // Cu^{+2} / Cu

Anode Cathode

The cell reaction is

$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$

Emf of cell i.e. $E^o_{cell} = E^o_{red}\ (cathode) - E^o_{red}\ (anode)$

$= +0.34 - (-0.76) = (+0.34 + 0.76) = +1.10\ V$

Hence, the emf of cell is +1.10 V.

53. **2068 Q.No. 24 What is meant by standard electrode potential? The standard electrode potential for the following electrode are;**

$Zn^{++} + 2e^- \longrightarrow Zn,\ E^o = -0.76V$

$Fe^{+++} + e^- \longrightarrow Fe^{++},\ E^o = +0.77V$

i. Represent a suitable galvanic cell and point out which one will be cathode?

ii. With 1 M solutions of the ions what will be emf? [5]

iii. Will the reaction $Zn^{++} + 2Fe^{++} \longrightarrow Zn + 2Fe^{+++}$ occur? Give reason.

Standard electrode potential: The potential of an electrode measured against normal hydrogen electrode under standard condition i.e. T = 298K, concentration = 1M, pressure = 1 atm is called standard electrode potential.

Numerical:

i. Representation of galvanic cell i.e. cell notation is

Zn, / Zn^{++} // Fe^{+++} / Fe^{++}

Anode Cathode

-ve charged +ve charged

Here,

$E^o_{Fe^{+++}/Fe^{++}} > E^o_{Zn^{++}/Zn}$

Zn acts as anode which undergoes oxidation and Fe acts as cathode where reduction takes place.

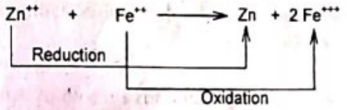
Net reaction is

$Zn + Fe^{+++} \longrightarrow Zn^{++} + 2Fe^{++}$

ii. Emf of cell i.e. $E^o_{cell} = E^o_{red}\ (cathode) - E^o_{red}\ (anode)$

$= (+0.77 - (-0.76)) = (+0.77 + 0.76) = +1.53\ V$

iii. The given reaction is



$Zn^{++} + Fe^{++} \longrightarrow Zn + 2Fe^{+++}$

No, in the given reaction Zn is reduced and Fe^{++} is oxidized which is not possible because standard electrode potential of Fe^{+++} / Fe^{++} is greater than Zn / Zn^{++}.

54. **2064 Q.No. 31(i) Write short notes on Variation of electrolytic conductances with concentration.** [5]

Please refer to 2073 Supp Q.No. 23

55. **2063 Q.No. 24 State and explain Faraday's second law of electrolysis. Show that the electric charge carried by transfer of 1 mole of electron is one Faraday.** [5]

Faraday's Second law of electrolysis: Please refer to 2072 Set E Q.No. 28

Numerical:

One Faraday is the charge required to deposit 1 g equivalent of the substance.

Let us suppose three different electronic reactions-

$Na^+ + e^- \longrightarrow Na$

1 mole 1 mole 1 mole

Equivalent Weight × Valency

Equivalent Weight × 1 = 1 g Equivalent Weight

$Cu^{++} + 2e^- \longrightarrow Cu$

2 mole 2 mole 1 mole

Equivalent Weight × Valency

Equivalent Weight × 2 = 2 g Equivalent Weight

$Co^{+++} + 3e^- \longrightarrow Co$

3 mole 3 mole 1 mole

Equivalent Weight × Valency

Equivalent Weight × 3 = 3 g Equivalent Weight

From these three reactions we can conclude that to deposite 1 g equivalent weight of the substance we need one mole of the electron. Therefore, 1 faraday charge is numerically equal to charge on one mole of the electron which is equal to 96500 C

1 Faraday = 1.6×10^{-19} C × 6.02×10^{23} = 96500 Coulomb

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56. 2061 Q.No. 26 Distinguish between (a) electrolytic and voltaic cells (b) oxidation and oxidizing agent. Four metals, labelled A, B, C and D react with each other and with acids in the following way: B displaces only C from solution. Only A and D displace hydrogen from 1M HCl. None of the metals will displace D from solution. Arrange the four metals in an activity series with hydrogen. **[5]**

a. Distinction between electrolytic cell and voltaic cell

Electrochemical Cell(Voltaic cell)	Electrolytic Cell
1. It is the apparatus in which a chemical redox reaction produces electricity.	1. It is the apparatus in which chemical decomposition reaction is carried out by electricity.
2. It converts chemical energy into electrical energy.	2. It converts electrical energy into chemical energy.

b. Distinction between oxidation and oxidizing agent:

Oxidation	Oxidizing agent
1. It involves the loss of electrons.	1. It is the chemical substance which oxidizes other substance but reduces itself.
2. Positive charge increases in the oxidized species.	2. It oxidizes others by accepting electrons.

According to the question, B displaces only C from solution. Only A and D displace hydrogen. B should be above than C but below than hydrogen in the seris. Thus, the series of metals with hydrogen are

H> B >C

Again, A and D displace hydrogen from acids i.e. both of them should be above than hydrogen in the series.

D >A >H>B> C

Again, none of the metals displace D from solution i.e. D should be at the top of series. Therefore, the arrangement of metal according to the reactivity are D>A>H>B>C

. 2060 Q.No. 27 How is single electrode potential originated? Predict which one of the following reactions occur spontaneously?

i. $2Fe^{+2} + Sn^{+4} \longrightarrow 2Fe^{+3} + Sn^{+2}$

ii. $2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$

Given standard reduction potentials of

Fe^{3+}/Fe^{2+} and Sn^{4+}/Sn^{2+} are + 0.77V and + 0.15V respectively. **[5]**

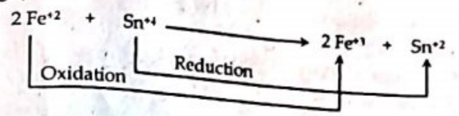
The single electrode potential is originated by the separation of charges between the netal electrode and its solution. When a metal is dipped into a solution of its own ions, he metal atom ionizes and the ions pass into the solution leaving behind the electrons in ie metal surface. This process results in the separation of charges. Similarly, if the metal ns have relatively greater tendency to take electrons from the electrode, the process is versed which result in the separation of charges. This causes the origin of single ctrode potential.

Numericals:

Given,

$E^o_{Fe^{+3}/Fe^{+2}} = + 0.77$ V

$E^o_{Sn^{+4}/Sn^{+2}} = + 0.15$ V



Cell notation is

Fe^{+2} / Fe^{+3} // Sn^{+4} / Sn^{+3}

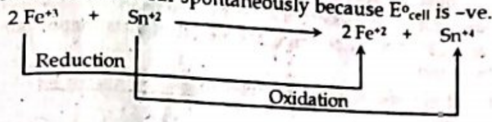
Anode Cathode

Emf of cell i.e. E^o_{cell} = E^o_{red} (cathode) – E^o_{red} (anode)

= (+0.15 – 0.77)

= – 0.62 V

Hence, the reaction does not occur spontaneously because E^o_{cell} is –ve.



Cell notation is

Sn^{+2} / Sn^{+4} // Fe^{+3} / Fe^{+2}

Anode Cathode

Emf of cell i.e. E^o_{cell} = E^o_{red} (cathode) – E^o_{red} (anode) = (+0.77 – 0.15) = +0.62 V

Hence, the reaction occurs spontaneously because E^o_{cell} is +ve.

NUMERICAL PROBLEMS:

58. 2073 Set D Q.No. 23 State Faraday's laws of electrolysis. Establish relationship between electrochemical equivalent and chemical equivalent. 0.197 g of copper is deposited by a current of 0.2 A in 50 minutes. Calculate its electrochemical equivalent. **[2+1+2]**

Faraday's laws of electrolysis: Please refer to **2072 Set E Q.No. 28**

Relationship between electrochemical equivalent (Z) and chemical equivalent (E):

We know from 1st law of electrolysis,

$W = ZIt$

If $I = 1$ A and $t = 1$ second

$W = Z$

We know form 2nd law of electrolysis,

$W \alpha E$

$\frac{W}{E} = \text{constant}$

Let, W_1 and W_2 are the amount of substance deposited or liberated and Z_1 and Z_2 are the electrochemical equivalent then

According to 1st law of electrolysis

$W_1 = Z_1$ and $W_2 = Z_2$

Combining both relations,

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} \quad \text{... (i)}$$

Similarly, according to 2nd law of electrolysis

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \quad \text{... (ii)}$$

From equatin (i) and (ii) we get

$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$ i.e. $Z \alpha E$

Hence, electrochemical equivalent (Z) of a substance is directly proportional to its chemical equivalent (E).

Numerical:

Given, Weight of copper deposited (W) = 0.197 g

Current in ampere (I) = 0.2 A

Time taken (t) = 50 minute = 50 × 60 = 3000 second

Electrochemical equivalent (Z) = ?

We know that,

W = ZIt

$$\text{Or, } Z = \frac{W}{It} = \frac{0.197}{0.2 \times 3000} = 0.00032 = 3.2 \times 10^{-4}\text{ g C}^{-1}.$$

Hence, the electrochemical equivalent of copper is 3.2×10^{-4} g C^{-1}.

---

59. **2070 Set C Q.No. 24 State Faraday's 2nd law of electrolysis. Equal amount of current was passed through an aqueous solution of trivalent metallic salt and dil. H_2SO_4. The volume of H_2 liberate was 96.5 mL at 27°C and 765 mm Hg pressure and weight of metal deposited was 0.74 g. Calculate atomic weight of the metal.** **[5]**

Faraday's 2nd law of electrolysis: Please refer to 2072 Set E Q.No. 28

Numerical:

Given,

Volume of hydrogen liberated (V_1) = 96.5 mL

Temperature (T_1) = 27°C = (27 + 273) = 300K

Pressure of gas (P_1) = 765 mm Hg

Weight of metal deposited (m) = 0.74 g

Valency of metal = 3

Atomic weight of metal (M) = ?

At standard condition

Temperature (T_2) = 273 K

Pressure (P_2) = 760 mm Hg

Volume of gas (V_2) = ?

According to the Combined gas equation,

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

$$\text{or, } V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

$$\text{or, } V_2 = \frac{765 \times 96.5 \times 273}{760 \times 300} = 88.39\text{ mL}$$

Hence, the standard volume of hydrogen gas is 88.39 mL

We know that,

22400 mL of hydrogen gas = 2 g of hydrogen gas

$$1\text{ mL of hydrogen gas} = \frac{2}{22400}\text{ g of hydrogen gas}$$

$$88.39\text{ mL of hydrogen gas} = \frac{2}{22400} \times 88.39\text{ g of hydrogen gas}$$

$$= 0.00789\text{ g}$$

Hence, the mass of hydrogen gas liberated is 0.00789 g

Equal amount of current was passed through an aqueous solution of trivalent metallic salt and dil. H_2SO_4. Faraday's 2nd law of electrolysis is applied.

$$\frac{\text{Weight of hydrogen gas liberated}}{\text{Equivalent weight of hydrogen}} = \frac{\text{Weight of metal deposited}}{\text{Equivalent weight of metal}}$$

$$\text{or, } \frac{0.00789}{1.008} = \frac{0.74}{\text{Equivalent weight of metal}}$$

$$\text{or, Equivalent weight of metal} = \frac{1.008 \times 0.74}{0.00789} = 94.53$$

We know that,

Atomic mass of metal = Equivalent weight × Valency = (94.53 × 3) = 283.61

Hence, the atomic weight of metal is 283.61 amu.

---

60. **2070 Set D Q.No. 4 How many number of coulombs are required to deposit 81 g of Aluminium when the electrode reaction is: $Al^{+++} + 3e^- \longrightarrow Al$?** **[2]**

The given reaction is

$$\underset{1\text{mole}}{Al^{+++}} + \underset{3\text{ mole}}{3e^-} \longrightarrow Al$$

Here,

1 mole of aluminium ion requires 3 moles of electrons i.e.

27 g aluminium = 3 mole electrons

$$1\text{ g aluminium} = \frac{3}{27}\text{ mole electrons}$$

$$81\text{ g aluminium} = \frac{3}{27} \times 81\text{ mole electrons} = 9\text{ mole of electrons}$$

Hence, 81 g of aluminium requires 9 moles of electrons.

We know that,

1 mole electron having charge 96500 coulomb

So, 9 mole of electron having charge 9 × 96500 coulomb = 868500 C

Therefore, 868500 coulomb charges are required to deposit 81 g of Al^{+3} into Al.

---

61. **2069 (Set A) Q.No. 25 Distinguish between electrochemical equivalent and chemical equivalent. A metallic spoon is coated with silver by passing a current of 5 ampere through $AgNO_3$ solution for 5 hrs. What is the thickness of silver plating if the area of the spoon is 12 cm^2 (density of silver is 10.5 g cm^{-3})?** **[5]**

Following are distinction between electrochemical equivalent and chemical equivalent:

Electrochemical equivalent	Chemical equivalent
1. The mass of substance deposited or liberated by one coulomb of charge or one ampere of current passed for one second.	1. The mass of substance deposited when one. Faraday of charge is passed through electrolytic solution.
2. It is denoted by Z	2. It is denoted by E

Numerical:

Given,

Current (I) = 5 A

Time (t) = 5 hrs = (5 × 60 × 60) = 18000 second

Area of spoon (A) = 12 cm^2

Density silver (d) = 10.5 g cm^{-3}

Equivalent wt. of silver (E) = 108

Weight of silver deposited (W) = ?

Thichness of silver plating = ?

We know that,

W = ZIt

$$\text{or, } W = \frac{E}{96500} \times It$$

$$\text{or, } W = \frac{108}{96500} \times 5 \times 18000$$

or, W = 100.72 g

Hence, the weight of silver deposited (W) = 100.72 g

We know that,

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{or, Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{100.72}{10.5} = 9.59\ \text{cm}^3$$

We know that,

Volume = Area × Thickness

$$\text{or, Thickness} = \frac{\text{Volume}}{\text{Area}} = \frac{9.59}{12} = 0.799\ \text{cm}$$

Hence, the thickness of silver plating is 0.799 cm.

---

62. 2069 (Set B) Q.No. 4 Convert the following:

i. Charge of 4.0×10^{12} electrons into coulombs.

ii. Chemical equivalent of Magnesium into Electro chemical equivalent. **[2]**

✍

i. We know that,

1 mole of electron = 6.022×10^{23} electrons

1 mole of electron = 96500 coulomb

So, 6.022×10^{23} electrons = 96500 coulomb

$$4.0 \times 10^{12}\ \text{electrons} = \frac{96500}{6.022 \times 10^{23}} \times 4.0 \times 10^{12}\ \text{C} = 6.409 \times 10^{-7}\ \text{C}$$

ii. Equivalent weight of magnesium metal (E) = 12

Electro chemical equivalent (Z) = ?

We know that,

$$Z = \frac{E}{96500} = \frac{12}{96500} = 1.24 \times 10^{-4}\ \text{gC}^{-1}$$

---

63. 2069 Supp. Set B Q.No. 26 State Faraday's first law of electrolysis and write the mathematical relation between electrochemical equivalent and chemical equivalent. 1.52 g of a trivalent metal Ⓜ was deposited at cathede by passing a current of 2.5 ampere through its salt solution (metal sulphate) for 30 minutes. What is the atomic mass of Ⓜ? **[5]**

✍ **Faraday's first law of electrolysis:** Please refer to 2072 Set E Q.No. 28

Relationship between electrochemical equivalent (Z) and chemical equivalent (E):

Please refer to 2073 Set D Q No. 23

Numerical:

Given,

Weight of metal (W) = 1.52 g

Valency of metal =3

Current (I) = 2.5 A

Time (t) = 30 minute = 30 × 60 = 1800 second

Atomic mass of metal = ?

Equivalent of metal (E) =?

We know that,

W = ZIt

$$\text{or, } W = \frac{E}{96500} \times It$$

$$\text{or, } 1.52 = \frac{E}{96500} \times 2.5 \times 1800$$

$$\text{or, } E = \frac{1.52 \times 96500}{2.5 \times 1800} = 32.59$$

We know that,

Atomic weight of metal = Equivalent weight × Valency

= 32.59 × 3 = 97.78

Hence, atomic weight of metal is 97.78 amu.

---

64. 2067 Q.No. 24 Define one Faraday's electricity. How many grams of silver could be plated out on a serving tray by passing electricity through a solution of Ag (I) salt for 8 hours at a current of 9 ampere? What is the area of the tray, if thickness of the silver platting is 0.002 cm? Density of silver is 10 g / cm³. (Atomic mass of Ag = 107.8). **[5]**

✍ **One Faraday Electricity:** Faraday is the quantity of charge which will deposit one gm equivalent of the substance. i.e. 1 Faraday of charge deposit 1 g equivalent or 96500 coulombs of charge deposit 1 g equivalent substance

$$1\ \text{C of charge deposit } \frac{E\ g}{96500}$$

Numerical:

Given, Current (I) = 9 A

Time (t) = 8 hrs = 8 × 60 × 60 = 28800 second

Thickness of silver platting (l) = 0.002 cm

Density of silver (d) = 10 g / cm³

Atomic mass = 107.8

Valency = 1

Equivalent weight of silver = 107.8

We know that,

$$W = ZIt = \frac{E}{F}\ It = \frac{107.8 \times 9 \times 28800}{96500} = 288.74\ \text{g}$$

Mass of silver (m) = 288.74 g

Volume of silver (v) = ?

We know that,

$$d = \frac{m}{v}$$

$$\text{or, } v = \frac{m}{d} = \frac{288.74}{10} = 28.874\ \text{cm}^3$$

We know that,

Volume = Area × thickness

$$\text{Area} = \frac{\text{Volume}}{\text{Tickness}} = \frac{28.874}{0.002} = 14437\ \text{cm}^2$$

Hence, the weight of silver deposited is 288.74 g and the area of thikness of tray is 14437 cm².

---

65. 2066 Q. No. 24 Define:

i. Electrochemical cell

ii. Equivalent Conductance

A current of 2.5 amphere passes through the solution of a metal sulphate for 30 minutes and deposits 1.52 g of metal at cathode. Find the equivalent weight of the metal. **[5]**

✍

i. **Electrochemical cell:** The arrangement of cell in which two electrodes are fitted in the same electrolyte or different electrolyte which is connected with salt bridge is called electrolytic cell.

ii. **Equivalent conductance:** The conducting power of all ions produced by 1 gram equivalent of an electrolyte in its solution is called equivalent conductance.

Numerical

Given,

Current (I) = 2.5 A

Time (t) = 30 minute = 30 × 60 second = 1800 second
Weight of metal deposited (w) = 1.52 g
Equivalent weight of metal (E) = ?

We know that,

$$W = ZIt = \frac{E}{F} It$$

or, $W \times F = EIt$

or, $E = \frac{W \times F}{It} = \frac{1.52 \times 96500}{2.5 \times 1800} = 32.6$

So, the equivalent weight of metal = 32.6.

---

66. **2065 Q.No. 24** **State Faraday's 1st Law of electrolysis. What current strength is required to ... whole copper from 1 litre of 1 M $CuSO_4$ solution by passing electricity through it in 10 minu...**

Faradays First law of electrolysis

Statement: "The amount of substance deposited or liberated at electrode d... electrolysis is directly proportional to the quantity of electricity passed throu... solution"

If W be the weight of substance deposited by the passage of Q coulombs of charge ...

$W \alpha Q$ where, Q is the quantity of charge.

$W = Zct$ Where, Z is the proportionality constant called Electrochemical Equival...

If 'c' be the current in ampere and 't' be the time in second then $c = \frac{Q}{t}$

or, $Q = ct$

When c = 1 ampere and t = 1 second then

$W = Z$

Therefore, the electrochemical equivalent of a substance is defined as the amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second i.e. 1 coulombs charge.

Numerical

Given, Volume of $CuSO_4$ = 1 litre = 1000 mL
Conc^n of $CuSO_4$ = 1 M
Time (t) = 10 minute = (10 × 60) = 600 second
Molecular wt. of $CuSO_4$ = 159.5 g
$CuSO_4$ ionizes as

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$Cu^{++} + 2e^- \longrightarrow Cu$$

1 mole   2 F   1 mole

1 mole of Cu = 63.5 g
1 mole of copper is deposited by 2 moles of electrons.
63.5 g of copper is deposited by 2 F of electricity
= 2 × 96500 C = 193000 C

Electricity required (Q) = 193000 C

We know that,

$Q = It$

or, $I = \frac{Q}{t} = \frac{193000}{600} = 321.66$ A

So, 321.66 ampere of current is required to deposit whole copper from 1 litre of 1M $CuSO_4$ solution.

---

67. **2064 Q.No. 14** **Calculate the equivalent conductance of 0.1 N KCl solution having specific resistance 83.3 Ohm cm^{-1}.** **[2]**

Given,
Specific resistance (ρ) = 83.3 ohm cm^{-1}
Normality of KCl = 0.1 N
Specific conductance (k) = ?
Equivalent conductivity (λ_{eq}) = ?

We know that,

$$\text{Specific conductance } (\kappa) = \frac{1}{\rho} = \frac{1}{83.3} = 0.012 \text{ ohm}^{-1}\text{cm}^{-1}$$

$$\text{Equivalent conductance } (\lambda_{eq}) = \frac{K \times 1000}{N} = \frac{0.012 \times 1000}{0.1} = 120 \text{ ohm}^{-1}\text{cm}^2\text{equiv}^{-1}$$

---

68. **2062 Q.No. 14** **Calculate the equivalent conductivity of 0.12 N solution of an electrolyte, whose conductivity is 0.024 S cm^{-1}.** **[2]**

Concentration of solution (C) = 0.12 N = 0.12 equivalent/dm^3
Conductivity (K) = 0.024 S cm^{-1}
Equivalent conductivity (λ_{eqv}) = ?

We know that,

$$\lambda_{eqv} = \frac{K \times 1000}{C} = \frac{0.024 \times 1000}{0.12} = 200 \text{ Scm}^2 \text{ eqv}^{-1}$$

Hence, equivalent conductivity of 0.12 N solution is 200 Scm^2 eqv^{-1}.

---

69. **2059 Q.No. 14** **Find out the molar conductivity of 0.01 M acetic acid having specific conductivity 1.46×10^{-4} ohm^{-1} cm^{-1} mol^{-1}.** **[2]**

Given,
Concentration of acetic acid (C) = 0.01 M
Specific conductance (K) = 1.46×10^{-4} $ohm^{-1}cm^{-1}mol^{-1}$
Molar conductivity (μ) = ?
We know that,

$$\mu = \frac{K \times 1000}{M} = \frac{1.46 \times 10^{-4} \times 1000}{0.01} = 14.6 \text{ ohm}^{-1}\text{ cm}^{-1}\text{mol}^{-1}$$

Hence, the molar colductivity of acetic acid is 14.6 $ohm^{-1}cm^{-1}mol^{-1}$

---

70. **2058 Q.No. 30** **State and explain Faraday's laws of electrolysis. How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with 0.005 mm thick layer? (Density of Ag = 10.5 g / cc).** **[10]**

Faraday's laws of electrolysis: Please refer to 2072 Set E Q.No. 28

Numerical:

Given,
Current (I) = 3A
Area of metal surface (A) = 80 cm^2
Thickness of metal = 0.005 mm = 0.0005 cm
Dendity of silver (d) = 10.5 g /cc
Equivalent wt. of silver (E) = 108
Time required to deposit metal (t) = ?

We know that,
Volume of metal = Area × Thickness = (80 × 0.0005) = 0.04 cm^3
Mass of silver deposited = Density × Volume = (10.5 × 0.04) = 0.42 g
According to Faraday first law of electrolysis

$W = ZIt$

$$\text{or, } t = \frac{W}{ZI} = \frac{W}{\frac{E}{96500} \times 1} = \frac{0.42}{\frac{108}{96500} \times 3} = \frac{0.42}{1.12 \times 10^{-3} \times 3} = \frac{0.42}{3.35 \times 10^{-3}} = 125.37 \text{ second}$$

Hence, the time required to deposit silver metal is 125.37 second.

---

71. 2057 Q.No. 26 You are given standard reduction potential of Cu^{+2}/Cu and Fe^{+2}/Fe as + 0.34V and – 0.44V respectively.

a. Construct a galvanic cell indicating anode and cathode

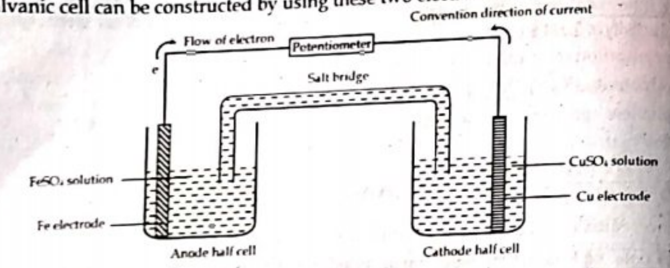
b. Write the cell reaction and calculate the standard emf of the cell. [5]

Given,

$E^{o}_{Cu^{+2}/Cu} = +0.34$ V

$Eo_{Fe^{+2}/Fe} = -0.44$ V

Galvanic cell can be constructed by using these two electrodes as:



Cell notation is

$Fe \; / \; Fe^{+2} \; // \; Cu^{+2} \; / \; Cu$

Anode Cathode

The cell reaction is

$Fe + Cu^{+2} \longrightarrow Fe^{+2} + Cu$

Emf of cell i.e. $E^{o}_{cell} = E^{o}_{red}\text{(cathode)} - E^{o}_{red}\text{(anode)}$

$= +0.34 - (-0.44) = (+0.34 + 0.44) = +0.78$ V

Hence, the emf of cell is +0.78 V.

---

72. 2056 Q.No. 4 How many coulombs of electricity are required to discharge 0.1 mole of Na^{+}? [2]

[1 Faraday = 96500 coulomb.]

Reduction of Na^{+} is

$Na^{+} + e^{-} \longrightarrow Na$

1 mole 1 mole

0.1 mole 0.1 mole

Thus, 0.1 mole of electron is required to discharge 0.1 mole of Na^{+}.

We know that,

One mole of electrons carry 96500 Coulomb charge.

So, 0.1 mole of electrons carry 0.1 × 96500 C = 9650 C charge.

WRITE SHORT NOTES ON:(5 MARKS)

73. 2062 Q.No. 31(d) Faraday's laws of electrolysis [5]

Faradays Law of Electrolysis: Michael Faraday in 1833 introduced the quantitative aspect of the decomposition of electrolyte by passing an electric current through them. He established a relationship between the amount of the electricity passed and the amount of the substance deposited at the electrode. His result can be expressed in the form of two laws called Faradays law of electrolysis.

Faradays First law of electrolysis:

Statement: "The amount of substance deposited or liberated at electrode during electrolysis is directly proportional to the quantity of electricity passed through the solution."

If W be the weight of substance deposited by the passage of Q coulombs of charge then,

$W \propto Q$ where, Q is the quantity of charge.

$W = Zct$ Where, Z is the proportionality constant called Electrochemical Equivalent.

If 'c' be the current in ampere and 't' be the time in second then $c = \frac{Q}{t}$

or, $Q = ct$

When c = 1 ampere and t = 1 second then,

$W = Z$

Therefore, the electrochemical equivalent of a substance is defined as the amount of substance in gram deposited at either of the electrode during electrolysis due to flow of 1 ampere current for 1 second i.e. 1 coulombs charge.

Faradays second law of electrolysis

Statement: If the same quantity of electricity is allowed to pass through the solutions of different electrolytes, then the amount of different substance or ions deposited or liberated at respective electrode are proportional to their chemical equivalent or equivalent weight.

Mathematically,

$W \propto E$

or, $W = KE$

or, $\frac{W}{E} = K$ (Where, K = constant)

Let us suppose two different electrolytic solutions i.e. $AgNO_3$ and $CuSO_4$ through which same quantity of electricity is passed then,

$W_{Ag} \propto E_{Ag}$ ... (i)

$W_{Cu} \propto E_{Cu}$ ... (ii)

From equation (i) and (ii)

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{Cu}}{E_{Cu}}$$

$$\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}}$$

This equation can be used to determine the equivalent wt. of substance.

❑❑❑

Unit

5

Energetics of Chemical Reactions

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 5 Define state function. Write any two examples of it.** [1+1]

The measurable property of a system which depends only upon the state of system called state function. Example: pressure and volume.

2. **2076 Set C Q.No. 5 2070 Set D Q.No. 5 2067 Q.No. 16 State the first law of thermodynamics.** [2]

Statement: Energy can neither be created nor destroyed but can be converted from one form to another.

3. **2075 GIE Q.No. 5 2074 Set A Q.No. 4 2074 Set B Q.No. 4 State the first law of thermodynamics and point out its limitation.** [1+1]

First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed.

Limitation: First law does not provide a clear idea about the direction of absorption or evolution of heat. The information's provided by the first law of thermodynamics are not enough to predict the spontaneity or feasibility of a process.

4. **2075 Set A Q.No. 5 Define the term 'internal energy'. Why is the internal energy of a system a state function?** [1+1]

Internal energy: It is defined as the energy associated with the random, disordered motion of molecules. Internal energy of ideal gases is a function of temperature only and internal energy of real gases is a function of temperature, pressure and volume. Since internal energy depends on quantities. Thus the internal energy of the system depends on the state of the system. It is therefore a state function.

5. **2075 Set B Q.No. 5 Define enthalpy of formation giving an example of it.** [2]

The heat change when one mole of a substance is formed from its own elements in their natural states is called heat of formation or enthalpy of formation. Example:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\ \Delta H = -286.2\ kJ$$

2074 Supp. Q.No. 4 Distinguish between extensive and intensive properties with an example of each. [2]

Following are the difference:

Extensive Properties	Intensive Properties
1. It depends on the nature and amount of substance.	1. It only depends on the nature of substance but not on the amount.
2. Examples: Volume, weight	2. Examples: density, pressure

2073 Supp Q.No. 5 Define enthalpy of combustion. Enthalpy of combustion of carbon to CO_2 is –393 kJ/mol. Calculate heat released upon formation of 33 g of CO_2 form carbon and oxygen. [1+1]

Enthalpy of combustion: The quantity of heat change involved when one mole of chemical substance is burnt completely with oxygen is called enthalpy of combustion.

$$C + O_2 \longrightarrow \underset{\underset{44\ g}{1\ mole}}{CO_2} + 393\ kJ$$

44 g of CO_2 requires 393 kJ heat energy

33 g of CO_2 requires $\frac{393}{44} \times 33\ kJ = 294.75\ kJ$

Hence, 294.75 kJ heat energy is released upon the formation of 33 g of CO_2 from carbon and oxygen.

2073 Set C Q.No. 5 Define standard enthalpy of formation. If heat change for the following reaction is 1648 KJ, what is the standard enthalpy of formation of Fe_2O_3

$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$ [2]

Standard Enthalpy of formation: The quantity of heat change is involved when one mole of chemical substance is formed from its constituent elements is known as standard enthalpy of formation. It is denoted by ΔH.

The given reaction is

$$\underset{0}{4\,Fe(s)} + \underset{0}{3\,O_2(g)} \longrightarrow \underset{H^\circ\, Fe_2O_3}{2\,Fe_2O_3(s)}\ ;\ \Delta H^\circ = +1648\ kJ$$

We know that

$\Delta H^\circ = \Delta H^\circ_{Product} - \Delta H^\circ_{Reactant}$

Or, $1648\ kJ = 2\Delta H^\circ\, Fe_2O_3 - [0 + 0]$

Or, $\Delta H^\circ\, Fe_2O_3 = \frac{1648}{2} = +824\ kJ\ mol^{-1}$

Hence, the standard enthalpy of formation of Fe_2O_3 is + 824 kJ mol^{-1}.

9. **2073 Set D Q.No. 5 What is meant by enthalpy of reaction? If standard enthalpy of formation of ammonia is 46 kJ mol^{-1}, what is the enthalpy change of the following reaction?** [1+1]

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Enthalpy of formation: The quantity of heat change is involved when one mole of chemical substance is formed from its constituent elements is known as enthalpy of formation. It is denoted by ΔH.

The given reaction is

$$\underset{0}{N_2(s)} + \underset{0}{3\,H_2(g)} \longrightarrow \underset{H^\circ\, NH_3}{2\,NH_3(s)}\ ;\ \Delta H^\circ = -46\ kJ$$

We know that

$\Delta H^\circ = \Delta H^\circ_{Product} - \Delta H^\circ_{Reactant}$

Or, Enthalpy change of reaction = $2\Delta H^\circ\, NH_3 - [0 + 0] = 2 \times (-46) = -92\ kJ$

Hence, the enthalpy change of reaction is -92 kJ mol^{-1}.

10. **2072 Supp. Q.No. 5 2071 Set C Q.No. 5 Calculate the standard enthalpy of formation of water in the following reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l),\ \Delta H = -136\ kcal$** [1+1]

In the balanced chemical equation 2 moles of water is formed. The enthalpy of formation of water i.e. $\Delta H_f H_2O = \frac{\Delta H}{2} = \frac{-136}{2} = -68\ KCal$

Hence, the enthalpy of formation of water is -68 KCal/mole.

11. **2072 Set C Q.No. 5 Distinguish between enthalpy of combustion and enthalpy of formation.** [1+1]

Following are the difference

Enthalpy of combustion	Enthalpy of formation
1. The amount of heat changed when one mole of any substance is completely burns in air or oxygen is called heat of combustion or enthalpy of combustion.	1. The heat change when one mole of a substance is formed from its own elements in their natural states is called heat of formation or enthalpy of formation.

2. Example: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $\Delta H = -94.5 kJ$	2. Example: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,$ $\Delta H = -286.2 kJ$

12. **2072 Set D Q.No. 5 What is meant by state function? Give its example.** [1+1]

Please refer to 2076 Set B Q.No. 5

13. **2072 Set E Q.No. 5 Distinguish between intensive and extensive property with examples.** [1+1]

Please refer to 2074 Supp. Q.No. 4

14. **2072 Set E Q.No. 6 The enthalpy of reaction for $N_2 (g) + 3H_2 (g) \longrightarrow 2NH_3 (g)$ is – 92.4 kJ. Calculate the enthalpy of formation of ammonia.** [2]

Enthalpy of formation is defined as the amount of heat energy released or absorbed during formation of one mole of a compound from its constituent elements. In the given reaction, two mole of ammonia are produced with the evolution of 92.4 kJ heat energy.

$N_2 (g) + 3H_2 (g) \longrightarrow 2NH_3 (g)$; $\Delta H = -92.4 kJ$

The enthalpy of formation ammonia i.e. $\Delta H_f NH_3 = \frac{dH}{2} = \frac{-92.4}{2} = -46.2 kJ$

Hence, enthalpy of formation of ammonia is – 46.2 kJ.

15. **2071 Supp. Q.No. 5 Distinguish between extensive and intensive properties giving one example of each.** [1+1]

Please refer to 2074 Supp. Q.No. 4

16. **2071 Set D Q.No. 5 Define state function and give any two correct examples of it.** [2]

Please refer to 2076 Set B Q.No. 5

17. **2070 Supp. Q.No. 5 State the first law of thermodynamics and write its mathematical relation.** [2]

Statement: Energy can neither be created nor destroyed but can be converted from one form to another.

$\Delta E = Q - W$

This is the mathematical representation of the first law of thermodynamics.

18. **2070 Set C Q.No. 6 Define the terms:**
i. Extensive properties ii. Internal energy [2]

i. **Extensive properties:** A property which depends on the nature and amount of the substance is known as as extensive property.e.g. volume, weight, quantity of current etc.

ii. **Internal energy:** The total of all the possible kinds of energy of a system is called its internal energy.

19. **2069 (Set A) Q.No. 6 2069 (Set B) Q.No. 5 Calculate the enthalpy of formation of NH_3 from the following equation.**

$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -186kJ$. [2]

In the balanced chemical equation 2 moles of ammonia gas is formed. The enthalpy of formation of ammonia i.e. $\Delta H_f NH_3 = \frac{\Delta H}{2} = \frac{-186}{2} = -93 kJ$

Hence, the enthalpy of formation of ammonia is -93kJ/mole.

20. **2069 Supp. Set B Q.No. 5 Under what conditions,**
i. reaction occur spontaneously
ii. free energy change become zero. [2]

We know that,

$\Delta G = \Delta H - T\Delta S$

For spontaneous change, $(\Delta G)_{T.P.} < 0$

Under equilibrium conditions $(\Delta G)_{T.P} = 0$

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21. **2065 Q.No. 16 State Hess's Law of constant heat summation.** [2]

Statement: The total amount of heat change in a reaction depends only upon the nature of the initial reactant and the nature of the final product and is independent of the path or the manner by which this change is brought about.

Let us consider a reaction

$$A \xrightarrow{Q} D$$

The reactant A changes to product D in one step and heat change is Q KJ.

Suppose, the same process is carried out in three steps.

$$A \xrightarrow{q_1} B \xrightarrow{q_2} C \xrightarrow{q_3} D$$

Suppose, the heat evolved in these steps are q_1, q_2, q_3. The total heat evolved = $q_1 + q_2 + q_3$

According Hess's Law, $Q = q_1 + q_2 + q_3$

22. **2062 Q.No. 16(i) Define the terms: Enthalpy of a reaction** [1]

Total heat content of a system is called enthalpy or heat content of reaction. It is represented by the symbol H. It is defined as relation, H = E + PV

23. **2059 Q.No. 17 How is free energy change of a reaction related to enthalpy change and entropy change?** [2]

Free energy change i.e. ΔG of a reaction is related to entropy ΔH change and entropy ΔS change as $\Delta G = \Delta H - T\Delta S$

The difference of ΔH change and ΔS change at constant temperature is free energy change.

24. **2058 Q.No. 17 Draw energy profile diagrams for exothermic and endothermic reactions.** [2]

Energy profile diagram of exothermic and endothermic reaction:

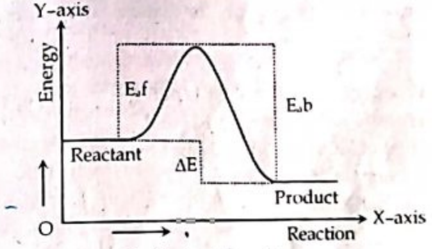

Fig: Exothermic reaction

In exothermic reaction, energy of the product < the energy of reactant.

Change of energy (ΔE) = $E_{product} - E_{reactant}$

= -ve value

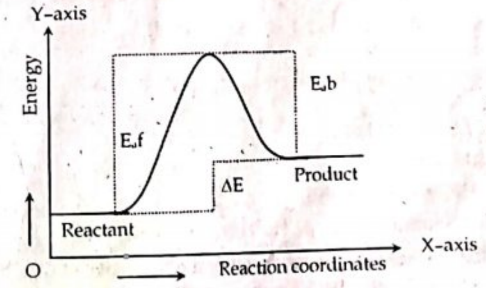

Fig: Endothermic reaction

In endothermic reaction, energy of product > energy of reactant

Change of energy (ΔE) = $E_{product} - E_{reactant}$ = +ve value

25. 2055 Q.No. 6 **Define exothermic and endothermic reaction.** [2]

Exothermic reaction: The reaction in which heat energy is liberated is called exothermic reaction. Example:

$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O, \Delta H = -890.4\ kJ$

Endothermic reaction: The reaction in which heat energy is absorbed is called endothermic reaction. Example:

$H_2 + I_2 \longrightarrow 2HI, \ \Delta H = +52.2\ kJ$

26. 2055 Q.No. 7 **State Hess's law of constant heat summation.** [2]

Please refer to 2065 Q No 16

27. 2054 Q.No. 7 **State whether the following properties are extensive properties or intensive properties**

a. Entropy b. Temperature [2]

a. **Entropy:** It is extensive property because it depends up on the amount of substance. It is the measure of ramdomness or disorder of a system.

b. **Temperature:** It is intensive property because it does not depend up on the quantity of water.

SHORT ANSWER QUESTIONS [5 MARKS]

28. 2076 Set B Q.No. 25 **Define bond dissociation energy. The bond dissociation energy of H_2 (g) and Cl_2 (g) are 435 KJ/mol and 243 KJ/mol respectively. The enthalpy of formation of HCl (g) = –92 KJ/mol. Calculate the bond dissociation energy of HCl (g).** [1+4]

Bond dissociation energy: Bond dissociation energy is the energy required to break a chemical bond. It is one means of quantifying the strength of a chemical bond. Bond dissociation energy equals bond energy only for diatomic molecules.

Numerical:

Given,

The bond dissociation energy of H_2 (g) = 435 KJ/mol

The bond dissociation energy of Cl_2 (g) = 243 KJ/mol

The enthalpy of formation of HCl (g) = –92 KJ/mol

The bond dissociation energy of HCl (g) = ?

The balanced chemical equation is

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl\ (g)$$

We know that

Enthalpy of formation of HCl = (Bond dissociation of reactant - Bond dissociation of product)

ΔH of HCl = $[\frac{1}{2}\Delta H$ of $H_2 + \frac{1}{2}\Delta H$ of $Cl_2] - [\Delta H$ of HCl]

or, $-92\ KJ = [\frac{1}{2} \times 435\ KJ + \frac{1}{2} \times 243\ KJ] - [\Delta H$ of HCl]

or, $-92\ KJ = [217.5 + 121.5] - [\Delta H$ of HCl]

or, $-92\ KJ = [339] - [\Delta H$ of HCl]

or, ΔH of HCl = (92 + 339) = +431 KJ/mol

Hence, the bond dissociation energy of HCl (g) is +431 KJ/mol

29. 2076 Set C Q.No. 25 **State enthalpy of combustion. If heat of formation of CO_2, H_2O and $C_6H_{12}O_6$ are –395 KJ mol^{-1}, –269.4 KJ mol^{-1} and –1169 KJ mol^{-1} respectively. Calculate the heat of combustion of glucose.** [1+4]

Enthalpy of combustion: The amount of heat changed when one mole of any substance is completely burns in air or oxygen is called heat of combustion or enthalpy of combustion.

Numerical:

Given,

Heat of formation of CO_2

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -395\ kJ$ ... (i)

Heat of formation of H_2O

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \Delta H = -269\ kJ$ (ii)

Heat of formation of $C_6H_{12}O_6$

$6C(s) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6, \Delta H = -1169\ kJ$ ... (iii)

Combustion of heat of glucose is as

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + \Delta H, \Delta H = ?$

Multiply equation (i) and (ii) by 6 and adding together, the resulting equation is subtracted from (iii) then we get,

$6C(s) + 6O_2(g) \longrightarrow 6CO_2(g), \Delta H = -2370kJ$

$6H_2(g) + 3O_2(g) \longrightarrow 6H_2O(l), \Delta H = -1614\ kJ$

$6C(s) + 6H_2(g) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l), \Delta H = -3984\ kJ$ ... (iv)

Subtracting equation (iii) from (iv) then we get,

$6C(s) + 6H_2(g) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l), \Delta H = -3984\ kJ$

$6C(s) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6, \quad \Delta H = -1169\ kJ$

$- \quad - \quad - \quad +$

$6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) - C_6H_{12}O_6, \Delta H = -2815\ kJ$

So, $C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l), \Delta H = -2815\ kJ$

The heat of combustion of $C_6H_{12}O_6$ is –2815 kJ

30. 2075 Set B Q.No. 24 **State Hess's law of constant heat summation. Heat of combustion of benzene (C_6H_6) is –3280 kJ. Heat of formation of CO_2 and water are – 395 kJ and – 286 kJ respectively. Calculate the heat of formation of benzene.** [1+4]

Hess's law of constant heat summation:

Statement: The total amount of heat change in a reaction depends only upon the nature of the initial reactant and the nature of the final product and is independent of the path or the manner by which this change is brought about.

Let us consider a reaction

$$A \xrightarrow{Q} D$$

The reactant A changes to product D in one step and heat change is Q KJ.

Suppose, the same process is carried out in three steps.

$$A \xrightarrow{q_1} B \xrightarrow{q_2} C \xrightarrow{q_3} D$$

Suppose, the heat evolved in these steps are q_1, q_2, q_3. The total heat evolved = $q_1+q_2+q_3$

According Hess's Law $Q = q_1 + q_2 + q_3$

Numerical:

Given,

The enthalpy of combustion of benzene (C_6H_6) ΔH_c = -3280 kJ

The heat of formation of CO_2 ΔH_f = - 395 kJ

The heat of formation of H_2O ΔH_f = - 286kJ

The heat of formation of benzene (C_6H_6) ΔH_f = ?

The oxidation of benzene is given as:

$$C_6H_6\ (l) + \frac{15}{2}O_2\ (g) \longrightarrow 3\ H_2O\ (l) + 6\ CO_2\ (g)$$

We know that

$\Delta H_c\ C_6H_6 = [3 \times \Delta H_f\ H_2O + 6 \times \Delta H_f\ CO_2 - \Delta H_f\ C_6H_6]$

or, $-3280 = [3 \times (-286) + 6 \times (-395) - \Delta H_f\ C_6H_6]$

or, $-3280 = [-858 - 2370 - \Delta H_f\ C_6H_6]$

or, $-3280 = [-3228 - \Delta H_f\ C_6H_6]$

or, $\Delta H_f\ C_6H_6 = 3280 - 3228 = +52$ kJ

Hence, heat of combustion of benzene is + 52 kJ.

31. **2074 Supp. Q.No. 25 State enthalpy of combustion. If heat of formation of CO_2, H_2O and $C_6H_{12}C_6$ are -395 KJ mol^{-1}, -269.4 KJ mol^{-1} and -1169 KJ mol^{-1} respectively. Calculate the heat of combustion of glucose.** **[1+4]**

Please refer to 2076 Set C Q.No. 25

32. **2074 Set A Q.No. 25 What is meant by enthalpy of combustion? If heat of formation of CO_2, H_2O and $C_6H_{12}O_6$ are -395 kJ mol^{-1}, -269 kJ mol^{-1} and -1169 kJ mol^{-1} respectively. Calculate the heat of combustion of glucose ($C_6H_{12}O_6$)** **[1+4]**

Please refer to 2076 Set C Q.No. 25

33. **2074 Set B Q.No. 25 Define bond enthalpy. The bond enthalpies of gases H_2, Cl_2 and HCl are 104 Kcal mol^{-1}, 58 Kcal mol^{-1} and 103 Kcal mol^{-1} respectively. Calculate enthalpy of formation of HCl (g).** **[1+4]**

Bond enthalpy: Bond enthalpy (also known as bond energy) is defined as the amount of energy required to break one mole of the stated bond.

Numerical:

The balanced chemical reaction is

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \quad \Delta H = ?$$

Given,

Bond enthalpy of H—H = 104 Kcal

Bond enthalpy of Cl—Cl = 58 Kcal

Bond enthalpy of H—Cl = 103 Kcal

We know that,

Enthalpy of formation of HCl = (Bond enthalpy of reactant – Bond enthalpy of product)

$$\Delta H \text{ of } HCl = [\frac{1}{2}\Delta H_{H-H} + \frac{1}{2}\Delta H_{Cl-Cl}] - [\Delta H_{H-Cl}]$$

or, ΔH of HCl $= [\frac{1}{2} \times 104 + \frac{1}{2} \times 58] - 103$

or, ΔH of HCl = -22 Kcal mol^{-1}

Hence, enthalpy of formation of HCl (ΔH of HCl) is – 22 Kcal.

34. **2072 Set D Q.No. 24 Define heat of formation. Heat of combustion of methane, carbon and hydrogen are –210 KCal, –94 KCal and –68 KCal respectively. Calculate the heat of formation of methane.** **[1+4]**

Heat of formation: The heat change when one mole of a substance is formed from its own elements in their natural states is called heat of formation. Example:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \ \Delta H = -210$ K Cal ... (i)

Heat of formation of carbondioxide (CO_2)

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -94$ K Cal ... (ii)

Heat of formation of water (H_2O)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \Delta H = -68$ K Cal ... (iii)

Heat of formation of methane (CH_4)

$C(s) + 2H_2(g) \longrightarrow CH_4(g), \Delta H = ?$

Adding equation (ii) and (iii) then we get,

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -94$ K Cal

$H_2(g) + \frac{1}{2}O(g) \longrightarrow H_2O(l), \Delta H = -68$ KCal] × 2

$2H_2(g) + 2O_2(g) + C(s) \longrightarrow CO_2(g) + 2H_2O(l), \Delta H = -230$ KCal ... (iv)

Subtracting equation (i) from equation (iv) then we get

$2H_2(g) + 2O_2(g) + C(s) \longrightarrow CO_2(g) + 2H_2O(l), \Delta H = -230$ KCal

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \Delta H = -210$ KCal

– – – +

$2H_2(g) + C(s) \longrightarrow CH_4(g), \Delta H = -20$ KCal

Hence, heat of formation of CH_4 is –20 KCal.

35. **2072 Set C Q.No. 24 Write any two applications of Hess's law. Heat of formation of ethyl alcohol, water and carbon dioxide are –64.1 K Cal, –68.5 K Cal and –95 K Cal. Calculate the heat of combustion of ethyl alcohol.** **[1+4]**

Two application of Hess's law:

i. It is used for determination of heat of formation of substance which cannot be determined experimentally.

ii. It is used for the calculation of heat of hydration.

Numerical:

Heat of formation of ethyl alcohol

$2CO_2(g) + 3H_2O(l) \longrightarrow C_2H_5OH(l) + 3O_2$ (g0, $\Delta H_f = -64.1$ KCal

Heat of formation of water

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta Hf = -68.5$KCal

Heat of formation of carbondioxide

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta Hf = -95$ KCal

Heat of combustion of ethyl alcohol

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l), \Delta Hc = ?$

We know that,

$\Delta Hc = \Sigma \Delta H_f$ (product) – $\Sigma \Delta H_f$ (reactant)

or, $\Delta Hc = 2 \times (-95) + 3 \times (-68.5) - (-64.1)$

$= -190 - 205.5 + 64.1 = -395.5 + 64.1 = -331.4$ KCal.

Hence, heat of combustion of ethyl alcohol is –331.4 KCal.

36. **2068 Q.No. 25 Mention the important applications of Hess's Law of constant heat summation. The standard heat of formation of SO_2(g) and SO_3(g) are - 296.6 kJ and -396 kJ respectively. Calculate ΔH for the reaction:** **[5]**

$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

Following are the important application of Hess's law of constant heat summation.

a. The most important consequence of Hess's law is that thermo chemical equation may be multiplied, added or substracted like ordinary algebraic equation.

Example:

$C + \frac{1}{2}O_2 \longrightarrow CO, \ \Delta H = -26.3$ Cal.

$CO + \frac{1}{2}O_2 \longrightarrow CO_2, \Delta H = -68$ Cal.

Net reaction

$C + O_2 \longrightarrow CO_2, \Delta H = -94.3$ Cal.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s), \Delta H = -42.1$ KCal.

$NH_4Cl(s) + aq. \longrightarrow NH_4Cl(aq.), \Delta H = +3.9$ KCal.

Net reaction

$NH_3(g) + HCl(g) + aq. \longrightarrow NH_4Cl(aq.), \Delta H = -38.2$ KCal.

b. Heat of reaction, heat of formation, heat of neutralization, heat of solution, bond energy may be obtained with the help of this law.

Example:

i. **Heat of solution:** The enthalpy change when one mole of a solute is dissolved in an excess of solvent at a given temperature so that further dilution involves no heat change. When KCl is added into water then its aqueous solution will be formed.

$KCl(s) + aq. \longrightarrow KCl\ (aq.), \Delta H = +18.6$ kJ

ii. **Heat of neutralization:** The enthalpy change when one gram equivalent of an acid is neutralized by base.

$NaOH + HCl \longrightarrow NaCl + H_2O, \Delta H = -57$ kJ

iii. **Heat of formation:** The heat change i.e. heat evolved or absorbed when one mole of substance is formed from its constituent element under a given temp. and pressure.

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -393.5$ kJ

Numerical

Given,

$$S(s) + O_2(g) \longrightarrow SO_2(g), \Delta H = -296.6\ kJ \qquad \text{... (i)}$$

$$S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g), \Delta H = -396kJ \qquad \text{... (ii)}$$

$$SO_2(s) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g), \Delta H = ?$$

Substracting equation (i) from (ii) then we get,

$$S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g), \Delta H = -396kJ$$

$$\underset{-}{S(s)} + \underset{-}{O_2(g)} \longrightarrow \underset{-}{SO_2(g)},\ \Delta H = \underset{+}{-296.6\ kJ}$$

$$\frac{1}{2}O_2(g) \longrightarrow SO_3(g) - SO_2(g), \Delta H = -99.4\ kJ$$

So, $SO_2(s) + \frac{1}{2}O_2(g)\ SO_3(g), \Delta H = -99.4$ kJ

Therefore, enthalpy of formation of SO_2 to SO_3 is –99.4 kJ.

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37. $\boxed{\text{2063 Q.No. 30a}}$ **Define enthalpy of a reaction. State and explain Hess Law of constant heat summation.** **[5]**

a. **Enthalpy of a reaction:** The amount of heat energy evolved or absorbed in a chemical reaction when the numbers of moles of reactant react completely to give the product at constant temperature is known as Enthalpy of reaction. Example:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g), \Delta H = -890.3$ kJ

Therefore, $\Delta H = \Sigma H\ (product) - \Sigma H\ (reactant)$

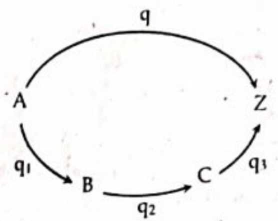
Hess's Law of constant heat of summation

Statement: The amount of heat evolved or absorbed in a process is the same whether the process is carried out in a single step or in several steps.

This law is a mere consequence of the first law of thermodynamics.

Theoretical proof: Let us suppose that a substance 'A' is directly converted into 'Z'.

$$A \longrightarrow Z + q$$



Where, q = amount of heat evolved

Now, suppose the system change from A to Z through three intermediate steps, shown as

$A \longrightarrow B + q_1$

$B \longrightarrow C + q_2$

$C \longrightarrow Z + q_3$

Where, q_1, q_2, q_3 are the heat evolved in three different steps.

According to Hess's Law

$q = q_1 + q_2 + q_3$

or, $q = Q$ (where, $q_1 + q_2 + q_3 = Q$)

If $q \neq Q$ then it will be $Q > q$ or $Q < q$

If $Q > q$ then by changing A to Z through different steps and back to A will gain heat = Q - q. Repeating this process again and again a large amount of heat will be stored which is against the law of conversion of energy or the first law of thermodynamics.

Experimental proof: This law has been tested experimentally and found to be true.

Example:

Formation of CO_2 from C and O_2

First way

$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -94.3$ Cal.

Second way

$$C + \frac{1}{2}O_2 \longrightarrow CO, \Delta H = -26.3 \text{ Cal. (1}^{st}\text{ step)}$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2, \Delta H = -68 \text{ Cal. (2}^{nd}\text{ step)}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -94.3 \text{ Cal.}$$

It is clear from both ways of chemical reaction that heat evolved in each steps is same.

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38. $\boxed{\text{2052 Q.No. 25}}$ **State and explain first law of: Thermodynamics, and, hence deduce H = E + PV, where all the symbols have their usual meanings.** **[5]**

The first statement of equivalence of heat and mechanical work was given by Robert Meyer and Helmholtz. They also stated the first law of thermodynamics in the form of law of conservation of energy, which may be stated in the following ways:

a. The internal energy of any material system can neither be increased nor decreased by any action between the parts of the system; through it may be changed from one form to another.

b. It is not possible to make a perpetual motion machine which would produce work without consuming energy.

c. Whenever a quantity of one kind of energy disappears, an exactly equivalent amount of another kind must be produced.

Mathematical statement of first law of thermodynamics:

When a system changes from one state to another, it may perform some type of external work, such as mechanical work of expansion, electrical work etc. Let a system A having an internal energy E_A passes into a new system having different internal energy E_B. Let

W be the external work done by the system and Q be the quantity of heat absorbed during such a change. Hence, according to the law of conservation of energy,

$E_B - E_A = Q - W$ ... (i)

$\Delta E = Q - W$

or, $Q = \Delta E + W$ ... (ii)

or, $\Delta E = Q - W$

Equation (ii) is the mathematical representation of the first law of thermodynamics.

Deduction of $H = E + PV$

Most of the thermodynamics change involves mechanical work of expansion or contraction and no electrical work. Then W will in general, be equal to PΔV. Where P is constant external pressure and ΔV is the change in volume. Hence, equation (ii) becomes

$Q = \Delta E + P\Delta V$ ... (iii)

When process occurs at constant volume, ΔV is equal to zero and equation (iii) becomes

$Q_V = \Delta E$

In case of process occurring at constant pressure, equation (iii) becomes

$Q_P = \Delta E + P\Delta V$ ... (iv)

If absorption of heat, Q_P at constant pressure increase the internal energy E_A to E_B and it also changes volume from V_A to V_B then,

$Q_P = (E_B - E_A) + P(V_B - V_A)$

$Q_P = (E_B + PV_B) - (E_A + PV_A)$

$Q_P = H_B - H_A$

$Q_P = \Delta H$ ... (v)

From equation (iv) and (v)

$\Delta H = \Delta E + P\Delta V$

Where, ΔH = enthalpy change
ΔE = Internal energy change
ΔV = Volume change

NUMERICAL PROBLEMS

39. 2072 Set E Q.No. 32a State first law of thermodynamics. What are its advantages and limitations? The enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and CH_4 (g) are -393.5, -286.2 and -74.8 kJ mol⁻¹ respectively. Calculate the enthalpy of combustion of methane. [1+1+1+2]

First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed.

Advantage and limitation of First law of thermodynamics:

Advantage: In the equation, q = -W Where W includes all types of work like mechanical, electrical, gravitational etc. if mechanical work is considered, $W = P.\Delta V$

Limitations:

i. *This law does not explain the extent and direction of convertibility of one form of energy to another.*

ii. *This law is unable to explain unidirectional nature of spontaneous process.*

Numerical:

Enthalpy of formation of CO_2

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_f = -393.5\ kJ$

Enthalpy of formation of H_2O

$H_2(g) + O_2(g) \longrightarrow 2H_2O(l);\ \Delta H_f = -286.2\ kJ$

Enthalpy of formation of methane (CH_4)

$C(s) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta H_f = -74.8\ kJ$

Enthalpy of combustion of CH_4

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H_c = ?$

Enthalpy of reaction

$\Delta H_c = \Sigma \Delta H_f\ (Product) - \Sigma \Delta H_f\ (Reactant)$

$\Delta H_c = [\Delta H_f\, CO_2 + 2\,\Delta H_f\, H_2O] - [\Delta H_f\, CH_4 + 2\,\Delta H_f\, O_2]$

$\Delta H_c = [-393.5 + 2(-286.2)] - [-74.8 + 0]$

$\Delta H_c = [-393.5 - 572.4] - [-74.8]$

$\Delta H_c = -965.9 + 74.8$

$\Delta H_c = -891.1\ kJ\ mol^{-1}$

Hence, the enthalpy of combustion of methane is $-891.1\ kJ\ mol^{-1}$.

40. 2070 Set C Q.No. 25 State Hess' law of constant heat summation. Calculate the enthalpy of formation of benzene, if enthalpy of combustion of benzene and carbon are -3280 kJ / mol and -395 kJ / mol respectively. The enthalpy of formation of water is -285 kJ / mol. [5]

Hess's law of constant heat summation: 2075 Set B Q.No. 24

Numerical:

Given,

The enthalpy of combustion of benzene (C_6H_6 or $\Delta H\ C_6H_6$) = $-3280\ kJmol^{-1}$

The enthalpy of combustion of carbon i.e. formation of CO_2 or $\Delta H_f\, CO_2 = -395\ kJmol^{-1}$

The enthalpy of formation of water $\Delta H_f H_2O = -285\ kJmol^{-1}$

The enthalpy of formation of benzene (C_6H_6) or $\Delta H_f C_6H_6$ = ?

Oxidation of bezene as

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 3H_2O(l) + 6CO_2(g)$$

We know that,

Enthalpy of combustion of benzene i.e. C_6H_6 = [Sum of enthalpy of products - Sum of enthalpy of reactants]

$\Delta H\ C_6H_6 = [3 \times \Delta H_f H_2O + 6 \times \Delta H_f CO_2 - \Delta H_f C_6H_6]$

or, $-3280 = [3 \times (-285) + 6 \times (-395) - \Delta H_f C_6H_6]$

or, $-3280 = [-855 - 2370 - \Delta H_f C_6H_6]$

or, $-3280 = [-3225 - \Delta H_f C_6H_6]$

or, $[3225 + \Delta H_f C_6H_6] = 3280$

or, $\Delta H_f C_6H_6 = 3280 - 3225$

or, $\Delta H_f C_6H_6 = +55\ kJ\ mol^{-1}$

Hence, enthalpy of formation of benzene i.e. C_6H_6 or $\Delta H_f\, C_6H_6$ is $+55\ kJ\ mol^{-1}$

41. 2069 Supp. Set B Q.No. 28 What is meant by enthalpy of combustion? Enthalpy of formation of benzene is 55 kJ, enthalpy of formation of water and carbondioxides are -395 kJ and -285 kJ respectively. Calculate the enthalpy of combustion of benzene. [5]

Enthalpy of combustion: The amount of heat changed when one mole of any substance is completely burns in air or oxygen is called heat of combustion or enthalpy of combustion.

Example: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$, $\Delta H = -94.5\ kJ$

The heat of combustion of methane is - 94.5 kJ per mole.

Numerical:

Given,

Enthalpy of formation of benzene

$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l),\ \Delta H = 55\ kJ$ ... (i)

Enthalpy of formation of water

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\,,\ \Delta H = -395\ kJ \qquad \ldots (ii)$$

Enthalpy of formation of carbondioxide

$$C(s) + O_2(g) \longrightarrow CO_2(g)\,,\ \Delta H = -285\ kJ \qquad \ldots (iii)$$

Enthalpy of combustion of benzene

$$C_6H_6(l) + \frac{15}{2}\,O_2(g) \longrightarrow 3H_2O(l) + 6CO_2(g),\ \Delta H = ?$$

Equation (ii) is multiplied by 3 and eqation (iii) is multiplied by 6, adding both th equation then we get,

$$3H_2(g) + \frac{3}{2}\,O_2(g) \longrightarrow 3\,H_2O(l)\,,\ \Delta H = -395 \times 3\ KJ = -1185\ kJ$$

$$\underline{6C(s) + 6O_2(g) \longrightarrow 6CO_2(g)\,,\ \Delta H = -285 \times 6\ KJ = -1710\ kJ}$$

$$6C(s) + \frac{15}{2}O_2(g) + 3H_2(g) \longrightarrow 6CO_2(g) + 3\,H_2O(l), \Delta H = -\,2895\ kJ \ldots (iv)$$

Substracting equation (i) form (iv) then we get,

$$6C(s) + \frac{15}{2}O_2(g) + 3H_2(g) \longrightarrow 6CO_2(g) + 3\,H_2O(l)\ ,\ \Delta H = -\,2895\ kJ$$

$$6C(s) \qquad + \quad 3H_2(g) \longrightarrow C_6H_6(l)\,, \qquad \Delta H = 55\ kJ$$

$$\underline{-\qquad\quad -\qquad\quad -\qquad\qquad\qquad -}$$

$$\frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3\,H_2O(l) - C_6H_6(l),\ \Delta H = -\,2950\ kJ$$

$$C_6H_6(l) + \frac{15}{2}\,O_2(g) \longrightarrow 6CO_2(g) + 3\,H_2O(l)\ ,\ \Delta H\ = -\,2950\ kJ$$

Hence, the enthalpy of combustion of benzene is -2950 kJ.

42. **2069 (Set A) Q.No. 24 Define enthalpy of combustion. Enthalpy of formation of benzene is 55kJ, enthalpy of formation of water and carbondioxide are –395 kJ and –285 kJ respectively. Calculate the enthalpy of combustion of benzene.** **[5]**

➣ Please refer to 2069 Supp. Set B Q.No. 28

43. **2066 Q. No. 26 Define Hess's Law of constant heat summation. Calculate the heat of combustion of glucose from the following data:**

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g),\ \Delta H = -395\ kJ$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l),\ \Delta H = -269\ kJ$$

$$6\,C\,(S) + 6\,H_2\,(g) + 3\,O_2\,(g) \longrightarrow C_6H_{12}O_6\,(s),\ \Delta H = -1169\ kJ$$

[5]

➣ **Hess's law of constant heat summation:** 2075 Set B Q.No. 24

Numerical: Please refer to 2076 Set C Q.No. 25

44. **2063 Q.No. 30(b) The standard enthalpy of formation of H_2O (*l*), CO_2 (g) and C_6H_6 (*l*) are – 286, – 393.5 and + 49.02 kJ mol^{-1} respectively at 298 K. Calculate the standard enthalpy of combustion of C_6H_6 (*l*) at the given temperature.** **[5]**

➣ Given,

The chemical equation involved

$$C(s) + O_2(g) \longrightarrow CO_2(g),\ \Delta H = -393.5kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\ \Delta H = -286\ kJ$$

$$6C\,(s) + 3H_2 \longrightarrow C_6H_6(l),\ \Delta H = +49.02\ kJ$$

$$C_6H_6(l) + 15/2\,O_2(g) \longrightarrow 6\,CO_2\,(g) + 3\,H_2O(l)\ ,\ \Delta H = ?$$

Given,

Standard enthalpy of formation of $CO_2 = \Delta H°f = -393.5$ kJ

Standard enthalpy of formation of $H_2O = \Delta H°f = -286$ kJ

Standard enthalpy of formation of $C_6H_6 = \Delta H°f = +49.02$ kJ

Standard enthalpy of combustion of C_6H_6, $\Delta H°f$ = ?

Equation is

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2\,(g) + 3\,H_2O(l)\ ;\ \Delta H°f\ =?$$

Enthalpy of the reaction

$$\Delta H° = \Sigma\Delta H°f\,(product) - \Sigma\Delta H°f\,(reactant)$$

$$\Delta H° = [6\Delta H°CO_2 + 3\Delta H°H_2O] - [\Delta H°C_6H_6 + \frac{15}{2}\Delta H°O_2]$$

$$= 6 \times (-393.5) + 3(-286) - (49.02 + 0)$$

$$= (-2361 - 858 - 49.02) = -\,3268.02\ kJ$$

So, the standard enthalpy of combustion of C_6H_6 is -3268.02 kJ.

45. **2062 Q.No. 24 What is meant by enthalpy of formation? Calculate the enthalpy of formation of ethane at 298 K, if the enthalpies of combustion of C, H and C_2H_6 are – 94.14, – 68.47 and – 373.3 KCal respectively.** **[5]**

➣ **Enthalpy of formation:** The heat change when one mole of a substance is formed from its own elements in their natural states is called heat of formation or enthalpy of formation. Example:

$$H_2(g) + ½\,O_2(g) \longrightarrow H_2O,\ \Delta H = -286.2\ kJ$$

Numerical:

Given,

Enthalpy of combustion of carbon i.e. formation of carbondioxide

$$C(s) + O_2(g) \longrightarrow CO_2(g)\,,\ \Delta H = -94.14\ KCal \qquad \ldots (i)$$

Enthalpy of combustion of hydrogen i.e. formation of water

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\,,\ \Delta H = -68.47KCal \qquad \ldots (ii)$$

Enthalpy of combustion of ethane i.e. C_2H_6

$$C_2H_6(g) + \frac{7}{2}\,O_2(g) \longrightarrow 3H_2O(l) + 2CO_2(g)\,,\ \Delta H = -373.3KCal \qquad \ldots (iii)$$

Enthalpy of formation of ethane

$$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)\,,\ \Delta H = ?$$

Equation (i) is multiplied 2 and eqation (ii) is multiplied by 3 and adding both the equation then we get,

$$2C(s) + 2O_2(g) \longrightarrow 2CO_2(g)\,,\ \Delta H = 2 \times -94.14\ KCal = -188.28\ KCal$$

$$\underline{3H_2(g) + \frac{3}{2}\,O_2(g) \longrightarrow 3H_2O(l)\,,\ \Delta H = 3 \times -68.47KCal = -205.41\ KCal}$$

$$3H_2(g) + 2C(s) + \frac{7}{2}\,O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)\,,\ \Delta H = -393.69\ KCal \qquad \ldots (iv)$$

Substracting equation (iii) form equation (iv) then we get,

$$3H_2(g) + 2C(s) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)\,,\ \Delta H = -393.69\ KCal$$

$$C_2H_6(g) + \frac{7}{2}\,O_2(g) \qquad \longrightarrow 3H_2O(l) + 2CO_2(g)\,,\quad \Delta H = -373.3KCal$$

$$\underline{-\quad -\qquad\qquad\qquad -\quad -\qquad\qquad +}$$

$$3H_2(g) + 2C(s) \qquad \longrightarrow C_2H_6(g)\,,\ \Delta H = -20.39\ KCal$$

Hence, enthalpy of formation of ethane is -20.39 KCal.

46. **2056 Q.No. 28**

i. **Distinguish between:**
   a. **Internal energy and enthalpy**
   b. **Exothermic and endothermic reaction.**

ii. Calculate the heat of formation of naphthalene from the following data:

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.405\,KCal.$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -68.3\,KCal$

$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$ $\Delta H = -1231.6\,KCal$
(Naphthalene) [5]

a. **Distinction between internal energy and enthalpy:**

Internal energy	Enthalpy
1. Every substance is associated with a definit amount of energy known as internal energy.	1. It is the heat content of the system.
2. It depends up on the property of state and chemical nature.	2. It depends up on the temperature and pressure of substance.
3. The heat supplied or absorbed by the system is equal to the change in internal energy at constant volume.	3. The heat supplied or absorbed or evolved in the system is equal to the change in enthalpy at constant pressure.
4. $Q_V = \Delta E$	4. $Q_P = \Delta H$

b. **Distinction between endothermic and exothermic reaction:**

Endothermic reaction	Exothermic reaction
a. The reaction in which heat energy is absorbed by the system.	a. The reaction in which heat energy is evolved form the system.
b. The value of change in enthalpy of system is +ve.	b. The value of change in enthalpy of system is -ve.
c. Reactants → Products, ΔH = +ve	c. Reactants → Products, ΔH = -ve

Numerical: Given,

Enthalpy of formation of carbondioxide

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.404\,KCal$ ... (i)

Enthalpy of formation of water

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -68.3\,KCal$ ... (ii)

Enthanpy of combustion of naphthalene ($C_{10}H_8$)

$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l);\ \Delta H = -1231.6\,KCal$ ...(iii)

Enthanpy of formation of naphthalene ($C_{10}H_8$)

$10C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s);\ \Delta H = ?$

Equation (i) is multiplied by 10 and equation is multiplied by 4 and adding both the equation then we get,

$10\,C(s) + 10\,O_2(g) \longrightarrow 10\,CO_2(g);\ \Delta H = -944.04\,KCal$

$4H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l);\ \Delta H = -273.2\,KCal$

$10\,C(s) + 4H_2(g) + 12\,O_2(g) \longrightarrow 10\,CO_2(g) + 4\,H_2O(l);\ \Delta H = -1217.24\,KCal$ ...(iv)

Substracting equation (iii) from equation (iv) then we get,

$10\,C(s) + 4H_2(g) + 12\,O_2(g) \longrightarrow 10\,CO_2(g) + 4\,H_2O(l);\ \Delta H = -1217.24\,KCal$

$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l);\quad \Delta H = -1231.6\,KCal$

$-\quad -\quad -\quad -\quad +$

$10\,C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s);\ \Delta H = +14.36\,KCal$

Hence, the enthalpy of formation of naphthalene i.e. $C_{10}H_8$ is + 14.36 KCal.

2054 Q.No. 23 Calculate the standard heat of formation of $CH_4(g)$ from the following informations.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(1)\ \Delta H = -890.3\,kJ$

$C(graphite) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5\,kJ$

$H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\Delta H = -571.7\,kJ$ [5]

Given,

Enthalpy of formation of carbondioxide

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\,kJ$ ... (i)

Enthalpy of formation of water

$2H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l);\ \Delta H = -571.7\,kJ$ ... (ii)

Enthanpy of combustion of methane (CH_4)

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H = -890.3\,kJ$ ... (iii)

Enthanpy of formation of methane (CH_4)

$C(s) + 2H_2(g) \longrightarrow CH_4(s);\ \Delta H = ?$

Adding eqation (i) and (ii) then we get,

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\,kJ$

$2H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l);\ \Delta H = -571.7\,kJ$

$2H_2(g) + 2O_2(g) + C(s) \longrightarrow CO_2(g) + 2\,H_2O(l);\ \Delta H = -965.2\,kJ$ ... (iv)

Substracting equation (iii) from equation (iv) then we get,

$2H_2(g) + 2O_2(g) + C(s) \longrightarrow CO_2(g) + 2\,H_2O(l);\ \Delta H = -965.2\,kJ$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H = -890.3\,kJ$

$-\quad -\quad -\quad +$

$2H_2(g) + + C(s) \longrightarrow CH_4(g);\ \Delta H = -74.9\,kJ$

Hence, the standard heat of formation of CH_4 is -74.9 kJ.

48. **2053 Q.No. 25(b) Estimate the enthalpy change for the reaction**

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Given: bond energy of H–H = 435 kJ / mol
bond energy of Cl–Cl = 243 kJ / mol
bond energy of H – Cl = 430 kJ / mol [5]

Let ΔH be the enthalpy change of given reaction

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

We know that,

The heat change in reaction i.e. enthalpy of reaction ΔH = (bond energy of reactant – bond energy of product)

or, $\Delta H = [(435 + 243) - (2 \times 430)]\,kJ$

or, $\Delta H = [678 - 860]\,kJ$

or, $\Delta H = -182\,kJ/mol$

Hence, the enthalpy change of given reaction is -182 kJ/mol.

WRITE SHORT NOTES ON [5MARKS]

49. **2075 GIE Q.No. 33i 2070 Set D Q.No. 33 d Hess's law of constant heat summation.** [5]

Please refer to 2063 Q.No. 30a

50. **2075 Set A Q.No. 33i 2073 Supp Q.No. 33iv 2073 Set C Q.No. 33iii 2073 Set D Q.No. 33iii 2072 Supp. Q.No. 33i 2071 Supp. Q.No. 33a Hess's law of constant heat summation and its applications.** [5]

Hess's law of Constant Heat Summation: Please refer to 2063 Q.No. 30a

Application of Hess's law:

Following are the application of Hess's law:

i. **Determination of heat of formation of substance which otherwise cannot be measured experimentally:** The substance like CO, CH_4, C_6H_6 cannot be prepared by combining their constituent elements. Therefore, it is not possible to determine the heat of formation directly. These can be determined indirectly by using Hess's law.

ii. **Determination of heat of transition:** The heat of transition of one allotropic from to another can also be calculated with the help of Hess's law.

iii. **Determination of heat of various reactions:** By using Hess's law, enthalpies of many reactions can be calculated which otherwise cannot be measured directly.

□□□

Unit 6

Chemical Thermodynamics

VERY SHORT ANSWER QUESTIONS: [2 MARKS]

1. **2076 Set B Q.No. 6 2076 Set C Q.No. 6 Calculate entropy change (ΔS) and free energy change (ΔG) for the conversion of ice into water at equilibrium condition when enthalpy change (ΔH) is 9 KJ/mol.** [2]

Given, Enthalpy change at equilibrium (ΔH) = 9 KJ/mol = 9 × 1000 J/mol

Entropy change (ΔS) =?

Free energy change (ΔG) = ?

Temperature (T_m) = 273K

We know that

$$\text{Entropy change } (\Delta S) = \frac{\Delta H}{T_m} = \frac{9 \times 1000}{273} = 32.96 \text{ J/mol}$$

We know that

Gibb's free energy (ΔG) = ΔH – TΔS = 9000 – (273 × 32.96) = 1.92 J/mol

Hence, the entropy change (ΔS) = 32.96 J/mol and Gibb's free energy (ΔG) = 1.92 J/mol

2. **2075 GIE Q.No. 6 2075 Set A Q.No. 6 Predict spontaneity and non spontaneity in term of ΔG, when ΔH and ΔS are positive.** [1+1]

The spontaneity can be determined by Gibb's free inergy. ΔG = ΔH - TΔS, Where the sign of ΔG depends on the signs of the changes in enthalpy (ΔH) and entropy (ΔS).

In cases where ΔG is

i. Negative, the process is spontaneous.

ii. Positive, the process is non-spontaneous.

By examining the signs of the *ΔS* and *ΔH*

i. When *ΔS* > 0 and *ΔH* < 0, the process is always spontaneous.

ii. When *ΔS* < 0 and *ΔH* > 0, the process is never spontaneous, but the reverse process is always spontaneous.

iii. When *ΔS* > 0 and *ΔH* > 0, the process will be spontaneous at high temperatures and non-spontaneous at low temperatures.

iv. When *ΔS* < 0 and *ΔH* < 0, the process will be spontaneous at low temperatures and non-spontaneous at high temperatures.

3. **2075 Set B Q.No. 6 Give reason:** [1+1]

   i. Gases have the highest absolute entropy among the three state of matter.

   ii. Decrease of enthalpy is the sole criterion for feasibility of a process.

i. As a gas expands in a system, entropy increases. If an atom has more space to bounce around, it will bounce more. Gases have the highest absolute entropy when compared to liquids and solids. Any chemical reaction that increases the number of gas molecules also increases entropy. A chemical reaction that increases the number of gas molecules would be a reaction that pours energy into a system. More energy gives you greater entropy and randomness of the atoms.

ii. We know that all physical and chemical processes are accompanied by energy changes. It is possible to interpret various spontaneous processes on the basis of changes in energy. The spontaneous processes proceed by decrease of energy. The state of lowest energy corresponds to the state of maximum stability. Therefore, the natural tendency of all systems in this universe to go from unstability to stability supports the fact that any process which involves a decrease in energy should have an inherent tendency to take place. The sign of ΔH may be taken as a criterion for the spontaneity of a process and decrease of enthalpy.

4. **2074 Supp. Q.No. 6 2074 Set B Q.No. 6 How would you apply the relation - ΔG = TΔS$_{total}$ to predict whether the process is spontaneous or non-spontaneous?** [2]

Gibb's free energy change ΔG indicates the chemical reaction is spontaneous or non-spontaneous.

ΔG > 0, the reaction is non-spontaneous.

ΔG < 0; the reaction is spontaneous.

If ΔG is negative, the reaction is spontaneous at low temperature. If ΔG is positive, the reaction is non-spontaneous at high temperature.

5. **2074 Set A Q.No. 6 Apply the relation -ΔG = TΔS$_{total}$ to predict whether the process is spontaneous or non-spontaneous?** [2]

Please refer to 2074 Supp. Q.No. 6

6. **2073 Supp Q.No. 6 2073 Set C Q.No. 6 Under what conditions the reaction expected to occur.**

   i. spontaneous.

   ii. non-spontaneous, if ΔH and ΔS are positive for the reaction? [1+1]

i. If ΔH > T ΔS, then ΔG is negative, the reaction is spontaneous at low temperature.

ii. If ΔH < T ΔS, then ΔG is positive, the reaction is non-spontaneous at high temperature.

7. **2073 Set D Q.No. 6 Under what conditions is the reaction expected to occur** [1+1]

   i. spontaneous

   ii. non- spontaneous, if ΔH and ΔS are negative

Please refer to 2073 Supp Q.No. 6

8. **2072 Supp. Q.No. 6 Mention the proper conditions of a chemical reaction to become spontaneous if its ΔH and ΔS are positive.** [2]

If the value of ΔH and ΔS are positive, the reaction becomes spontaneous and the reaction occurs only TΔS > ΔH.

9. **2072 Set C Q.No. 6 How would you predict the spontaneity of a system in term of free-energy change?** [2]

The relation of Gibb's free energy with E, H, S and T are given by equation.

ΔG = ΔH - TΔS

Gibb's free energy change ΔG indicates the chemical reaction is spontaneous or non-spontanesous.

ΔG > 0, reaction is non-spontaneous

ΔG < 0, reaction is spontaneous

10. **2072 Set D Q.No. 6 Calculate ΔS and ΔG for conversion of ice into water when they are equilibrium at 0°C(ΔH = 4 kJ/mole)** [1+1]

Given, ΔH = 4kJ/mol = 4 × 1000 J/mol

Entropy change $\Delta S = ?$

Temperature i.e. melting point in Kelvin $(T_m) = (0 + 273)\ K = 273\ K$

We know that

$$\text{Entropy change } (\Delta s) = \frac{\Delta H}{T_m} = \frac{4 \times 1000}{273} = 14.65\ J\ mol^{-1}k^{-1}$$

Gibb's free energy change $(\Delta G) = ?$

We know that

$$\Delta G = \Delta H - T\Delta S$$
$$= (4 \times 1000 - 273 \times 14.65) = (4 \times 1000 - 3999.45) = 0.55\ J\ mol^{-1}$$

Hence, the entropy change (ΔS) is 14.65 J mol^{-1} K^{-1} and free energy change (ΔG) is 0.55 J mol^{-1}.

11. **2071 Supp. Q.No. 6 Predict the criteria of spontaneity in light of free-energy change.** [2]

Prediction about a reaction

Condition for spontaneity

ΔH	ΔS	Occurrence of a reaction
+(increase)	+(increase)	Reaction occurs only if $T\Delta S > \Delta H$
–(decrease)	–(decrease)	Reaction occurs only if $\Delta H > T\Delta S$
+(increase)	–(decrease)	Occurrence impossible
–(decrease)	+(increase)	Reaction occurs

Prediction about the sign for ΔH

A reaction which gives of heat to the surroundings is said to be exothermic. So, ΔH has a negative value.

Example:

$H_2O\ (g) \longrightarrow H_2O(l),\ \Delta H = -49.93\ kJ$

A reaction which absorbs heat from the surrounding is said to be endothermic. So, that ΔH has a positive value.

Example:

$H_2O\ (l) \longrightarrow H_2O(g),\ \Delta H = +49.93\ kJ$

Reaction in which bonds are formed are invariably exothermic.

Example:

$I(g) + I(g) \longrightarrow I_2(g)$

Prediction about the sign for ΔS

ΔS would be positive if disorder increase.

Example:

i. ΔS would be positive for a reaction where the number of products molecules exceeds the number of reactants molecules.

$2NH_3 \longrightarrow N_2 + 3H_2$

ii. ΔS would be positive when a solid melts or when a liquid evaporates.

12. **2071 Set C Q.No. 6 Mention the proper conditions of a chemical reaction to become spontaneous if its ΔH and ΔS are positive.** [2]

Please refer to 2072 Supp. Q.No. 6

13. **2071 Set D Q.No. 6 Predict the criteria of spontaneity in light of entropy change.** [2]

Please refer to 2071 Supp. Q.No. 6

14. **2070 Supp. Q.No. 6 Distinguish spontaneous and non spontaneous process giving an example of each.** [2]

Distinction between spontaneous and non spontaneous process:

Spontaneous	Non-spontaneous
1. Process that proced in a definite direction on their own are spontaneous.	1. Process that requires energy input are non-spontaneous.
2. Example- water converting into ice.	2. Electricity is required to convert water to H_2 gas and O_2 gas.

15. **2070 Set C Q.No. 5 What is meant by spontaneous process? Write an example for it.** [2]

The process which occurs with its own effort without the aid of any external agency is called spontaneous process. It means the process which is possible under the given set of conditions. Example: diffusion of gas, evaporation of liquid, rusting of iron, melting of ice etc.

16. **2070 Set D Q.No. 6 How would you predict the spontaneity using the relation?** [2]

$T\Delta S_{total} = -\Delta G_{sys}$

The given relation:

$T\Delta S_{total} = -\Delta G_{sys}$

For the spontaneous process, the total change in entropy is always positive.

$T\Delta S_{total} = +ve$

For spontaneous process, the Gibb's energy of a system is always negative.

$\Delta G_{sys} = -ve$

17. **2069 (Set A) Q.No. 5 Define Gibbs free–energy change. Write the mathematical relation to predict the spontaneity.** [2]

Gibb's free energy: Any part of energy which can be converted into useful work is called Gibb's free energy. It is denoted by the symbol G. its relations with E, H, S and T are given by the following equations.

$G = H - TS$

$G = E + PV - TS$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta E + P\Delta V - T\Delta S$

For spontaneous change, $(\Delta G)_{T,P} < 0$

18. **2069 Set B Q.No. 6 Give the physical meaning of entropy. Write its unit.** [2]

The physical meaning of entropy is the degree of disorder or randomness of the molecules of a system. It is denoted by S. The unit of rate constant of entropy is $JK^{-1}mol^{-1}$.

19. **2068 Q.No. 15 Name the two criteria which must be met for a process to be spontaneous regardless of the temperature.** [2]

Following are the two criteria which must be met for a process to be spontaneous regardless of the temperature:

Enthalpy change of a system is negative i.e. $\Delta H = -ve$

Entropy change of a system is positive i.e. $\Delta S = +ve$

20. **2066 Q. No. 16 Comment the statement "The decrease of enthalpy is not the sole criterian for the feasibility of the process."** [2]

In early development of thermodynamics, it was assumed that a spontaneous process occurs with the decrease in enthalpy of the system. These assumptions could explain why a ball rolls down the hill and why a hot object cools down. This could also explain the feasibility of some chemical reaction. For example, combustion of methane gas and neutralization of acid by a base is feasible because these reactions are accompanied by evolution of heat and decrease in energy of the system.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (g),\ \Delta H = -890.4\ kJ$

$H^+ + OH^- \longrightarrow H_2O,\ \Delta H = -56.2\ kJ$

Both reactions are exothermic, it is not necessary that an exothermic reaction is feasible. Some endothermic reactions are also feasible.

Example: melting of ice at higher temperature is feasible process and ammonium nitrate is dissolved in water by the absorption of heat.

$NH_4NO_3 \longrightarrow NH_4^+ + NO_3^-,\ \Delta H = 25\ kJ$

The above assumption fails to explain the feasible process. Thus decrease of enthalpy is not the sole criterion for the feasibility of process.

21. **2063 Q.No. 14** **Define thermodynamic efficiency of heat engine. How is second law of thermodynamics stated in the light of this term?** **[2]**

Thermodynamic efficiency of heat engine: The extent of conversion of heat into work by engine is called thermodynamic efficiency of heat engine.

Mathematically, it is defined as the ratio of the external work obtained to the amount of heat energy absorbed from the heat source.

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Where, T_1 = Temperature of source.

T_2 = Temperature of sink.

The efficiency $\frac{W}{Q_1}$ of the heat engine is denoted by η

$$\therefore \eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Where, W = Work done.

Q_1 = Quantity of heat taken from the source.

2nd Law of thermodynamic is stated in the light of efficiency of heat engine, heat efficiency of a practical thermodynamics engine is always less than 100%.

22. **2062 Q.No. 16 (ii)** **Define the terms: Standard free energy of a reaction** **[2]**

Standard free energy of a reaction: The free energy change in a chemical reaction where the reactant and product are in their standard state. It is denoted by $\Delta G°$

$\Delta G° = \Sigma G°\ (product) - \Sigma G°\ (reactant)$

23. **2061 Q.No. 14** **In order for a reaction to occur spontaneously, what is the criterion?** **[2]**

For a reaction to occur spontaneously, the change in free energy i.e. ΔG is negative. If $\Delta H > T\Delta S$, then ΔG is -ve.

$\Delta G = -\bar{v}e$ (or < 0)

24. **2060 Q.No. 17** **What is entropy? State the effect of increased temperature on the entropy of a substance.** **[2]**

Entropy: The degree of randomness or disorder of the molecules in a system is known as entropy. Greater the randomness of the molecules in a system, greater would be the entropy and vice-versa.

Effect of temperature on the entropy of substance: Gas has higher entropy than liquid and liquid has higher entropy than solid.

Entropy of gas > Entropy of liquid > Entropy of solid

The change of entropy of a system between two states can be determined by

$$\text{Entropy change } (\Delta S) = \frac{dQ_{rev}}{T}$$

Where, dQ_{rev} = reversible heat change.

T = Kelvin scale temperature

Entropy of substance is changed with changing temperature.

25. **2057 Q.No. 17** **What is the physical concept of entropy?** **[2]**

Please refer to **2069 Set B Q.No. 6**

SHORT ANSWER QUESTIONS: [5 MARKS]

26. **2069 Set B Q.No. 26** **Define Gibbs free energy. How is spontaneity of a reaction predicted in light of free energy change, enthalpy change and entropy change?** **[5]**

Gibb's free energy: Any part of energy which can be converted into useful work is called Gibb's free energy. It is denoted by the symbol G. its relation with E,H,S and T are given by the following equation.

$G = H - TS$

If the system is changed from one state to another state then

$G_1 = H_1 - T_1S_1$ ... (i)

$G_2 = H_2 - T_2S_2$ ... (ii)

The change of free energy is given by

$G_2 - G_1 = (H_2 - H_1) - (T_2S_2 - T_1S_1)$

If the system is carried out at constant temperature then $T_1 = T_2 = T$

$\Delta G = \Delta H - T\Delta S$ ... (iii)

The equation (iii) is called Gibb's Helmholtz equation and useful for predicting the spontaneity of a process.

From 1st law of thermodynamics

or, $\Delta Q = \Delta E + \Delta W$

or, $\Delta Q = \Delta E + W_{exp} + W_{useful}$

or, $\Delta Q = \Delta E + P\Delta V + W_{useful}$ $[W_{exp} = P\Delta V]$

or, $\Delta Q = \Delta H + W_{useful}$ $[\Delta E + P\Delta V = \Delta H]$

or, $\Delta Q = \Delta H + W_{useful}$ ... (iv)

We know that,

$$\Delta S = \frac{\Delta Q_{rev}}{T}$$

$\Delta Q = T\Delta S$

Equation (iv) becomes

$T\Delta S = \Delta H + W_{useful}$

$\Delta H - T\Delta S = -W_{useful}$

or, $\Delta G = -W_{useful}$

Prediction about a reaction:

Condition for spontaneity

ΔH	ΔS	Occurrence of a reaction
+ (increase)	+ (increase)	Reaction occurs only if TΔS > ΔH
- (decrease)	- (decrease)	Reaction occurs only if ΔH > TΔS
+ (increase)	- (decrease)	Occurrence impossible
- (decrease)	+ (increase)	Reaction occurs

Prediction about the sign for ΔH

A reaction which gives of heat to the surroundings is said to be exothermic. So, ΔH has a negative value.

Example:

$H_2O\ (g) \longrightarrow H_2O(l),\ \Delta H = -49.93\ kJ$

A reaction which absorbs heat from the surrounding is said to be endothermic. So, th ΔH has a positive value.

Example:

$H_2O(l) \longrightarrow H_2O(g)$, $\Delta H = +49.93$ kJ

Reaction in which bonds are formed are invariably exothermic.

Example:

$I(g) + I(g) \longrightarrow I_2(g)$

Prediction about the sign for ΔS

ΔS would be positive if disorder increase.

Example:

i. ΔS would be positive for a reaction where the number of products molecules exceeds th number of reactants molecules.

$2NH_3 \longrightarrow N_2 + 3H_2$

ii. ΔS would be positive when a solid melts or when a liquid evaporates.

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27. 2067 Q.No. 26 What is meant by free–energy change? Write the relation between entropy and enthalpy change. How does this relation help in predicting the spontaneity of a reaction? [5]

✍ **Free energy:** The amount of energy released or absorbed during the chemical reaction at constant temp. is known as free energy.

Gibb's Free energy: Any part of energy which can be converted into useful work is called Gibb's free energy. It is denoted by the symbol G. its relation with E,H,S and T are given by the following equation.

$G = H - TS$

or, $G = E + PV - TS \quad [H = E + PV]$

or, $\Delta G = \Delta E + P\Delta V - T\Delta S$

or, $\Delta G = \Delta H - T\Delta S$

$\therefore (\Delta G)_{T.P} = \Delta H - T\Delta S$

Gibb's free energy ΔG indicates the chemical reaction is spontaneous or non-spontaneous.

If the Gibb's free energy ΔG is less than 0 i.e. $\Delta G < 0$ i.e. in –ve value then the reaction is spontaneous.

If the Gibb's free energy ΔG is more than 0 i.e. $\Delta G > 0$ i.e. in +ve value then the reaction is non–spontaneous.

If the Gibb's free energy is equal to zero then the process in equilibrium state.

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28. 2065 Q.No. 26 What is free energy change? How it is related with enthalpy change and entropy change? How would you predict whether a reaction is spontaneous, non spontaneous and equilibrium in term of free energy change? [5]

✍ Please refer to 2067 Q.No. 26

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29. 2064 Q.No. 24 Define Gibb's free energy. How is the feasibility of exothermic and endothermic reactions predicted in the light of free energy change and entropy change? [5]

✍ Please refer to 2069 (Set B) Q.No. 26

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30. 2061 Q.No. 27 State and explain second law of thermodynamics. How does free energy change depend on the equilibrium constant? [5]

✍ **Second law of thermodynamics:** First law of thermodynamics is failed to explain the direction and feasibility of a process. So, 2nd law has been formulated the concept of energy which measure the randomness or disorderness of a system.

2nd law of thermodynamics may be stated as in various way, all the statement appear to be different from one another. The modified statement "all forms of energy are converted into heat but the heat so obtained cannot be converted into other forms of energy by any process"

For isolated system: The criteria of spontaneity and equilibrium of an isolated system are:

Entropy Change	Sign	Process
ΔS	+ve	Spontaneous
ΔS	-ve	Non-spontaneous
ΔS	0	Equilibrium

For a spontaneous process the entropy change of the universe should be always positive.

- **Relationship between free energy change and equilibrium constant**

$\Delta G^\circ = - RT \ln K$

or, $\Delta G^\circ = - 2.303\, RT \log K$

Where, R = Universal gas constant.

For spontaneous reaction ΔG° should be negative.

Therefore, log K must be +ve.

So, for a spontaneous reaction $K > 1$

Thus, free energy change depends upon the value of equilibrium constant K.

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31. 2060 Q.No. 25 Define free energy. Derive an expression to relate Gibb's free energy change with work. [5]

✍ **Free energy:** The amount of energy released or absorbed during the chemical reaction at constant temperature is known as free energy.

Gibb's Free energy: Please refer to 2069 (Set B) Q.No. 26

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32. 2059 Q.No. 24 State second law of thermodynamics. How would you explain the law in the light of entropy change? [5]

✍ **Second law of thermodynamics:** Please refer to 2061 Q.No. 27

Second Part: Please refer to 2069 (Set B) Q.No. 26

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33. 2058 Q.No. 25 Discuss the criteria of spontaneity, non spontaneity and equilibrium of exothermic and endothermic reactions on the basis of free energy and entropy change. [5]

✍ Criteria of spontaneity and and equilibrium of exothermic and endothermic reaction can be predicted in terms of ΔG free energy change, ΔH enthalpy change and ΔS entropy change.

According to Gibb's Helmholtz equation

$\Delta G = \Delta H - T\Delta S$

Where, ΔG = Free energy change
ΔH = Enthalpy change
ΔS = Entropy change

a. For exothermic reaction:

ΔH is always –ve.

i. If ΔS is positive, the value of ΔG is –ve and the process is spontaneous at all temperature.

ii. If ΔS is –ve, the value of ΔG is is ± i.e. either +ve or –ve at high temperature.

Thus, at high temperature, the process is non-spontaneous and at low temperature the process is spontaneous.

b. For endothermic reaction:

ΔH is always + ve.

i. If ΔS is negative, the value of ΔG is +ve and the process is non-spontaneous.

ii. If ΔS is +ve, the value of ΔG may be +ve or –ve.

At high temperature $T\Delta S > \Delta H$

ΔG = -ve, the process is spontaneous.

At low temperature $T\Delta S < \Delta H$

ΔG = +ve, the process is non-spontaneous.

Hence, exothermic reaction is favoured at low temperature but endothermic reaction is favoured at high temperature.

c. If the value of $\Delta G = 0$, the value of ΔH is equal to $T\Delta S$. The process is in equilibrium.

34. **2057 Q.No. 24 State and explain second law of thermodynamics.** **[5]**

✎ **Second law of thermodynamics:** Please refer to 2061 Q.No. 27

Entropy and spontaneity: According to 2nd law of thermodynamics, a process will occur spontaneously if entropy of the universe increase.

LONG ANSWER QUESTIONS [10 MARKS]

35. **2070 Set D Q.No. 32 a How is the free energy change of a reaction related with the enthalpy change and entropy change? Discuss the criteria of spontaneity and non-spontaneity of a reaction on the basis of its energy change.** **[5]**

✎ Please refer to 2067 Q.No. 26 and 2069 (Set B) Q.No. 26

NUMERICAL PROBLEMS:

36. **2064 Q.No. 17 The latent heat of fusion of ice is 336 Jg^{-1}. Calculate the molar entropy of fusion of ice at its normal melting point.** **[2]**

✎ Given,

Latent heat of fusion of ice(ΔH_{fus})= 336 Jg^{-1} = 336 × 18 J mol^{-1}

Normal melting point of ice(T_{fus}) = 273 K

Molar entropy of fusion of ice (ΔS_{fus}) = ?

We know that,

$$\Delta S_{fux} = \frac{\Delta H_{fus}}{T_{fus}} = \frac{336 \times 18}{273} = 22.15 \text{ J mol}^{-1}\text{K}^{-1}$$

Hence, the molar entropy of fusion of ice is 22.15 J mol^{-1}K^{-1}.

WRITE SHORT NOTES ON [5 MARKS]

37. **2072 Set E Q.No. 33iv Prediction for the feasibility of reaction in terms of ΔG and ΔS.** **[5]**

✎ **Prediction of the feasibility of reaction in terms of ΔG and ΔS:**

The Gibb Hem-Holtz equation is $\Delta G = \Delta H - T\Delta S$. This equation includes both change in enthalpy and change in entropy. The interplay of enthalpy change and entropy change is the prediction of feasibility of reaction.

ΔS	$\Delta G = \Delta H - T\Delta S$	Behaviour
+ ve	- ve	Spontaneous
- ve	If $\|\Delta H\| > \|T.\Delta S\|, \Delta G$ =-ve	Spontaneous
- ve	If $\|\Delta H\| < \|T.\Delta S\|, \Delta G$ =+ve	Non spontaneous
- ve	If $\|\Delta H\| = \|T.\Delta S\|, \Delta G = 0$	Equilibrium
- ve	+ ve	Non spontaneous
+ ve	If $\|\Delta H\| < \|T.\Delta S\|, \Delta G$ =-ve	Spontaneous
+ ve	If $\|\Delta H\| > \|T.\Delta S\|, \Delta G$ =+ve	Non spontaneous
+ ve	If $\|\Delta H\| = \|T.\Delta S\|, \Delta G = 0$	Equilibrium

From the table given above it is concluded that

i. If the reaction is exothermic and entropy change of system is positive, the change in Gibb's free energy is always negative and the reaction occurs spontaneously at all temperature.

ii. If the reaction is exothermic but the entropy change of the system is negative then different case arises.

a. At low temperature: Gibb's free energy becomes positive and the process is non-spontaneous.

b. At high temperature: Gibb's free energy becomes negative and the process is spontaneous.

iii. If the reaction is endothermic, the entropy change of reaction is negative and change in Gibb's free energy always become +ve irrespective temperature. The process is non-spontaneous.

38. **2071 Set C Q.No. 33 a 2071 Set D Q.No. 33 a Second law of thermodynamics** **[5]**

→ **Second law of thermodynamics:** It states that "Whenever a spontaneous process takes place, it is accompanied by increase in the total energy of the universe"

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} > 0$

According to second law, when an irreversible spontaneous process occurs, the entropy of system and surrounding increase i.e. $\Delta S_{uni} > 0$. When a reversible process occurs the entropy of the system remains constant $\Delta S_{uni} = 0$. Since the entire universe is undergoing spontaneous change, the second law can be stated as, "The entropy of the system is constantly increasing"

According to second law of thermodynamics, for a spontaneous process, there must be increase in entropy of the universe i.e. $\Delta S_{uni} > 0$

Now, for spontaneous process

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur} > 0$

or, $\Delta S_{uni} = \Delta S_{sys} - \dfrac{\Delta H_{sys}}{T} > 0$

or, $T\Delta S_{uni} = T\Delta S_{sys} - T\Delta H_{sys} > 0$

For spontaneous process, there must be increase in entropy of the universe i.e. it must be positive.

Hence, $T\Delta S_{uni} = -\Delta G$

If ΔG = -ve, there is increase in entropy of the universe. Hence the process is spontaneous.

If ΔG = +ve, there is decrease in entropy of the universe. Hence the process is non-spontaneous.

If $\Delta G = 0$, the system is at equilibrium state.

39. **2070 Supp. Q.No. 33 a Spontaneity in light of entropy change, enthalpy change and free-energy change.** **[5]**

✎ Please refer to 2069 (Set B) Q.No. 26

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Unit 7

Chemical Kinetics

VERY SHORT ANSWER QUESTIONS: [2 MARKS]

1. 2076 Set B Q.No. 7 2076 Set C Q.No. 7 **You are given a rate law equation, Rate = k $[A]^2$ [B]. By how many times will the rate increase or decrease for the reaction if**
   - i. **Concentration of Ⓐ is doubled while that of Ⓑ made constant.**
   - ii. **Concentration of Ⓐ is kept constant that of Ⓑ is doubled?** [1+1]

✍ The given rate law equation is

$\text{Rate} = k[A]^2[B]$

i. If the concentration of A is doubled while that of B made constant, the new rate equation may be

New Rate = $k[2A]^2 = 4k[A]^2$ = 4 times the initial rate

ii. If the concentration of A is kept constant that of B is doubled, the new rate equation may be

Rate = $k[2B] = 2k[B]$ = 2 times the initial rate

2. 2075 GIE Q.No. 7 **For a reaction, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$. If the rate of formation of Oxygen is 2×10^{-1} mol $L^{-1}Sec^{-1}$, what will be the rate of disappearance of N_2O_5?** [2]

✍ The given reaction is $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

The rate of disappearance of $N_2O_5 = \frac{-1}{2}\frac{d[N_2O_5]}{dt}$

The rate of formation of $O_2 = \frac{d[O_2]}{dt}$

We know that,

The rate of disappearance of N_2O_5 = The rate of formation of O_2

$$\frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt}$$

or, $\frac{-1}{2}\frac{d[N_2O_5]}{dt} = 2 \times 10^{-1}$

or, $\frac{d[N_2O_5]}{dt} = 2\times2 \times 10^{-1} = 4 \times 10^{-1}$

Hence, the rate of disappearance of N_2O_5 is 4×10^{-1}.

3. 2075 Set A Q.No. 7 **A reaction is I^{st} order w.r. to A and II^{nd} order w.r. to B.** [1+1]
   - I. **Write the rate law equation.**
   - II. **How many times will the rate increase when the concentration of B is tripled?**

✍ The reaction according to question may be

$A + 2B \longrightarrow \text{Product}$

i. The rate law equation is

Rate = $K[A]^1[B]^2$

ii. Rate = $K[B]^2$ or Rate = Kb^2, if [B] = 3b then new rate = $K(3b)^2 = 9b^2$

Hence, the rate of reaction will be increased by 9 times.

4. 2075 Set B Q.No. 7 **A hypothetical reaction $P + Q \longrightarrow Z$ is a third order reaction. Write its possible rate law expression.** [2]

✍ The possible rate law expressions for third order reaction are:

Rate = $k[P]^0[Q]^3$

Rate = $k[P]^3[Q]^0$

Rate = $k[P]^1[Q]^2$

Rate = $k[P]^2[Q]^1$ Where, k = rate constant

5. 2074 Supp. Q.No. 7 **For a reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, The rate of disappearance of N_2O_5 is 4×10^{-6} mol $L^{-1}s^{-1}$, what will be the rate of formation of NO_2?** [2]

✍ The given reaction is $2N_2O_5 \longrightarrow 4NO_2 + O_2$

The rate of disappearance of $N_2O_5 = \frac{-1}{2}\frac{d[N_2O_5]}{dt}$

The rate of formation of $NO_2 = \frac{1}{4}\frac{d[NO_2]}{dt}$

The rate of formation of $O_2 = \frac{d[O_2]}{dt}$

We know that,

The rate of disappearance of N_2O_5 = The rate of formation of NO_2

$$\frac{-1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

Or, $\frac{-1}{2} 4 \times 10^{-6} = \frac{1}{4}\frac{d[NO_2]}{dt}$

Or, $\frac{d[NO_2]}{dt} = 2 \times 4 \times 10^{-6} = 8 \times 10^{-6}$ mol $L^{-1}s^{-1}$

Hence, rate of formation of NO_2 is 8×10^{-6} mol $L^{-1}s^{-1}$ which is double of the rate of disappearance of N_2O_5

6. 2074 Set A Q.No. 7 **For a reaction $2HI \longrightarrow H_2 + I_2$ If the rate of formation of I_2 is 9.1×10^{-6} mol $L^{-1}s^{-1}$, What will be the rate of disappearance of HI?** [2]

✍ The rate of disappearance of HI = $-\frac{1}{2}\frac{d[HI]}{dt}$

The rate of formation of $H_2 = +\frac{d[H_2]}{dt}$

The rate of formation of $I_2 = +\frac{d[I_2]}{dt}$

We know that,

The rate of disappearance of HI = rate of formation of H_2 = rate of formation of I_2

Or, $-\frac{1}{2}\frac{d[HI]}{dt} = +\frac{d[H_2]}{dt} = +\frac{d[I_2]}{dt}$

Or, $-\frac{1}{2}\frac{d[HI]}{dt} = +\frac{d[I_2]}{dt}$

Or, $-\frac{1}{2}\frac{d[HI]}{dt} = 9.1 \times 10^{-6}$ mol $L^{-1}s^{-1}$

Or, $-\frac{d[HI]}{dt} = 2 \times 9.1 \times 10^{-6}$ mol $L^{-1}s^{-1}$

Hence, the rate of disappearance of HI is $2 \times 9.1 \times 10^{-6}$ mol $L^{-1}s^{-1}$ which is double of rate of formation of I_2.

7. **2074 Set B Q.No. 7 Write the rate expression for the following reaction 2 HI $\longrightarrow$ $H_2 + I_2$ If the rate of formation of I_2 is 9.1×10^{-6} mol L^{-1} s^{-1}, what will be the rate of disappearance of HI?** [1+

➣ The rate of disappearance of HI = $-\frac{1}{2}\frac{d[HI]}{dt}$

The rate of formation of H_2 = $+\frac{d[H_2]}{dt}$

The rate of formation of I_2 = $+\frac{d[I_2]}{dt}$

We know that,

The rate of disappearance of HI = rate of formation of H_2 = rate of formation of I_2

or, $-\frac{1}{2}\frac{d[HI]}{dt} = +\frac{d[H_2]}{dt} = +\frac{d[I_2]}{dt}$

or, $-\frac{1}{2}\frac{d[HI]}{dt} = +\frac{d[I_2]}{dt}$

or, $-\frac{1}{2}\frac{d[HI]}{dt} = 9.1 \times 10^{-6}$ mol L^{-1} s^{-1}

or, $-\frac{d[HI]}{dt} = 2 \times 9.1 \times 10^{-6}$ mol L^{-1} s^{-1}

Hence, the rate of disappearance of HI is $2 \times 9.1 \times 10^{-6}$ mol L^{-1} s^{-1} which is double of rate of formation of I_2.

8. **2073 Supp Q.No. 7 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is**
   - **i. doubled**
   - **ii. reduced to half** [1+1]

➣ For a second order reaction

Initial rate = $k_2[A]^2$

i. If the concentration of reactant is doubled

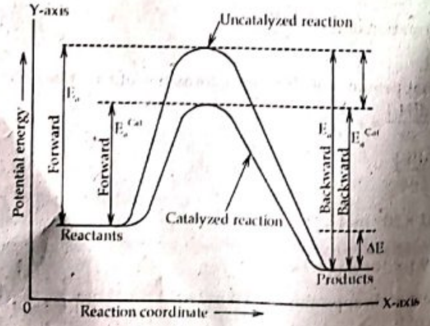
New rate = $k_2[2A]^2 = 4k_2[A]^2 = 4 \times$ initial rate

ii. If the concentration of reactant is reduced to half $\frac{1}{2}$

New rate = $k_2\left[\frac{1}{2}A\right]^2 = \frac{1}{4}k_2[A]^2 = \frac{1}{4} \times$ initial rate

9. **2073 Set C Q.No. 7 Draw an energy profile diagram to show influence of catalyst in the rate of chemical reaction.** [2]

➣ The energy profile diagram of catalyzed and uncatalyzed reaction is



E_a(forward) = Forward reaction for uncatalyzed reaction

E_a(backward) = Backward reaction for uncatalyzed reaction

E_a^{Cat}(forward) = For catalyzed reaction

E_a^{Cat}(backward) = For catalyzed reaction

10. **2073 Set D Q.No. 7 What are the essential conditions for the effective collision of reacting species?** [2]

➣ Following are the essential condition for the effective collision of reacting species:

i. They collide with proper orientation.

ii. The colliding species must have sufficient kinetic energy.

11. **2072 Supp. Q.No. 7 Write the rate expression of each components in the following reaction:**
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
What is the unit of reaction rate? [1.5+0.5]

➣ The given reaction is

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Rate of reaction in terms of $N_2(r) = -\frac{d[N_2]}{dt}$

Rate of reaction in terms of $H_2(3r) = -\frac{d[H_2]}{dt}$ or $r = -\frac{d[H_2]}{3dt}$

Rate of reaction in terms of $NH_3(2r) = \frac{d[NH_3]}{dt}$ or $r = \frac{d[NH_3]}{2dt}$

The equivalence rate of reaction is also expressed as

Rate of reaction $= -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{3dt} = \frac{d[NH_3]}{2dt}$

Unit of reaction rate: molL^{-1} time^{-1}

12. **2072 Set C Q.No. 7 What is meant by instantaneous rate of reaction? Write the expression for the rate of the following reaction:** [1+1]
$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

➣ **Instantaneous rate of reaction:** The rate of chemical reaction at any particular instant of time during chemical change is known as instantaneous rate of reaction.

The given reaction is

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

Rate of reaction $= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

13. **2072 Set D Q.No. 7 Define the terms** [1+1]
   - **i. activated complex**
   - **ii. rate of reaction**

➣

i. **Activated complex:** An activated complex is an intermediate state that is formed during the conversion of reactants into products. An activated complex is the structure that results at the maximum energy point along the reaction path. The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants.

ii. **Rate of reaction:** A mathematical expression in which observed rate of reaction is related with concentration of reacting species is called rate of reaction.

Let us consider a reaction

$aA + bB \longrightarrow$ Product

Rate α $[A]^a[B]^b$

Rate = $k[A]^a[B]^b$

14. 2072 Set E Q.No. 7 **The following hypothetical reaction is second order,**

$A + B \longrightarrow Z$

Write possible rate law expression. [2]

The hypothetical reaction for second order is

$A + B \longrightarrow Z$

The possible rate law expression for second order reaction may be

$Rate = k[A]^0[B]^2$

$Rate = k[A]^2[B]^0$

$Rate = k[A]^1[B]^1$ Where, k is the rate constant.

15. 2071 Supp. Q.No. 7 **Define 1st order reaction and write the unit of rate constant in the first order reaction.** [1+1]

First order reaction: The reaction whose rate depends upon the concentration of only one reactant is said to be 1st order.

Let us consider a reaction

$A + B \longrightarrow Product$

$Rate = k\,[A]^1\,[B]^0$ Where, k is rate constant

The order of reaction is (1 + 0) = 1 i.e. 1st order.

Unit of rate constant (k)

$$k = \frac{Rate}{[A]^1} = \frac{Mol\,L^{-1}\,s^{-1}}{Mol\,L^{-1}} = s^{-1}$$

Hence, rate constant (k) for 1st order reaction is s^{-1}.

16. 2071 Set C Q.No. 7 **Identify reaction orders if the units of rate constant are:** [2]

a. min^{-1}

b. $molL^{-1}\,min^{-1}$

a. Unit of rate constant = min^{-1}

The rate law expression for a reaction is as

$Rate = k[Reactant]^x$, Where, k = rate constant x = order of reaction

$$[Reactant]^x = \frac{Rate}{k}$$

or, $[mol.L^{-1}]^x = \frac{Mol\,L^{-1}min^{-1}}{min^{-1}}$

or, $[mol.L^{-1}]^x = [mol\,L^{-1}]$ [minute is cancelled]

or, $[mol.L^{-1}]^x = [mol.\,L^{-1}]^1$

or, $x = 1$

Hence, the reaction having rate constant min^{-1} is first order.

b. unit of rate constant = $Mol\,L^{-1}min^{-1}$

$$[Reactant]^x = \frac{Rate}{k}$$

or, $[mol.L^{-1}]^x = \frac{MolL^{-1}\,min^{-1}}{Mol\,L^{-1}\,min^{-1}}$

or, $[mol.L^{-1}]^x = 1$

or, $[mol.L^{-1}]^x = (mol.L^{-1})^0$

or, $x = 0$

Hence, the reaction having rate constant $Mol\,L^{-1}min^{-1}$ is zero order.

17. 2071 Set D Q.No. 7 **Rate of reaction is doubled when concentration of A is doubled but there is no effect in rate with change in concentration of B.**

a. Write rate law

b. Find out unit of the reaction. [2]

The concentration of A is douled, rate is also doubled so it is 1st order with A and zero order with B. The concentration of B is no change.

The rate law becomes

$Rate = k[A]^1[B]^0$ where, k = rate constant

Unit of rate constant k

$$k = \frac{Rate}{[A]^1[B]^0} = \frac{Mol\,L^{-1}s^{-1}}{[Mol\,L^{-1}]^1\,[Mol\,L^{-1}]^0}$$

or, $k = s^{-1}$ or $time^{-1}$

18. 2070 Supp. Q.No. 7 **For a hypothetical reaction $A + B \longrightarrow Z$. The rate of above reaction is doubled when concentration of A is doubled but there is no effect of change of concentration of B.**

i. Write down the rate law.

ii. What is the unit of rate constant? [2]

Please refer to 2071 Set D Q.No. 7

19. 2070 Set C Q.No. 7 **For the reaction**

$P + Q \longrightarrow$ product is a third order.

Write the possible rate law expressions for the above reaction. [2]

The possible rate law expression for the above third order reaction may be:

$Rate = k[P]^0[Q]^3$

$Rate = k[P]^3[Q]^0$

$Rate = k[P]^1[Q]^2$

$Rate = k[P]^2[Q]^1$, Where, k is the rate constant.

20. 2070 Set D Q.No. 7 **Draw energy profile diagram for catalyzed and uncatalyzed reactions.** [2]

Please refer to 2073 Set C Q.No. 7

21. 2069 (Set A) Q.No. 7 **What is meant by effective collision of reacting species? Mention any one condition for a collision.** [2]

Effective collision: The collision between reacting molecules resulting in the formation of product is called effective collision. There are many factors that affecting in the effective collision which of one is the **orientation** of the reacting molecules.

22. 2069 (Set B) Q.No. 7 **Write the rate law for a first order reaction. What is the unit of the reaction?** [2]

Let us consider a reaction: $A \longrightarrow$ product

Rate law expression for first order reaction is written as:

$Rate = k\,[A]^1$

Where, k = rate constant

Unit of rate constant

$$k = \frac{Rate}{[A]} = \frac{Mol\,L^{-1}s^{-1}}{MolL^{-1}} = s^{-1}$$

23. 2069 Supp. Set B Q.No. 7 **Define**

i. Effective collision **ii. Proper orientation** [2]

i. **Effective collision:** The collision between reacting molecules resulting in the formation of product is called effective collision.

ii. **Proper orientation:** The reacting molecule must have a particular geometry which result in effective collision is called proper orientation.

24. 2068 Q.No. 16 **Define the half-life period of a reaction. The half-life periods of two reactions A and B are 3.21×10^2 minute and 569 minute respectively. Which of these is a faster reaction?** [2]

Half life period: The time required to complete the half of the initial amount of the reactant by any chemical change is known as half life. It is denoted by $t_{1/2}$.

$A = 3.21 \times 10^2 = 321$ minute

$B = 569$ minute

Smaller the value of half life period of reaction, reaction rate will be faster. Because concentration of reactant will decrease faster and formation of product is faster. So, rate of reaction A is faster than B.

25. **2067 Q.No. 15** **What is the order of reaction whose rate constant has same unit as the rate of reaction?** [2]

Let us consider a reaction

$A \longrightarrow$ product

If it is zero order reaction

Rate = $k[A]^0$

or, $-\frac{d[A]}{dt} = k$

or, $\frac{Mol\ L^{-1}}{S} = k$

or, $k = Mol\ L^{-1}S^{-1}$

So, k has same units as rate of reaction.

Hence, order of reaction is zero order.

26. **2066 Q. No. 15** **Write the rate expression for the following reaction:** [2]

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

The given reaction is $2N_2O_5 \longrightarrow 4NO_2 + O_2$

The rate of disappearance of N_2O_5 (r_1) = $\frac{-1}{2}\frac{d[N_2O_5]}{dt}$

The rate of formation of $NO_2(r_2) = \frac{1}{4}\frac{d[NO_2]}{dt}$

The rate of formation of O_2 (r_3) = $\frac{d[O_2]}{dt}$

Rate of reaction = $-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$

27. **2065 Q.No. 15** **Write the possible rate Law equations of the following Second order reaction:** [2]

$P + Q \longrightarrow$ Product

The possible rate law expression for the above second order reaction may be:

Rate = $k[P]^0[Q]^2$

Rate = $k[P]^2[Q]^0$

Rate = $k[P]^1[Q]^1$,Where k is the rate constant.

28. **2064 Q.No. 18** **Draw a labeled energy profile diagram to show the influence of catalyst in the rate of chemical reaction.** [2]

Please refer to **2073 Set C Q.No. 7**

29. **2063 Q.No. 17** **Define zero order reaction and find the unit of its rate constant.** [2]

Zero order: The reaction whose rate does not depend upon the concⁿ of the reactants is called zero order reaction. For a photochemical reaction which is zero order:

$H_2(g) + Cl_2(g) \longrightarrow 2HCl\,(g)$

Rate $\left(-\frac{dx}{dt}\right) = k[H_2]^0[Cl_2]^0$, Where, k is the rate constant.

Unit:

Rate constant (k) = $\frac{\text{Unit of concentration}}{\text{Unit of time}} = mol.L^{-1}s^{-1}$

30. **2062 Q.No. 17** **What is half life period of a reaction? Calculate the half life period of a first order reaction when the rate constant is 5 year⁻¹.** [2]

Half life period: The time required to complete the half of the initial amount of the reactant by any chemical change is known as half life. It is denoted by $t_{1/2}$.

Numerical:

Given,

Rate constant (k) = 5 year⁻¹

Half life $t_{1/2}$ = ?

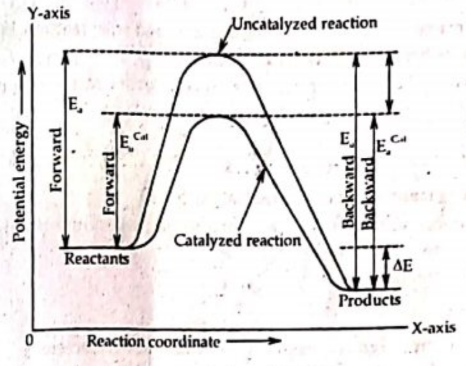
We know that,

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5} = 0.1386$ year.

Hence, the half life period is 0.1386 year.

31. **2061 Q.No. 16** **How does a Catalyst increase rate of reaction?** [2]

The catalyst increases the rate of reaction by lowering the activation energy.



E_a(forward) = Forward reaction for uncatalyzed reaction

E_a(backward = Backward reaction for uncatalyzed reaction

E_a^{Cat}(forward) = For catalyzed reaction

E_a^{Cat}(backward) = For catalyzed reaction

32. **2059 Q.No. 18** **Give one example of a reaction where order and moleculary are equal.** [2]

Example: $H_2(g) + I_2(g) \longrightarrow 2HI(g)$. This reaction is 2nd order and bimolecular i.e. order and molecularity are equal.

33. **2058 Q.No. 18** **Identify the order of the reaction if the unit of its rate constant is lit mol⁻¹ S⁻¹.** [2]

The rate law expression for a reaction is as

Rate = $k[Reactant]^x$, Where, k = rate constant

X = order of reaction

$[Reactant]^x = \frac{Rate}{k}$

or, $[mol.L^{-1}]^x = \frac{Mol\ L^{-1}s^{-1}}{L\ moL^{-1}s^{-1}}$

or, $[mol.L^{-1}]^x = [mol.^2L^{-2}]$ [second is cancelled]

or, $[mol.L^{-1}]^x = [mol.\ L^{-1}]^2$

or, $x = 2$

Hence, the reaction having rate constant L mol⁻¹s⁻¹ is second order.

34. **2057 Q.No. 18** **Give the rate law for a reaction which is second order in A and zero order in B.** [2]

Let us consider a reaction:

$A + B \longrightarrow$ Product

Rate = $k[A]^2[B]^0$ Where, k is rate constant.

The order of reaction is (2 + 0) = 2 i.e. second order.

35. **2056 Q.No. 3** **Give the factors which influence the rate of a reaction.** [2]

Following are the factors that influence the rate of reaction:

i. Temperature
ii. Catalyst
iii. Size of reactants
iv. Concentration of reactants

36. **2056 Q.No. 7** **Calculate the half-life period of a first order reaction when the rate constant is 5 year^{-1}.** [2]

Given, rate constant (K) = 5 years^{-1}

For first order reaction, half-life period $(t_{1/2}) = \frac{0.692}{k} = \frac{0.692}{5} = 0.1386$ years.

Hence, half life period of a first order reaction is 0.1386 years.

37. **2055 Q.No. 5** **The reaction X + Y ⟶ products is a second order reaction. Write three different rate law expressions which may be true to the above reaction.** [2]

The three rate law expression for the above second order reaction may be:

Rate = $k[X]^0[Y]^2$
Rate = $k[X]^2[Y]^0$
Rate = $k[X]^1[Y]^1$ Where, k is the rate constant.

38. **2054 Q.No. 6** **What is meant by rate of a chemical reaction?** [2]

The change in concentration of reactant or product with time is called rate of chemical reaction.

Let us consider a reaction:

$A \longrightarrow B$

Rate = $\frac{-d[A]}{dt}$ Negative sign shows the concentration of A decrease.

Rate = $\frac{+d[B]}{dt}$ Positive sign shows the concentration of B increase.

39. **2053 Q.No. 11** **What is an activation energy?** [2]

The amount of energy in which the reactant must absorb to pass over this activated state is known as activation energy.

40. **2053 Q.No. 16** **Define the half life of a reaction.** [2]

The time period of reaction in which the initial concentration of the reactant is decreased to half is called half-life period. It is denoted by $t_{1/2}$.

Half-life for 1st order reaction is

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

41. **2052 Q.No. 5** **Give a chemical reaction to show reaction of first order.** [2]

If the rate of chemical depends upon the only one concentration of reactant is said to be first order.

Let us consider a reaction:

$A + B \longrightarrow$ Product

Rate = $k[A]^1[B]^0$ Where, k is rate constant.

The order of reaction is (1 + 0) = 1 i.e. first order.

Decomposition of ammonium nitrite is first order reaction.

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Rate = $k[NH_4NO_2]^1$

SHORT ANSWER QUESTIONS [5 MARKS]

42. **2073 Supp Q.No. 26** **Define the terms.**
i. Half-life period of a reaction.
ii. First order reaction.
A first order reaction is 90% complete in 30 minutes. How long would it take to be 99% complete? [2+3]

i. **Half life period:** The time required to complete the half of the initial amount of the reactant by any chemical change is known as half life. It is denoted by $t_{1/2}$.

ii. **First order reaction:** The reaction whose rate depends upon the concentration of only one reactant is said to be 1st order.

Numerical:

For 90 % decomposition,
Initial concentration of reactant (a) = 100 (suppose)
After 100 minutes the concentration of reactant becomes
(a – x) = (100 – 90) = 10
Time taken (t) = 30 min.
Rate constant (k) = ?
For first order reaction,

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

$$K = \frac{2.303}{t}\log\frac{100}{100-90}$$

$$\text{or, } K = \frac{2.303}{t}\log\frac{100}{10}$$

$$\text{or, } K = \frac{2.303}{30}\log(10)$$

$$\text{or, } K = \frac{2.303}{30}\times 1$$

$$\text{or, } K = 7.67\times10^{-2}\ \text{min}^{-1}$$

For 99% completion,
Initial concentration (a) = 100
Final concentration (a – x) = 100 – 99 = 1
Time taken for completion (t) = ?
For first order reaction,

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

$$\text{or, } 7.67\times10^{-2} = \frac{2.303}{t}\log\frac{100}{100-99}$$

$$\text{or, } 7.67\times10^{-2} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\text{or, } 7.67\times10^{-2} = \frac{2.303}{t}\log 100$$

$$\text{or, } 7.67\times10^{-2} = \frac{2.303}{t}\times 2$$

$$\text{or, } t = \frac{2.303\times2}{7.67\times10^{-2}} = 60 \text{ minute}$$

Hence, the time taken for the completion of 99% is 60 minute.

43. **2073 Set C Q.No. 26** **Define**
i. Rate law **ii. Half-life period of a reaction.**
In a first order reaction 40% of reactant gets converted into product in 30 minutes. What time would it require to convert 75% into product? [1+1+3]

i. **Rate law:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

ii. **Half life period:** The time required to complete the half of the initial amount of reactant by any chemical change is known as half life. It is denoted by $t_{1/2}$.

Numerical:

For 40 % decomposition

Initial concentration of reactant (a) = 100 (suppose)

After 30 minutes the concentration of reactant become (a – x) = (100 – 40) = 60

Time taken (t) = 30 minutes

Rate constant (k) = ?

For 1st order reaction

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

$$\text{or, } k = \frac{2.303}{t}\log\frac{100}{60}$$

$$\text{or, } k = \frac{2.303}{t}\log(1.66)$$

$$\text{or, } k = \frac{2.303}{30}\log(1.66)$$

$$\text{or, } k = \frac{2.303}{30}\times 0.22$$

$$\text{or, } k = 0.0169 = 1.69\times 10^{-3}\text{min}^{-1}$$

For 75 % completion

Initial concentration (a) = 100

Final concentration (a – x) = 100 – 75 = 25

Time taken for completion (t) = ?

For 1st order reaction

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

$$\text{or, } k = \frac{2.303}{t}\log\frac{100}{25}$$

$$\text{or, } k = \frac{2.303}{t}\log(4)$$

$$\text{or, } k = \frac{2.303}{t}\times 0.60$$

$$\text{or, } t = \frac{2.303}{k}\times 0.60$$

$$\text{or, } t = \frac{2.303}{0.0169}\times 0.60 = 81.76 \text{ minute.}$$

Hence, the time required to convert 75% into product is 81.76 minute.

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44. **2073 Set D Q.No. 26** **Define rate law. The reaction P + Q ⟶ Z is first order with respect to Ⓟ and zero order with respect to Ⓠ. If so, fill in the blanks in the following.** **[1+4]**

Expt	[P] M	[Q] M	Initial rate of formation [Z] M min^{-1}
I	0.1	0.1	2×10^{-2}
II	–	0.2	4×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2×10^{-2}

Rate law: The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

Numerical:

The given reaction is $P + Q \longrightarrow Z$

First order with respect to P and zero order with respect to Q

Therefore, the rate of reaction is given by,

$\text{Rate} = k[P]^1[Q]^0$

$\text{Rate} = k[P]$

From experiment I, we obtain

$\text{Rate} = k[P]$

$2.0\times10^{-2} = k[0.1]$

$$\text{Or, } k = \frac{2.0\times10^{-2}}{0.1} = 0.2\text{ min}^{-1}$$

From experiment II, we obtain

$\text{Rate} = k[P]$

$\text{Or, } 4.0\times10^{-2} = 0.2[P]$

$$\text{Or, } [P] = \frac{4.0\times10^{-2}}{0.2} = 0.2\text{ mol L}^{-1}$$

From experiment III, we obtain

$\text{Rate} = k[P]$

$\text{Rate} = 0.2\times0.4 = 0.08\text{ mol L}^{-1}\text{min}^{-1} = 8.0\times10^{-2}\text{ mol L}^{-1}\text{min}^{-1}$

From experiment IV, we obtain

$\text{Rate} = k[P]$

$\text{Or, } 2.0\times10^{-2} = 0.2[P]$

$$\text{Or, } [P] = \frac{2.0\times10^{-2}}{0.2} = 0.1\text{ mol L}^{-1}$$

---

45. **2072 Supp. Q.No. 24** **Define the terms:**

i. Rate law ii. Order of a reaction iii. Molecularity of a reaction

A first order reaction will take 100 minutes to complete 60% of reactant into product. What time will it take to complete 75% of the reactant into product? **[1+1+1+2]**

Define:

i. **Rate law:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

ii. **Order of reaction:** The sum of powers of concentration terms of reacting subastance which is appearing in its rate law equation is called order of reaction.

iii. **Molecularity of a reaction:** The total number of atoms or molecules which take part in any chemical reaction is called molecularity of a reaction.

Numerical:

For 60 % decomposition,

Initial concentration of reactant (a) = 100 (suppose)

After 100 minutes the concentration of reactant becomes

(a – x) = (100 – 60) = 40

Time taken (t) = 100 min.

Rate constant (k) = ?

For first order reaction,

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

$$K = \frac{2.303}{t}\log\frac{100}{100-60}$$

$$\text{or, } K = \frac{2.303}{t}\log\frac{100}{40}$$

$$\text{or, } K = \frac{2.303}{100}\log(2.5)$$

or, $K = \frac{2.303}{100} \times 0.397$

or, $K = 9.16 \times 10^{-3}\ min^{-1}$

For 75% completion,

Initial concentration (a) = 100

Final concentration (a - x) = (100 - 75) = 25

Time taken for completion (t) = ?

For first order reaction,

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

or, $9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{100-75}$

or, $9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{25}$

or, $9.16 \times 10^{-3} = \frac{2.303}{t} \log 4$

or, $9.16 \times 10^{-3} = \frac{2.303}{t} \times 0.602$

or, $t = \frac{2.303 \times 0.602}{9.16 \times 10^{-3}} = 151.35$ minute

Hence, the time taken for the completion of 75% is 151.35 minute.

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46. **2071 Supp. Q.No. 24** **Define the term.** **[1+1+1+2]**

i. Rate law equation **ii. Instantaneous rate**

What will be the initial rate of a reaction if its rate constant is $1 \times 10^{-3}\ min^{-1}$ and the concentration of the reactant is $0.2\ mol\ L^{-1}$? How much the reactant will be converted into the product in 500 minute?

✍

i. **Rate law equation:** The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

ii. **Instantaneous rate:** The rate of chemical reaction at any particular instant of time during chemical change is known as instantaneous rate.

$$A \longrightarrow B$$

Instantaneous rate = $(\text{Average})_{t \to 0}$

$$R_t = \left(-\frac{\Delta[A]}{\Delta t}\right)_{t \to 0}$$

$$R_t = \left(\frac{\Delta[B]}{\Delta t}\right)_{t \to 0}$$

$$R_t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Where d[A], d[B] and dt being infinitesimally small change in concentration of A and B and that of time respectively.

Numerical:

Given, Rate constant (k) = $1 \times 10^{-3}\ min^{-1}$

Concentration of reactant = $0.2\ mol\ L^{-1}$

Initial rate of a reaction = ?

We know that

Rate = k [concentration of reactant]

Rate = 1×10^{-3} [0.2]

Rate = $2 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}$

Again, t = 500 minute

Initial concentration of reactant (a) = $0.2\ mol\ L^{-1}$

Final concentration of reactant (a - x) = ?

The concentration of reactant converted into product (x) = ?

For 1st order reaction

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

or, $1 \times 10^{-3} = \frac{2.303}{500} \log \frac{0.2}{(a-x)}$

or, $\log \frac{0.2}{a-x} = \frac{1 \times 10^{-3} \times 500}{2.303} = 0.217$

or, $\frac{0.2}{(a-x)} = \log^{-1}(0.217)$

or, $\frac{0.2}{(a-x)} = 1.64$

or, $\frac{0.2}{(0.2-x)} = 1.64$

or, $0.328 - 1.64x = 0.2$

or, $1.64x = 0.328 - 0.2$

or, $1.64x = 0.128$

or, $x = \frac{0.128}{1.64} = 0.078\ mol\ L^{-1}$

Hence, the concentration of reactant is converted into product (x) = $0.078\ mol\ L^{-1}$.

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47. **2071 Set C Q.No. 24** **Define the term:**

a. Rate law

b. Order of reaction

c. Activated complex

The rate of a first order reaction is $1.5 \times 10^2\ mol\ L^{-1}\ min^{-1}$ at 0.5 M concentration of the reaction. What is the half-life of the reaction? **[5]**

✍

a. **Rate law:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

b. **Order of reaction:** The sum of powers of concentration terms of reacting subastance which is appearing in its rate law equation is called order of reaction.

c. **Activated complex:** An activated complex is an intermediate state that is formed during the conversion of reactants into products. An activated complex is the structure that results at the maximum energy point along the reaction path. The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants.

Numerical:

Given,

Rate of a first order reaction= $1.5 \times 10^2\ mol\ L^{-1} min^{-1}$

Concentration of reactant = 0.5 M

We know that,

Rate = k[concentration of reactant] where, k = rate constant of reaction

or, $1.5 \times 10^2 = K[0.5]$

or, $k = \frac{1.5 \times 10^2}{0.5} = 3 \times 10^2$ minute

We know that,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^2} = 2.31 \times 10^{-3} \text{ minute}$$

Hence, the half life of a reaction is 2.31×10^{-3} minute.

---

48. 2071 Set D Q.No. 24 What is instantaneous rate of reaction? How do concentration and surface area of reactant affect the rate of reaction? A first order reaction will take 100 minutes to complete 60% of reactant into product. What time will it take to complete 90% of reactant into product? [5]

Instantaneous rate: Please refer to 2071 Supp. Q No. 24

Affect of concentration and surface area of reactant:

i. **Concentration of reactants:** It is clear from collision theory that more molecules in a given volume mean more collision per unit of time and therefore a greater chance of reactions where as less molecules in a given volume mean less collision and less chance for reactions. So, we can say that concentration of reactants certainly influence the rate of reaction.

ii. **Surface area of reactants:** This factor is only applicable or hererogeneous reactions. The smaller particles (larger surface area) react more rapidly than the larger particle (smaller surface area).

For example: coal dust (smaller particle or larger surface area) burns in air more rapidly than that of large lumps of coal.

Numerical:

For 60 % decomposition,

Initial concentration of reactant (a) = 100 (suppose)

After 100 minutes the concentration of reactant becomes

$(a - x) = (100 - 60) = 40$

Time taken (t) = 100 minute

Rate constant (k) = ?

For first order reaction,

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

$$K = \frac{2.303}{t} \log \frac{100}{100-60}$$

$$\text{or, } K = \frac{2.303}{t} \log \frac{100}{40}$$

$$\text{or, } K = \frac{2.303}{100} \log (2.5)$$

$$\text{or, } K = \frac{2.303}{100} \times 0.397$$

$$\text{or, } K = 9.16 \times 10^{-3} \text{ min}^{-1}$$

For 90% completion,

Initial concentration (a) = 100

Final concentration $(a - x) = (100 - 90) = 10$

Time taken for completion (t) = ?

For first order reaction,

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

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{100-90}$$

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \log \frac{100}{10}$$

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \log 10$$

$$\text{or, } 9.16 \times 10^{-3} = \frac{2.303}{t} \times 1$$

$$\text{or, } t = \frac{2.303}{9.16 \times 10^{-3}} = 251.41 \text{ minute}$$

Hence, the time taken for the completion of 90% is 251.41 minute.

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49. 2065 Q.No. 31 iv Describe Factors affecting on reaction rate. [5]

Following are the important factors which influence rate of reactions:

i. **Nature of reactant:** Rate of reactions are certainly governed by the nature of reactants. Different reactants have different composition, different shape and size, different chemical bond etc. these properties of substance greatly influence the rate of chemical reaction. For example:

$$Na + HCl \longrightarrow \text{reacts violently}$$

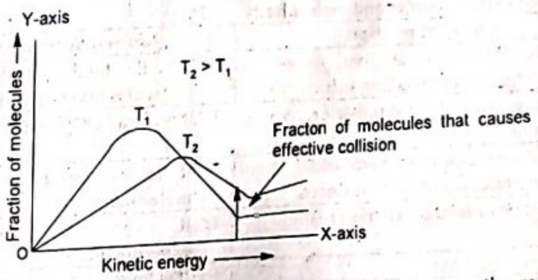
$$Sn + HCl \longrightarrow \text{reacts very slowly}$$

The change in rate of reaction of above chemical reaction is due to different nature of Na and Sn.

ii. **Concentration of reactants:** It is clear from collision theory that more molecules in a given volume mean more collision per unit of time and therefore a greater chance of reactions where as less molecules in a given volume mean less collision and less chance for reactions. So, we can say that concentration of reactants certainly influence the rate of reaction.

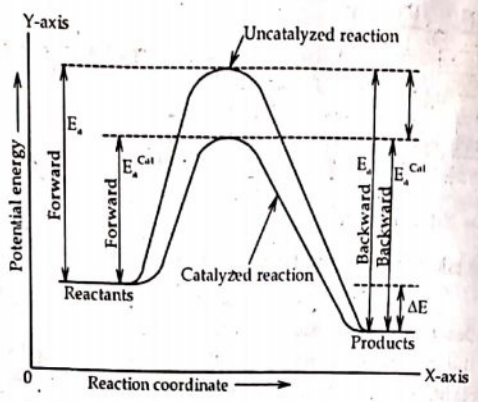
iii. **Temperature:** It is a well known fact that the rate of chemical reaction increase with rise in temperature. In homogeneous reactions, the rate becomes doubled or tripled for each 10°C rise of temperature.

As the temperature is increased the molecules move more rapidly, therefore collisions are more frequent and increase the rate of chemical reaction.



iv. **Catalyst:** It is clear from the definition of catalyst that it increase the rate of chemical reaction without under going any change and can be recovered after completion of the reaction.

It has been found from the theoretical study of catalyst that it lowers the activation energy of a reaction there by increasing the rate of reaction. So, we can say that catalyst influence the rate of reaction.



v. **Surface area of reactants:** This factor is only applicapable or hererogeneous reactions. The smaller particles (larger surface area) react more rapidly than the larger particle (smaller surface area).

For example: coal dust (smaller particle or larger surface area) burns in air more rapidly than that of large lumps of coal.

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50. 2059 Q.No. 25 Define the rate of chemical reaction. How do concentration, temperature, catalyst and surface area of reactants affect the rate of reaction? [5]

Rate of reaction: A mathematical expression in which observed rate of reaction is related with concentration of reacting species is called rate of reaction.

Let us consider a reaction

$aA + bB \longrightarrow \text{Product}$

Rate $\alpha\ [A]^a[B]^b$

Rate $= k[A]^a[B]^b$

Affect of concentration and surface area of reactant: Please refer to 2071 Set D Q.No. 24

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51. 2058 Q.No. 24 Define rate of reaction. Distinguish between order and molecularity of a reaction. [5]

Rate of reaction: A mathematical expression in which observed rate of reaction is related with concentration of reacting species is called rate of reaction.

Difference between order and molecularity

Order of reaction	Molecularity of reaction
1. It is the sum of the power of concentration of reacting substance.	1. It is the total number of atoms or molecules taking part in reaction.
2. It may be a whole number or zero or fraction.	2. It is always a whole number.
3. It is expressed as zero order, first order, second order, nth order etc.	3. It is expressed as uni, bi, tri, molecular etc.
4. It can be obtained experimentally.	4. It can not be obtained experimentally.
5. It is real number.	5. It is imaginary quantity.
6. It has no connection with the stoichiometric equation of a reaction.	6. It has great connection with the stoichiometric equation of a reaction.
7. $2N_2O_5 \longrightarrow 4NO_2 + O_2$ It is first order reaction not bimolecular.	7. $2N_2O_5 \longrightarrow 4NO_2 + O_2$ It is bimolecular reaction.

LONG ANSWER QUESTIONS

52. 2076 Set B Q.No. 32 Define the terms (i) activation energy (ii) order of reaction (iii) molecularity of reaction (iv) effective collision (v) rate law equation.

Why does powder sugar dissolve faster than grain sugar?

The following data were obtained for a hypothetical reaction $x + y \longrightarrow z$

Expt.	[x] mol L^{-1}	[y] mol L^{-1}	formation of z mol L^{-1} S^{-1}
1	0.20	0.20	3×10^{-3}
2	0.40	0.20	1.2×10^{-2}
3	0.20	0.40	6×10^{-3}
4	0.60	0.20	9×10^{-3}

Calculate the rate constant and find out rate of disappearance of y when [x] = 0.2 mol L^{-1} and [y] = 0.4 mol L^{-1}. [5+1+2+2]

i. **Activation energy:** The minimum energy over the average energy which must be gained by the reacting molecules before they could react to form the product is called activation energy.

ii. **Order of reaction:** The sum of powers of concentration terms of reacting subastance which is appearing in its rate law equation is called order of reaction.

iii. **Molecularity of a reaction:** The total number of atoms or molecules which take part in any chemical reaction is called molecularity of a reaction.

iv. **Effective collision:** Effective collisions are those that result in a chemical reaction. In order to produce an effective collision, reactant particles must possess some minimum amount of energy. This energy, used to initiate the reaction, is called the activation energy.

v. **Rate law equation:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

Numerical:

The reaction $x + y \longrightarrow z$

Rate $= k[x]^m[y]^n$

Therefore,

$3\times10^{-3} = k[0.2]^m[0.2]^n$ ...(i)

$1.2\times10^{-2} = k[0.4]^m[0.2]^n$ ... (ii)

$6\times10^{-3} = k[0.2]^m[0.4]^n$ ...(iii)

$9\times10^{-3} = k[0.6]^m[0.2]^n$ ...(iv)

Dividing equation (ii) by (i) we get

$$\frac{1.2\times10^{-2}}{3\times10^{-3}} = \frac{k[0.4]^m[0.2]^n}{k[0.2]^m[0.2]^n}$$

or, $4 = 2^m$

or, $2^2 = 2^m$

or, $m = 2$

The reaction is 2nd order with respect to x

Again, dividing equation (iii) by (i) we get

$$\frac{6\times10^{-3}}{3\times10^{-3}} = \frac{k[0.2]^m[0.4]^n}{k[0.2]^m[0.2]^n}$$

or, $2^1 = 2^n$

or, $n = 1$

The reaction is 1st order with respect to y

Hence, the rate law expression is

Rate $= k[x]^2[y]^1$

The overall reaction is (2+1) = 3

The value of rate constant k can be determined by

$3\times10^{-3} = k[0.2]^2[0.2]^1$

or, $k = \dfrac{3\times10^{-3}}{0.04\times0.2} = 0.375\ L^2mol^{-2}s^{-1}$

Hence, the rate constant (k) is 0.375 $L^2mol^{-2}s^{-1}$

The rate of disappearance of y is determined by

$Rate = k[0.2]^2[0.4]^1$

$Rate = 0.375[0.2]^2[0.4]^1 = 0.375\times0.04\times0.4 = 6\times10^{-3}$

Hence, Rate of disappearance of y = 6×10^{-3} mol $L^{-1}s^{-1}$

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53. **2075 GIE Q.No. 32** **Define rate law. What are the effects of (i) concentration (ii) temperature (iii) Catalyst and (iv) surface area of reactants on rate of reaction? Why is order of reaction an experimental parameter?**

The reaction between Ⓧ and Ⓨ is of 1st order w.r. to ⓧ and zero order w.r. to ⓨ. Fill in the banks in the following table. [1+4+1+4]

Expt. No.	[x] mol L^{-1}	[y] mol L^{-1}	initial rate mol L^{-1} min^{-1}
1	0.1	0.1	2×10^{-2}
2	-	0.2	4×10^{-2}
3	0.4	0.4	-
4	-	0.2	2×10^{-2}

a. **Rate law:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

Affect of concentration, temperature, catalyst and surface area of reactant on rate of reaction: Please refer to 2065 Q.No. 31iv

Order of a reaction is an experimentally determined quantity. It corresponds to the stoichiometric coefficients only for an elementary reaction. A complex reaction occurs in series of elementary reactiosns. Some steps are very fast as they do not reauire much energy. These steps do not affect the overall rate of reaction. Hence, the rate of reaction is mainly determined by the slowest step of the reaction. Order of a reaction in case of a complex reaction, corresponds to the stoichiometric coefficients of this rate determining step.

b. The reaction is given as:

$X + Y \longrightarrow Product$

First order w.r.t. X and Zero order w.r.t. Y

Therefore, the rate of reaction is given as

$Rate = K[X]^1[Y]^0$

$Rate = K[X]$

From Experiment I, we obtain

$Rate = K[X]$

or, $2\times10^{-2} = K[0.1]$

or, $K = \dfrac{2\times10^{-2}}{0.1} = 0.2\ min^{-1}$

From Experiment II, we obtain

$Rate = K[X]$

or, $4\times10^{-2} = 0.2[X]$

or, $[X] = \dfrac{4\times10^{-2}}{0.2} = 0.2\ mol\ L^{-1}$

From Experiment III, we obtain

$Rate = K[X]$

$Rate = 0.2\times0.4 = 0.08\ mol\ L^{-1}min^{-1} = 8\times10^{-2}\ mol\ L^{-1}min^{-1}$

From Experiment IV, we obtain

$Rate = K[X]$

or, $2\times10^{-2} = 0.2[X]$

or, $X = \dfrac{2\times10^{-2}}{0.2} = 0.1\ mol\ L^{-1}$

Thus, the given table looks like

Expt.	(X) molL^{-1}	(Y) molL^{-1}	Initial rate molL^{-1} min^{-1}
1	0.1	0.1	2×10^{-2}
2	0.2	0.2	4×10^{-2}
3	0.4	0.4	8×10^{-2}
4	0.1	0.2	2×10^{-2}

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54. **2075 Set A Q.No. 32**

a. **Define rate law. How do (i) concentration (ii) temperature (iii) catalyst (iv) surface area of reactant affect the rat of reaction? Why is order of reaction a experimental parameter?** [1+4+1+4]

b. **The reaction between x and y is of 1st order with respect to x and of zero order with respect to y. Fill in the blanks in the following table.**

Expt.	(X) molL^{-1}	(Y) molL^{-1}	Initial rate molL^{-1} min^{-1}
1	0.1	0.1	2×10^{-2}
2	-	0.2	4×10^{-2}
3	0.4	0.4	-
4	-	0.2	2×10^{-2}

Please refer to 2075 GIE Q.No. 32

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55. **2074 Supp. Q.No. 32** **Define:**

i. **Rate law equation**

ii. **Half life period for a reaction**

How is order of a reaction different from molecularity of reaction?

The following rate data were obtained for the reaction $2A + B \longrightarrow C$

Exp.No.	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of C mol L^{-1}
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-4}
4	0.4	0.1	2.4×10^{-2}

Calculate the rate of formation of C, When [A] = 0.5 mol L^{-1} and [B] = 0.2 mol L^{-1}. [2+4+4]

i. **Rate law equation:** The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

ii. **Half life period for a reaction:** The time period of reaction in which the initial concentration of the reactant is decreased to half is called half-life period. It is denoted by $t_{1/2}$.

Half-life for 1st order reaction is

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

Difference between order and molecularity of reaction: Please refer to 2058 Q.No. 24

Numerical:

Reaction $2A + B \longrightarrow C$

$\text{Rate} = k[A]^m[B]^n$

Therefore,

$6.0 \times 10^{-3} = k[0.1]^m[0.1]^n$ ... (i)

$7.2 \times 10^{-2} = k[0.3]^m[0.2]^n$ ... (ii)

$2.88 \times 10^{-1} = k[0.3]^m[0.4]^n$ ... (iii)

$2.4 \times 10^{-2} = k[0.4]^m[0.1]^n$... (iv)

Dividing equation (iv) by (i) we get

$$\frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

or, $4 = 4^m$

or, $4^1 = 4^m$

$\therefore$ m = 1

The reaction is first order with respect to A.

Again, dividing equation (iii) by (ii) we get,

$$\frac{2.88 \times 10\text{–}1}{7.2 \times 10\text{–}2} = \frac{k[0.3]^m[0.4]^n}{k[0.3]^m[0.2]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

$\therefore$ n = 2

The reaction is 2nd order with respect to B.

Hence, the rate law expression is

$\text{Rate} = k[A]^1[B]^2$

The overall reaction is (1 + 2) = 3 order

Rate of formation of C when

$[A] = 0.5 \text{ mol L}^{-1}$

$[B] = 0.2 \text{ mol L}^{-1}$

$\text{Rate} = k\ [0.5]^1\ [0.2]^2$

The value of rate constant K can be determined by

$6 \times 10^{-3} = k\ [0.1]^1\ [0.1]^2$

$$k = \frac{6 \times 10\text{–}3}{[0.1]1\ [0.1]2} = 6 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

$\text{Rate} = 6 \times 0.5 \times 0.04$

$= 0.12 \text{ mol}^2 \text{ L}^{-2} \text{ s}^{-1}$

Hence, rate of formation of C is $0.12 \text{ mol}^2 \text{ L}^{-2} \text{ s}^{-1}$.

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56. **2074 Set A Q.No. 32** **Define the terms;**

i. Rate Law equation **ii. Activated complex**

How is order of reaction differed from molecularity of reaction?

The following data were obtained for the reaction $2A + B \longrightarrow C$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	[Initial rate] mol $L^{-1}s^{-1}$
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

Calculate the rate of formation of C when $[A] = 0.5 \text{ mol L}^{-1}$ and $[B] = 0.2 \text{ mol L}^{-1}$ **[2+4+4]**

i. **Rate law equation:** The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

ii. **Activated complex:** An activated complex is an intermediate state that is formed during the conversion of reactants into products. An activated complex is the structure that results at the maximum energy point along the reaction path. The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants.

Difference between order and molecularity of reaction: Please refer to **2058 Q No.24**

Numerical:

Reaction $2A + B \longrightarrow C + D$

$\text{Rate} = k[A]^m[B]^n$

Therefore,

$6.0 \times 10^{-3} = k[0.1]^m[0.1]^n$ ... (i)

$7.2 \times 10^{-2} = k[0.3]^m[0.2]^n$ ... (ii)

$2.88 \times 10^{-1} = k[0.3]^m[0.4]^n$ ... (iii)

$2.4 \times 10^{-2} = k[0.4]^m[0.1]^n$ ... (iv)

Dividing equation (iv) by (i) we get

$$\frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

or, $4 = 4^m$

or, $4^1 = 4^m$

$\therefore$ m = 1

The reaction is first order with respect to A.

Again, dividing equation (iii) by (ii) we get,

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^m[0.4]^n}{k[0.3]^m[0.2]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

$\therefore$ n = 2

The reaction is 2nd order with respect to B.

Hence, the rate law expression is

$\text{Rate} = k[A]^1[B]^2$

The overall reaction is (1 + 2) = 3 order

The rate constant of reaction is calculated by putting the value of 'm' and 'n' in the equation (i)

$6.0 \times 10^{-3} = k[0.1]^1[0.1]^2$

Or, $6.0 \times 10^{-3} = k[0.1][0.01]$

Or, $k = \frac{6.0 \times 10^{-3}}{0.001} = 6 \text{ s}^{-1}$

Rate of formation of $C = k[A]^1[B]^2 = 6[0.5]^1[0.2]^2 = 6[0.5][0.04] = 0.12 \text{ mol L}^{-1}\text{s}^{-1}$.

---

57. **2074 Set B Q.No. 32** **Define**

i. Activation energy **ii. Rate law equation**

What are the difference between order and molecularity of reaction? From the following data for the reaction between (A) and (B). **[2+4+4]**

$2A + B_2 \longrightarrow 2\ AB$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	[Initial rate] mol L^{-1} s^{-1}
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

Calculate the rate of formation of AB When $[A] = 2 \text{ mol L}^{-1}$ and $[B] = 4 \text{ mol L}^{-1}$.

i. **Activation energy:** The minimum energy over the average energy which must be gained by the reacting molecules before they could react to form the product is called activation energy.

ii. **Rate law equation:** The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

Difference between order and molecularity of reaction: Please refer to 2058 Q.No.24

Numerical:

Reaction is given as:

$2A + B_2 \longrightarrow 2AB$

Rate = $k[A]^m[B]^n$

Therefore,

$1.6 \times 10^{-4} = k[0.50]^m[0.50]^n$ ... (i)

$3.2 \times 10^{-4} = k[0.50]^m[1.00]^n$ ... (ii)

$3.2 \times 10^{-4} = k[1.00]^m[1.00]^n$ ... (iii)

Dividing equation (ii) by (i) then we get

$$\frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}} = \frac{k[0.50]^m[1.00]^n}{k[0.50]^m[0.50]^n}$$

Or, $2 = 2^n$

Or, $2^1 = 2^n$

$\therefore$ n = 1

The reaction is first order with respect to B.

Again, dividing equation (iii) by (ii) we get,

$$\frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}} = \frac{k[1.00]^m[1.00]^n}{k[0.50]^m[1.00]^n}$$

Or, $1 = 2^m$

Or, $2^0 = 2^m$

$\therefore$ m = 0

The reaction is zero order with respect to A.

The overall reaction is (0+ 1) = 1 i.e. first order.

The value of rate constant can be calculated by putting the value of 'm' and 'n' in equation (i)

Or, $1.6 \times 10^{-4} = k[0.50]^0[0.50]^1$

Or, $1.6 \times 10^{-4} = k \times 1 \times 0.5$

So, $k = \frac{1.6 \times 10^{-4}}{0.50} = 3.2 \times 10^{-4}\ s^{-1}$

The rate of formation of AB When [A] = 2 mol L^{-1} and [B] = 4 mol L^{-1}.

Rate = $k[A]^0[B]^1 = 3.2 \times 10^{-4}\ [2]^0[4]^1 = 3.2 \times 10^{-4} \times 4 = 1.28 \times 10^{-3}$

Hence, the rate of formation of AB is 1.28×10^{-3} mol L^{-1} s^{-1}

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58. **2070 Set C Q.No. 32 a Distinguish between order and molecularity of reaction. What is meant by second order reaction? Write its units.** **[5]**

Distinction between order and molecularity of reaction: Please refer to 2058 Q.No. 24

Second order reaction: The reaction in which the rate is determined by the variation of two concentration terms.

A $\longrightarrow$ product

Rate = $k[A]^2$

Where, k = rate constant

Unit of rate constant:

$$k = \frac{Rate}{[A]^2}$$

$$k = \frac{Mol\ L^{-1}s^{-1}}{[MolL^{-1}]^2} = Mol^{-1}Ls^{-1}$$

---

59. **2069 (Set A) Q.No. 30a Define rate law and rate of a reaction. How does temperature, catalyst, concentration of reactant and surface area of reactant affect the rate of reaction?** **[5]**

Rate law equation: The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

Rate of reaction: A mathematical expression in which observed rate of reaction is related with concentration of reacting species is called rate of reaction.

Let us consider a reaction

$aA + bB \longrightarrow$ Product

Rate $\alpha\ [A]^a[B]^b$

Rate = $k[A]^a[B]^b$

Second part: Please refer to 2065 Q.NO. 31iv

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60. **2063 Q.No. 31(i) Write short notes on Effect of temperature and catalyst on the rate of reaction.** **[5]**

Please refer to 2065 Q NO. 31iv

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61. **2054 Q.No. 27(a) In a reaction $H_2 + I_2 \rightleftharpoons 2HI$ the rate of disappearance of I_2 is found to be 10^{-6} mole per litre per second. What would be corresponding rate of appearance HI?** **[5]**

The balance given equation is given as,

$H_2(g) + I_2(g) \rightleftharpoons 2\,HI\,(g)$

Now,

The rate of disappearance of $H_2 = -\frac{d[H_2]}{dt}$

The rate of disappearance of $I_2 = -\frac{d[I_2]}{dt} = 10^{-6} moleL^{-1}s^{-1}$

The rate of appearance of $HI = +\frac{1}{2}\frac{d[HI]}{dt} = ?$

We know that,

The rate of disappearance of H_2 = the rate of disappearance of I_2 = the rate of appearance of HI

or, $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$

or, $-\frac{d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$

or, $10^{-6} moleL^{-1}S^{-1} = +\frac{1}{2}\frac{d[HI]}{dt}$

or, $\frac{d[HI]}{dt} = 2 \times 10^{-6} moleL^{-1}s^{-1}$

Hence, the rate of appearance of HI is $2 \times 10^{-6} moleL^{-1}s^{-1}$ which is double of rate of disappearance of I_2.

NUMERICAL PROBLEMS

62. **2072 Set C Q.No. 30 Give any four points of difference between molecularity and order of a chemical reaction. What is meant by pseudo first order reaction? Write an example of it.** **[4+2+1.5+1+1.5]**

The experimental data for the reaction

$2A + B \longrightarrow C$ is

Expt no.	Initial Concentration of		Rate of reaction mol $L^{-1} s^{-1}$
	[A] mol L^{-1}	[B] mol L^{-1}	
1	0.1	0.1	7×10^{-3}
2	0.3	0.2	8.4×10^{-2}
3	0.3	0.4	3.36×10^{-1}
4	0.4	0.1	2.8×10^{-2}

Determine:

i. **Over all order of reaction**

ii. **Rate law equation**

iii. **Calculate the rate of formation of C when concentration of [A] and [B] are 0.6 mol L^{-1} and 0.3 mol L^{-1} respectively.**

✍ **Difference between molecularity and order of reaction:** Please refer to 2058 Q.No. 24

Pseudo first order reaction: In bimolecular reaction, the rate of reaction depends on the concentration of only one reactant is called pseudo first order reaction.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

Rate = k (Ester)

Numerical

Reaction $2A + B \longrightarrow C$

Rate = k $[A]^m [B]^n$

Therefore,

i. $7.0 \times 10^{-3} = k[0.1]^m [0.1]^n$ ... (i)

$8.4 \times 10^{-2} = k[0.3]^m [0.2]^n$ ... (ii)

$3.36 \times 10^{-1} = k[0.3]^m [0.4]^n$ ... (iii)

$2.8 \times 10^{-2} = k[0.4]^m [0.1]^n$ ... (iv)

Dividing equation (iv) by (i), we get

$$\frac{2.8 \times 10^{-2}}{7.0 \times 10^{-3}} = \frac{K[0.4]^m [0.1]^n}{K[0.1]^m [0.1]^n}$$

or, $4 = 4^m$

or, $4^1 = 4^m$

∴ $m = 1$

The reaction is first order w.r.t. A.

Again, dividing equation (iii) by (ii) we get

$$\frac{3.36 \times 10^{-1}}{8.4 \times 10^{-2}} = \frac{K[0.3]^m [0.4]^n}{K[0.3]^m [0.2]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

∴ $n = 2$

The reaction is 2nd order w.r.t. B.

The over all order of reaction is (m + n) = (1 + 2) = 3

ii. The rate law equation can be expressed as

Rate = k $[A]^1 [B]^2$

iii. Rate of formation of C when

[A] = 0.6 mol L^{-1}

[B] = 0.3 mol L^{-1}

Rate = k $[0.6]^1 [0.3]^2$

The value of rate constant K can be determined by

$7 \times 10^{-3} = k[0.1]^1 [0.1]^2$

$$k = \frac{7 \times 10^{-3}}{[0.1]^1 [0.1]^2} = 7 \text{ mol}^{-2} L^2 s^{-1}$$

Rate $= 7 \times 0.6 \times 0.09$

$= 0.378 \text{ mol}^2 L^{-2} s^{-1}$

Hence, rate of formation of C is 0.378 $\text{mol}^2 L^{-2} s^{-1}$.

63. 2072 Set E Q.No. 32b **For the reaction $Cl_2 + 2NO \longrightarrow 2NOCl$, the data obtained are:**

Expt no.	Initial Concentration of		Initial rate of reaction mol $L^{-1} s^{-1}$
	[Cl_2] mol L^{-1}	[NO] mol L^{-1}	
1	0.020	0.010	2.40×10^{-4}
2	0.020	0.030	2.16×10^{-3}
3	0.040	0.030	4.32×10^{-3}

[3+2]

Determine:

i. **Order of reaction with respect to Cl_2 and NO and the overall reaction.**

ii. **If the concentration of Cl_2 is [0.50] molL^{-1} and NO is [0.40] molL^{-1}, What is the rate?**

✍ The reaction is

i. $Cl_2 + 2NO \longrightarrow 2NOCl$

Rate = $k[Cl_2]^m[NO]^n$

Therefore,

$2.40 \times 10^{-4} = k[0.020]^m[0.010]^n$ ... (i)

$2.16 \times 10^{-3} = k[0.020]^m[0.030]^n$ ... (ii)

$4.32 \times 10^{-3} = k[0.040]^m[0.030]^n$ ... (iii)

Dividing equation (iii) by (ii) then we get

$$\frac{4.32 \times 10^{-3}}{2.16 \times 10^{-3}} = \frac{k[0.040]^m[0.030]^n}{k[0.020]^m[0.030]^n}$$

or, $2 = 2^m$

or, $2^1 = 2^m$

or, $m = 1$

The reaction is 1st order with respect to Cl_2.

Again, dividing equation (ii) by (i) then we get

$$\frac{2.16 \times 10^{-3}}{2.40 \times 10^{-4}} = \frac{k[0.020]^m[0.030]^n}{k[0.020]^m[0.010]^n}$$

or, $9 = 3^n$

or, $3^2 = 3^n$

or, $n = 2$

The reaction is 2nd order with respect to NO.

The overall reaction order is (1+2) =3 i.e. 3rd

ii. The concentration of Cl_2 = [0.50] molL^{-1}

The concentration of NO = [0.40] molL^{-1}

From equation (i)

$2.40 \times 10^{-4} = k[0.020]^1[0.010]^2$

or, $$k = \frac{2.40 \times 10^{-4}}{[0.020]^1[0.010]^2} = \frac{2.40 \times 10^{-4}}{2 \times 10^{-6}} = 120 \text{ mol}^{-2}L^2s^{-1}$$

Now,

Rate = $k[0.50]^1[0.40]^2$

Rate = $120[0.50]^1[0.40]^2 = 9.6 \text{ mol}L^{-1}s^{-1}$

Hence, the rate of reaction is 9.6 mol$L^{-1}s^{-1}$.

64. 2070 Supp. Q.No. 32 **How does (i) temperature (ii) concentration of reactant and (iii) catalyst affect the rate of reaction? Write any three points to distinguish order from molecularity of a reaction. For a first order reaction, it takes 4 minute for initial concentration of 0.8 mol/L to become 0.2 mol/L. What time will it take to become the concentration to 0.04 mol / L?** [10]

Affect of temperature, concentration and catalyst on the rate of reaction:

Please refer to 2065 Q.NO. 31iv

Distinction of order and molecularity: Please refer to 2058 Q.No. 24

Numerical:

For 1st order reaction

Time taken (t) = 4 minute

Initial concentration (a) = 0.8 mol/L

Final concentration (a - x) = 0.2 mol/L

We know that,

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

$$\text{or, } K = \frac{2.303}{4} \log \frac{0.8}{0.2}$$

$$\text{or, } K = \frac{2.303}{4} \log 4$$

$$\text{or, } K = \frac{2.303}{4} \times 0.602$$

or, $K = 0.346\ min^{-1}$

Hence, rate constant of reaction (K) = $0.346\ min^{-1}$

Again,

Time taken (t) = ?

Initial concentration (a) = 0.8 mol/L

Final concentration (a - x) = 0.04 mol/L

We know that,

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

$$\text{or, } 0.346 = \frac{2.303}{t} \log \frac{0.8}{0.04}$$

$$\text{or, } 0.346 = \frac{2.303}{t} \log 20.$$

$$\text{or, } 0.346 = \frac{2.303}{t} \times 1.30$$

$$\text{or, } t = \frac{2.303 \times 1.30}{0.346}$$

or, t = 8.65 minutes

Hence, time taken to become 0.04 mol/L concentration is 8.65 minutes.

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65. 2070 Set C Q.No. 32 b. The following rate data were obtained at 303 K for the reaction **[5]**

$2A + B \longrightarrow C + D$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of [D] mol L^{-1} min^{-1}
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

i. What is the rate law?
ii. Write the order with respect to each reactant and overall order.
iii. Find the unit of the overall reaction.

Reaction $2A + B \longrightarrow C + D$

Rate = $k[A]^m[B]^n$

Therefore,

$6.0 \times 10^{-3} = k[0.1]^m[0.1]^n$ ... (i)

$7.2 \times 10^{-2} = k[0.3]^m[0.2]^n$ ... (ii)

$2.88 \times 10^{-1} = k[0.3]^m[0.4]^n$ ... (iii)

$2.4 \times 10^{-2} = k[0.4]^m[0.1]^n$ ... (iv)

Dividing equation (iv) by (i) we get

$$\frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

or, $4 = 4^m$

or, $4^1 = 4^m$

$\therefore m = 1$

The reaction is first order with respect to A.

Again, dividing equation (iii) by (ii) we get,

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^m[0.4]^n}{k[0.3]^m[0.2]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

$\therefore n = 2$

The reaction is 2nd order with respect to B.

Hence, the rate law expression is

Rate = $k[A]^1[B]^2$

The overall reaction is (1 + 2) = 3 order

Unit of rate constant is

Rate = $k[A]^1[B]^2$

$$k = \frac{Rate}{[A]^1[B]^2}$$

$$= \frac{molL^{-1}\,S^{-1}}{[Mol\ L^{-1}]\,[molL^{-1}]^2} = mol^{-2}L^2s^{-1}$$

---

66. 2070 Set D Q.No. 32 b For a reaction, $2X + Y \longrightarrow X_2Y$, the following data were obtained by experiment. **[5]**

Experiment	[X] mol L^{-1}	[Y] mol L^{-1}	Rate, mol $L^{-1}s^{-1}$
1	0.10	0.10	1.3×10^{-4}
2	0.10	0.20	2.6×10^{-4}
3	0.20	0.20	1.04×10^{-3}

i. Find the order of reaction with respect to X, Y and overall reaction.
ii. Find the value of rate constant with its units.
iii. What is the initial rate of the reaction when the initial concentration of X and Y are 1M and 0.5 M respectively?

i. Reaction $2X + Y \longrightarrow X_2Y$

Rate = $k[X]^m[Y]^n$

Therefore,

$1.3 \times 10^{-4} = k[0.10]^m[0.10]^n$ ... (i)

$2.6 \times 10^{-4} = k[0.10]^m[0.20]^n$ ... (ii)

$1.04 \times 10^{4} = k[0.20]^m[0.20]^n$ ... (iii)

Dividing equation (iii) by (i) then we get

$$\frac{2.6 \times 10^{-4}}{1.3 \times 10^{-4}} = \frac{k[0.10]^m[0.20]^n}{k[0.10]^m[0.10]^n}$$

or, $2 = 2^n$

or, $2^1 = 2^n$

∴ $n = 1$

The reaction is first order with respect to Y.

Again, dividing equation (iii) by (ii) we get,

$$\frac{1.04 \times 10^{-3}}{2.6 \times 10^{-4}} = \frac{k[0.20]^m[0.20]^n}{k[0.10]^m[0.20]^n}$$

or, $4 = 2^m$

or, $2^2 = 2^m$

∴ $m = 2$

The reaction is 2^{nd} order with respect to X.

The overall reaction is (2 + 1) = 3

ii. Find the value of rate constant with its units.

Value of rate constant (k) and unit is obtained by putting the value of m and n

$1.3 \times 10^{-4} = k[0.10]^2[0.10]^1$

$$k = \frac{1.3 \times 10^{-4}}{[0.01]^3} = \frac{1.3 \times 10^{-4}}{1.0 \times 10^{-3}} = 0.13\ mol^{-2}L^2s^{-1}$$

iii. What is the initial rate of reaction when the initial concentration of X and Y are 1M and 0.5M respectively.

The initial rate is calculated as:

Rate = $k[X]^2[y]^1 = 0.13[1]^2[0.5]^1 = 6.5 \times 10^{-2}\ mol\ L^{-1}s^{-1}$

Hence, initial rate = $6.5 \times 10^{-2}\ mol\ L^{-1}s^{-1}$

---

67. 2069 (Set A) Q.No. 30b From the following experimental data for the reaction: [5]

$2A + B \longrightarrow 2AB$

Experiment	[A], $molL^{-1}$	[B], $molL^{-1}$	Rate, $mol\ L^{-1}s^{-1}$
1	0.5	0.5	1.6×10^{-4}
2	0.5	1	3.2×10^{-4}
3	1	1	3.2×10^{-4}

i. Find overall order of reaction.

ii. Find the rate constant.

Reaction $2A + B \longrightarrow 2AB$

Rate = $k[A]^m[B]^n$

Therefore,

$1.6 \times 10^{-4} = k[0.5]^m[0.5]^n$ ... (i)

$3.2 \times 10^{-4} = k[0.5]^m[1]^n$ ... (ii)

$3.2 \times 10^{-4} = k[1]^m[1]^n$ ... (iii)

Dividing equation (ii) by (i) then we get

$$\frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}} = \frac{k[0.5]^m[1]^n}{k[0.5]^m[0.5]^n}$$

or, $2 = 2^n$

or, $2^1 = 2^n$

∴ $n = 1$

The reaction is first order with respect to B.

Again, dividing equation (iii) by (ii) we get,

$$\frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}} = \frac{k[1]^m[1]^n}{k[0.5]^m[1]^n}$$

or, $1 = 2^m$

or, $2^0 = 2^m$

∴ $m = 0$

The reaction is zero order with respect to A.

The overall reaction is (0 + 1) = 1 i.e. first order.

Find the rate constant.

The value of rate constant can be calculated by putting the value of m and n in equation (i)

$1.6 \times 10^{-4} = k[0.5]^0[0.5]^1$

$1.6 \times 10^{-4} = k \times 1 \times 0.5$

$$So,\ k = \frac{1.6 \times 10^{-4}}{0.5} = 3.2 \times 10^{-4}\ s^{-1}$$

Hence, rate constant (k) = $3.2 \times 10^{-4}\ s^{-1}$

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68. 2069 (Set B) Q.No. 32

a. Define the terms:

i. First order reaction **ii. Rate law**

iii. Effective collision **iv. Activation energy**

v. Half-life period of a reaction **vi. Instantaneous rate.**

b. The following data are given for the reaction [10]

$2x + y \longrightarrow$ product (Z)

Expt. No.	[X], $molL^{-1}$	[Y], $molL^{-1}$	Rate of formation of (Z) $molL^{-1}s^{-1}$
1	0.1	0.1	7.0×10^{-3}
2	0.3	0.2	8.4×10^{-2}
3	0.3	0.4	3.36×10^{-1}
4	0.4	0.1	2.8×10^{-2}

i. Calculate the order of reaction with respect to X and Y.

ii. Half-life of reaction with respect to X.

iii. The rate of formation of 'Z'

when [X] = 0.6 $molL^{-1}$; [Y] = 0.3 $molL^{-1}$

i. **First order reaction:** Reaction in which rate is determined by the variation of only one concentration the reactant is called 1^{st} order reaction.

ii. **Rate law:** The mathematical expression that gives the true rate of reaction in terms of concentration which influences the rate of reaction is called rate law.

iii. **Effective collision:** The collision between reacting molecules resulting in the formation of product is called effective collision. There are many factors that affecting in the effective collision which of one is the **orientation** of the reacting molecules.

iv. **Activation energy:** The minimum amount of energy in which the reactant molecules must have in order to react is called activation energy.

v. **Half-life period of a reaction:** The time period of reaction in which the initial concentration of the reactant is decreased to half is called half-life period. It is denoted by $t_{1/2}$.

Half-life for 1^{st} order reaction is

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

vi. **Instantaneous rate:** The rate of chemical reaction at any particular instant of time during chemical change is known as instantaneous rate.

$A \longrightarrow B$

Instantaneous rate = $(Average)_{t \to 0}$

$$R_t = \left(-\frac{\Delta[A]}{\Delta t}\right)_{t \to 0}$$

$$R_t = \left(-\frac{\Delta[B]}{\Delta t}\right)_{t \to 0}$$

$$R_t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Where d[A] , d[B] and dt being infinitesimally small change in concentration of A and B and that of time respectively.

Numerical:

Reaction $2X + Y \longrightarrow Z$

Rate = $k[X]^m[Y]^n$

Therefore,

$7.0 \times 10^{-3} = k[0.1]^m[0.1]^n$ ... (i)

$8.4 \times 10^{-2} = k[0.3]^m[0.2]^n$ ... (ii)

$3.36 \times 10^{-1} = k[0.3]^m[0.4]^n$ ... (iii)

$2.8 \times 10^{-2} = k[0.4]^m[0.1]^n$ ... (iv)

Dividing equation (iv) by (i) we get

$$\frac{2.8 \times 10^{-2}}{7.0 \times 10^{-3}} = \frac{k[0.4]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

or, $4 = 4^m$

or, $4^1 = 4^m$

$\therefore$ m = 1

The reaction is first order with respect to X.

Again, dividing equation (iii) by (ii) we get,

$$\frac{3.36 \times 10^{-1}}{8.4 \times 10^{-2}} = \frac{k[0.3]^m[0.4]^n}{k[0.3]^m[0.2]^n}$$

or, $4 = 2^n$

or, $2^2 = 2^n$

$\therefore$ n = 2

The reaction is 2nd order with respect to Y.

The rate law equation can be expressed as

Rate = $k[X]^1[Y]^2$

Half-life of reaction with respect to X.

To calculate the half-life period the value of rate constant is needed.

$7.0 \times 10^{-3} = k[0.1]^1[0.1]^2$

$$k = \frac{7.0 \times 10^{-3}}{[0.1]^1[0.1]^2} = \frac{7.0 \times 10^{-3}}{0.001} = 7 \text{ mol}^{-2}\text{L}^2\text{s}^{-1}$$

Half-life period with respect to X is calculated as

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7} = 0.099 \text{ second}$$

The rate of formation of Z, when [X] = 0.6 molL^{-1} and [Y] = 0.3 molL^{-1}

The rate of formation of Z is

Rate = $K[0.6]^1[0.3]^2 = 7 \times 0.6 \times 0.09 = 0.378 \text{ mol L}^{-1}\text{s}^{-1}$

Hence, the rate of formation of Z is $0.378 \text{ mol L}^{-1}\text{s}^{-1}$.

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69. 2066 Q. No. 30 What is the rate law of reaction? How does order of a reaction differ from molecularity of a reaction, Rate of reaction $A + B \longrightarrow P$, is given below as a function of different initial concentration of A and B.

[A] mol L^{-1}	[B] mol L^{-1}	Rate mol L^{-1}s^{-1}
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

i. Determine the order of reaction with respect to A and B respectively.
ii. What is overall order of reaction?
iii. Write rate Law equation.

iv. Find value of rate constant.
v. What is the half-life of A? **[10]**

Rate law equation: The equation which shows the relationship between the rate of reaction and actual variation of concentration of reactant which is determined experimentally is called rate law equation.

Difference between order and molecularity of reaction: Please refer to 2058 Q.No. 24

Numerical:

Reaction is $xA + yB \longrightarrow$ product

Rate = $k[A]^x[B]^y$

Therefore,

$0.005 = k[0.01]^x[0.01]^y$ ... (i)

$0.010 = k[0.02]^x[0.01]^y$ ... (ii)

$0.005 = k[0.01]^x[0.02]^y$ ... (iii)

Dividing equation (iii) by (i) then we get

$$\frac{0.005}{0.005} = \frac{k[0.01]^x[0.02]^y}{k[0.01]^x[0.01]^y}$$

or, $1 = 2^y$

or, $2^0 = 2^y$

or, y = 0

Dividing equation (ii) by (i) then we get

$$\frac{0.010}{0.005} = \frac{k[0.02]^x[0.01]^y}{k[0.01]^x[0.01]^y}$$

or, $2^1 = 2^x$

or, x = 1

Hence, the rate equation is

Rate = $k[A]^1[B]^0$

So, the reaction is 1st order w.r.t. A and zero order w.r.t. B and overall order is (1 + 0) = 1 i.e. 1st order.

Substituting the value of x and y in the equation (i) we get

$0.005 = k[0.01]^1[0.01]^0$

or, $k = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$

We know that,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ minute}$$

Hence, the half life of a reaction is 1.386 minute.

---

70. 2064 Q.No. 25 Define Instantaneous rate of reaction. Compare the rate of reaction of all the components of the following reaction:

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

Find the rate of each component in mol s^{-1}, when 2.24 litre of O_2 at NTP are produced in 30 minutes. [5]

Instantaneous rate of reaction: Please refer to 2071 Supp. Q.No. 24

Numerical:

Volume of O_2 = 2.24 litre at NTP

$$\text{No. of mole of } O_2 = \frac{\text{Volume of } O_2 \text{ at NTP}}{22.4} = \frac{2.24}{22.4} = 0.1 \text{ mol}$$

Time of O_2 = 30 minute = (30 × 60) = 1800 second

Given,

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Here, $\frac{\Delta[O_2]}{\Delta t} = \frac{0.1}{1800} = 5.5 \times 10^{-5}\ \text{mol s}^{-1}$

Again,

$$-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\therefore \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 5.5 \times 10^{-5}\ \text{mol S}^{-1} = 1.11 \times 10^{-4}\ \text{mol s}^{-1}$$

Similarly,

$$\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\therefore \frac{\Delta[NO_2]}{\Delta t} = 4 \times 5.5 \times 10^{-5}\ \text{mol S}^{-1} = 2.22 \times 10^{-4}\ \text{mol s}^{-1}$$

So, Rate of formation of $O_2 = 5.5 \times 10^{-5}$ mol s^{-1}
Rate of disappearance of $N_2O_5 = 1.11 \times 10^{-4}$ mol s^{-1}
Rate of formation of $NO_2 = 2.22 \times 10^{-4}$ mol s^{-1}

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71. 2063 Q.No. 16 The half life period of first order reaction is 3 hours. Find the time required to complete 87.5% of the reaction. **[2]**

Given,

Half life $t_{1/2} = 3$ hrs

Time required to complete 87.5% = ?

We know that,

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

$$\text{or, } 3 = \frac{0.693}{k}$$

$$\text{or, } k = \frac{0.693}{3} = 0.231\ \text{hr}^{-1}$$

Suppose, initial concentration = a_o

Final concentration (x) $= a_o - 87.5\ \%$ of a_o

$$= a_o - \frac{87.5}{100}a_o = \frac{100a_0 - 87.5a_0}{100} = \frac{12.5a_0}{100} = 0.125\ a_o$$

For 1st order reaction

$$t = \frac{2.303}{k}\log\frac{a_0}{x} = \frac{2.303}{0.231}\log\frac{a_0}{0.125\ a_0} = \frac{2.303}{0.231}\log 8 = \frac{2.303}{0.231} \times 0.903$$

$t = 9.003$ hrs.

So, the time required to complete 87.5% of reaction is 9.003 hrs.

---

72. 2062 Q.No. 25 The rate of a reaction, A + B ⟶ product is given below as a function of different initial conc^n. of A and B. **[5]**

Expt.	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol L^{-1} min^{-1}
1.	0.01	0.01	0.005
2.	0.02	0.01	0.010
3.	0.01	0.02	0.005

i. Determine the order of reaction with respect to A and B..
ii What is the half life of A in the reaction?

Numerical: Please refer to 2066 Q. No. 30

73. 2061 Q.No. 25 Suppose that the rate law for the reaction A ⟶ B has been found to be of the form Rate = k[A]^m.
From the following data, determine the overall order of the reaction and the order with respect to A. [5]

Initial Concentration of A (M)	Initial Rate (M/Sec)
0.05	3×10^{-5}
0.10	12×10^{-5}
0.20	48×10^{-5}

Given,
Reaction is A ⟶ B
Rate = $k[A]^m$

Therefore,

$$3 \times 10^{-5} = k[0.05]^m \qquad \dots (i)$$
$$12 \times 10^{-5} = k[0.10]^m \qquad \dots (ii)$$
$$48 \times 10^{-5} = k[0.20]^m \qquad \dots (iii)$$

Dividing equation (ii) by (i), then we get

$$\frac{12 \times 10^{-5}}{3 \times 10^{-5}} = \frac{k[0.10]^m}{k[0.05]^m}$$

or, $4 = (2)^m$
or, $(2)^2 = (2)^m$
So, m = 2

Therefore, the order of reaction with respect to A is second and the overall reaction order is second.

---

74. 2060 Q.No. 16 What is meant by order of a reaction? State the order of reaction having rate constant 2×10^{-2} mol L^{-1}s^{-1}. **[2]**

Order of reaction: The sum of power of concentration of reactants species in the chemical reaction at the rate determining step of reaction is called order of reaction.

Let us consider a reaction:

A + B ⟶ product

Rate = $k[A]^o[B]^o$ Where, k is rate constant.

The order of reaction is zero.

$$\text{Rate constant(k)} = \frac{\text{Unit of concentration}}{\text{Unit of time}} = \text{molL}^{-1}\text{s}^{-1}$$

The order of reaction having rate constant 2×10^{-2} mol L^{-1}s^{-1} is zero order.

---

75. 2060 Q.No. 30 For the gaseous reaction,

$A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$

It is found that, rate = $k[A]^2\ [B]^1$

How many times does the rate of reaction increase or decrease if (a) the partial pressure of both A and B are doubled, (b) the partial pressure of A doubles but that of B remains constant. (c) the volume of reacting vessel is doubled (d) an inert gas is added which doubles the overall pressure while the partial pressure of A and B remains constant. (e) the temperature rises by 30°C. **[10]**

Given,

Equation is A(g) + B(g) ⟶ C(g) + D(g)

Rate = $k[A]^2[B]^1$ Where, k = rate constant

If P_A and P_B are the partial pressure of two gases A and B respectively, then the rate constant becomes

$$\text{Rate} = k[P_A]^2[P_B]^1 \qquad \dots (i)$$

a. If the partial pressure of both A and B are doubled, then the equation becomes

$$\text{Rate} = k[2P_A]^2[2P_B]^1 = 8k[P_A]^2[P_B]^1$$

The rate of reaction is increased by 8 times, if both the reactant A and B are doubled.

b. If the partial pressure of A is doubled and that of B remains constant, the rate constant becomes

$\text{Rate} = k[2P_A]^2[P_B]^1 = 4k[P_A]^2[P_B]^1$

The rate of reaction is increased by 4 times, if the reactant A is doubled and B remains constant.

c. We know that the volume of gas at constant temperature is inversely proportional to its pressure. When the volume of reaction vessel is doubled, the partial pressure of A and B is decreased by half and the new pressure becomes $\frac{P_A}{2}$ and $\frac{P_B}{2}$ respectively.

$$\text{Rate} = k\left[\frac{P_A}{2}\right]^2\left[\frac{P_B}{2}\right]^1 = \frac{1}{8}k\,[2P_A]^2[P_B]^1$$

The rate of reaction is decreased by 8 times.

d. If the inert gase is added to the gaseous vessel, there is no change in partial pressure of reactant A and B i.e. the partial pressure of A and B remains constant.

e. Experimentally, it is found that the rate of reaction increase or decrese by 2 or 3 times for every 10°C rise or fall in temperature.

Suppose, 'r' be the initial rate of reaction. If the temperature of reaction is increased by 10°C, the rate becomes 2r or 3r.

Again, if temperature of reaction is increased by 10°C, the rate will be 2 or 3 times of 2r or 3r.

$2 \times 2r = 4r$ or $3 \times 3r = 9r$

If temperature of reaction is further increased by 10°C, the rate will be 2 or 3 of 4r of 9r.

$2 \times 4r = 8r$ or $3 \times 9r' = 27r$

Therefore, if the temperature of reaction is increased by 30°C, the rate of reaction increases from 8 to 27 times.

---

76. **2055 Q.No. 28**

a. List the factors that affect the rate of a reaction.

b. Hydrogen and nitrogen oxide react according to the following equation.

$2H_2(g) + 2NO\,(g) \longrightarrow H_2O\,(g) + N_2(g)$

Experiments were performed at 800°C in order to determine the order of reaction and the following results were obtained. **[5]**

Initial concentration of nitrogen oxide (mol L^{-1})	Initial concentration of hydrogen (mol L^{-1})	Initial rate of production of nitrogen (mol L^{-1} s^{-1})
6×10^{-3}	1×10^{-3}	3×10^{-3}
6×10^{-3}	2×10^{-3}	6×10^{-3}
6×10^{-3}	3×10^{-3}	9×10^{-3}
1×10^{-3}	6×10^{-3}	0.5×10^{-3}
2×10^{-3}	6×10^{-3}	2.0×10^{-3}
3×10^{-3}	6×10^{-3}	4.5×10^{-3}

a. What is the order of this reaction with respect to (i) nitrogen oxide (ii) hydrogen?

b. Write the rate equation for the reaction of nitrogen oxide with hydrogen.

c. What is the unit of rate constant, k?

d. Why are chemists interested in obtaining order of reaction and rate equations?

➣ Reaction $2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$

$\text{Rate} = k[NO]^m[H_2]^n$

Therefore,

$3 \times 10^{-3} = k[6 \times 10^{-3}]^m[1 \times 10^{-3}]^n$ ... (i)

$6 \times 10^{-3} = k[6 \times 10^{-3}]^m[2 \times 10^{-3}]^n$ ... (ii)

$9 \times 10^{-3} = k[6 \times 10^{-3}]^m[3 \times 10^{-3}]^n$ ... (iii)

$0.5 \times 10^{-3} = k[1 \times 10^{-3}]^m[6 \times 10^{-3}]^n$ ... (iv)

$2 \times 10^{-3} = k[2 \times 10^{-3}]^m[6 \times 10^{-3}]^n$ ... (v)

$4.5 \times 10^{-3} = k[3 \times 10^{-3}]^m[6 \times 10^{-3}]^n$ ... (vi)

Dividing equation (i) by (ii) then we get,

$$\frac{3 \times 10^{-3}}{6 \times 10^{-3}} = \frac{k[6 \times 10^{-3}]^m\,[1 \times 10^{-3}]^n}{k[6 \times 10^{-3}]^m\,[2 \times 10^{-3}]^n}$$

or, $\left(\frac{1}{2}\right) = \left(\frac{1}{2}\right)^n$

$\therefore$ $n = 1$

The reaction is first order with respect to (w.r.t.) H_2

Again, dividing equation (iv) by (v) then we get,

$$\frac{0.5 \times 10^{-3}}{2 \times 10^{-3}} = \frac{k[1 \times 10^{-3}]^m\,[6 \times 10^{-3}]^n}{k[2 \times 10^{-3}]^m\,[6 \times 10^{-3}]^n}$$

or, $\left(\frac{5}{20}\right)^1 = \left(\frac{1}{2}\right)^m$

or, $\left(\frac{1}{4}\right)^1 = \left(\frac{1}{2}\right)^m$

or, $\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^m$

$\therefore$ $m = 2$

The given reaction is second order w.r.t. NO

The rate equation is given as

$\text{Rate} = k[NO]^m[H_2]^n$

$\text{Rate} = k[NO]^2[H_2]^1$

The unit of rate constant k is given as,

$$k = \frac{\text{Sec}^{-1}}{(\text{mol L}^{-1})^2} = s^{-1}\text{mol}^{-2}L^2$$

The chemist are interested in obtaining the order of reaction and rate equation to find out the path of reaction and change in concentration of reactant with change in time period.

---

77. **2053 Q.No. 25(a)** **What is meant by the term rate of reaction? How is it expressed?** **[2.5]**

➣ Please refer to 2054 Q.No. 6

WRITE SHORT NOTES ON [5 MARKS]

78. **2075 Set B Q.No. 33ii** **2072 Set D Q.No. 33a** **Order and molecularity of reaction.** **[5]**

➣ **Order of reaction:** It is the sum of the power of concentration of reacting substance. It may be a whole number or zero or fraction. It is expressed as zero order, first order, second order, nth order etc. It can be obtained experimentally. It is real number. It has no connection with the stoichiometric equation of a reaction.

Example, $2N_2O_5 \longrightarrow 4NO_2 + O_2$

It is first order reaction not bimolecular.

Molecularity of reaction: It is the total number of atoms or molecules taking part in reaction. It is always a whole number. It is expressed as uni, bi, tri, molecular etc. It can not be obtained experimentally. It is imaginary quantity. It has great connection with the stoichiometric equation of a reaction. Example, $2N_2O_5 \longrightarrow 4NO_2 + O_2$

It is bimolecular reaction.

---

79. **2068 Q.No. 31iv** **Rate of chemical reaction and Rate Law** **[5]**

➣ **Rate of chemical reaction:** The rate of reaction is a measure of how fast a reactant is used up or a product formed or we can say rate of reaction means the slowness and fastness of reaction. When reaction progress, the concentration of reactants decrease and that of product increase with increase time. Therefore, the rate at which reaction proceeds can be measured either by rate of decrease of reactant concentration or by rate of increase of product concentration. Let us consider the reaction:

$$R\ (\text{Reactant}) \xrightarrow{\text{Reaction}} P\ (\text{Product})$$

If $[R]_1$ and $[R]_2$ be the concentration of reactant R at time t_1 and t_2 respectively, then

$$\text{Rate} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = -\frac{\Delta[R]}{\Delta t}$$

The square bracket [ ] is used to indicate molar concentration. The –ve sign shows that the concentration of reactant keeps on decreasing with time and +ve sign implies the increase in concentration of product with time.

Rate Law: Rate law equation is the equation showing the relationship between the rate of reaction and actual variation of concentration of reactant or reactants which is determined experimentally. It is obtained when the experimental rate law of the reaction is converted into an equation after incorporating the rate constant (k). The rate law is not obtained theoretically as per overall chemical equation because the rate equation has no empirical relationship with the overall chemical equation rather it is determined experimentally. The rate of reaction is always measured with the help of the slowest step of that reaction. The rate of reaction is proportional to the product of molar concentrations of reactant participating in its slowest step.

For the following reaction:

$$2A \longrightarrow \text{products}$$

We have the following experimental data:

[A]	Rate of reaction
1M	10
2M	20
3M	30

The theoretical rate of reaction will be = $k[A]^2$

But the experimental rate of reaction = $k[A]$

Because by doubling the concentration of A, the rate of reaction gets doubled i.e. the rate of reaction is directly proportional to the concentration of A.

---

80. 2067 Q.No. 31 ii 2054 Q.No. 30(b) Collision theory of reactions rate [5]

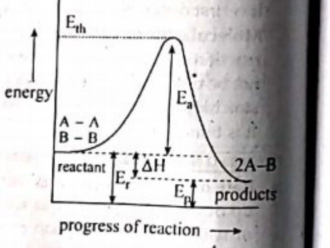
This theory provides the basic requirements for chemical reaction to occur. According to this theory a chemical reaction takes place only due to collision between reactant molecules. Only certain fractions of total collisions are capable to give products, such collisions are called effective collisions or fruitful collision. Conditions for effective collisions are

i. The colliding molecules must possess sufficient kinetic energy to cause a reaction.
ii. The reactant molecules must collide with proper orientation.

To explain the collision theory, Let us consider a chemical reaction,

$$A - A + B - B \longrightarrow 2A - B$$

For chemical reaction, old bonds of reactants are broken and new bonds are formed to give products. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision. The energy profile diagram is

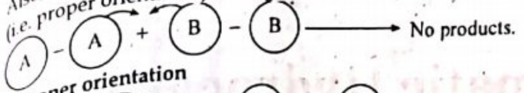


Where,

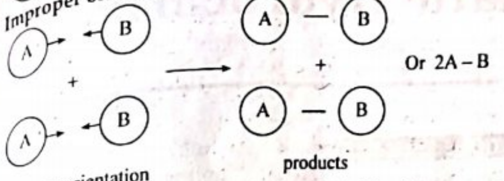
E_r = Energy of reactant
E_p = Energy of product
E_{th} = Threshold energy
E_a = Activation energy
ΔH = Heat of reaction.

Only the molecules which collide with kinetic energy greater than E_a, are able to overcome the barrier of threshold energy and give product. The molecules colliding with kinetic energy less than Ea, fail to cross the threshold energy barrier and products are not formed. Such collisions are called ineffective or unproductive collision.

Also, for effective collision, reactants molecules should approach in their favourable sites (i.e. proper orientation) during collision.



Improper orientation



proper orientation

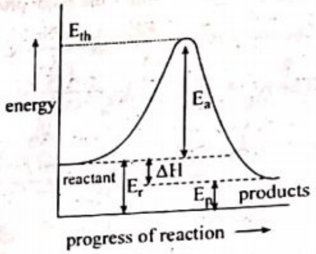
Thus, only the molecules colliding with kinetic energy greater than E_a and with proper orientation can cause reaction.

Activation energy

From collision theory, it is seen that the reactant molecules must overcome the barrier of threshold energy to give products. The additional energy above the average energy of reactants which must be supplied or gained to cross threshold energy barrier by reactant molecule is called activation energy.

In other words, the additional energy required to produce effective collision is called activation energy.

Greater the activation energy, slower will be the rate of reaction and lower the activation energy faster will be the rate of reaction. A reaction with zero activation energy is nearly explosive.



Where,

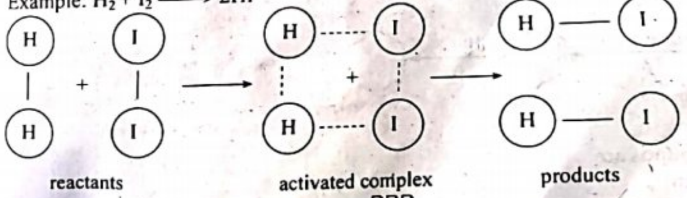
E_r = Energy of reactant
E_p = Energy of product
E_{th} = Threshold energy
E_a = Activation energy
ΔH = Heat of reaction.

Mathematically, $E_a = E_{th} - E_r$

Activated Complex

The reactant molecules after absorbing activation energy attain a complex structure at the top of energy barrier. At this step, original bonds of reactants are in the process of breaking and new bonds of products are in the process of formation. This short life molecular complex midway between reactants and products at the top of energy barrier is called activated complex. It decomposes as soon as it forms to give products.

Example: $H_2 + I_2 \longrightarrow 2HI$



❑❑❑

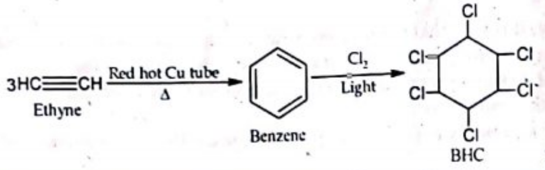
Unit 8

Aromatic Hydrocarbon

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 8** **Write down correct reactions for the conversion of ethyne into BHC.** [2]

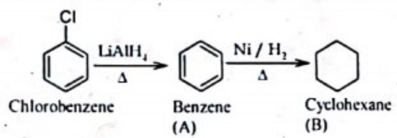
➢



2. **2075 GIE Q.No. 8** **Identify the major products Ⓐ and Ⓑ in the following reaction sequence.** [1+1]

$$\text{Chlorobenzene} \xrightarrow[\Delta]{LiAlH_4} Ⓐ \xrightarrow[\Delta]{Ni/H_2} Ⓑ$$

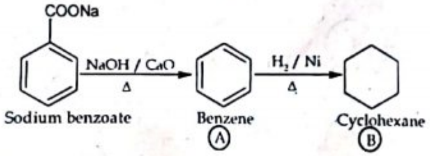
➢ The reaction sequence is



3. **2075 Set A Q.No. 8** **Identify the major products Ⓐ and Ⓑ in the following reaction sequence** [1+1]

$$\text{Sodium benzoate} \xrightarrow[\Delta]{NaOH+CaO} Ⓐ \xrightarrow[\Delta]{H_2/Ni} Ⓑ$$

➢ The reaction sequence is given as:



The compounds are

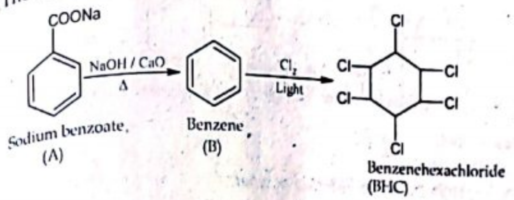
Ⓐ = Benzene

Ⓑ = Cyclohexane

4. **2075 Set B Q.No. 8** **Identify Ⓐ and Ⓑ in the following reaction sequence.** [1+1]

$$Ⓐ \xrightarrow[\Delta]{NaOH/CaO} Ⓑ \xrightarrow[light]{Cl_2} C_6H_6Cl_6$$

➢ The reaction sequence is given as:



The compounds are

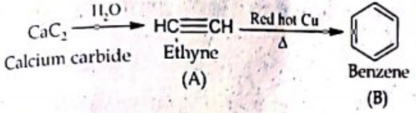
A = Sodium benzoate

B= Benzene

5. **2074 Supp. Q.No. 8** $CaC_2 \xrightarrow{H_2O} A \xrightarrow[\Delta]{\text{Red hot Cu}} B$

Identify A and B in the above reaction. [1+1]

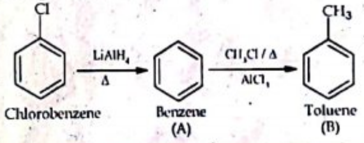
➢ The reaction sequence is given as



6. **2074 Set A Q.No. 8** **Identify the major product (A) and (B) in the following reaction sequence.** [1+1]

$$\text{Chlorobenzene} \xrightarrow[\Delta]{LiAlH_4} (A) \xrightarrow[AlCl_3]{CH_3Cl / \Delta} (B)$$

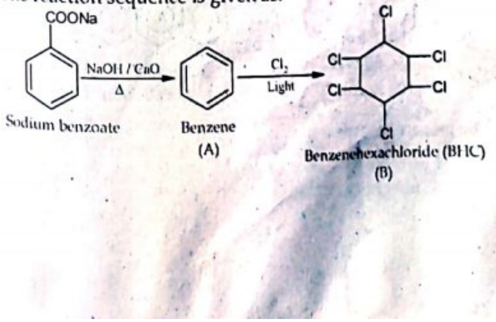
➢ The reaction sequence is given as:



7. **2074 Set B Q.No. 8** **Identify the major product (A) and (B) in the following reaction sequence.** [1+1]

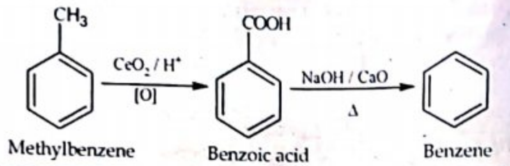
$$\text{Sodium benzoate} \xrightarrow[\Delta]{NaOH / CaO} (A) \xrightarrow[light]{Cl_2} (B)$$

➢ The reaction sequence is given as:



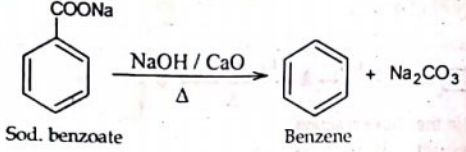
8. 2073 Supp Q.No. 8 **How is benzene obtained form toluene?** [2]

When toluene is oxidized with oxidizing agent like CeO_2/H^+, benzoic acid is obtained which on heating with soda-lime benzene is obtained.

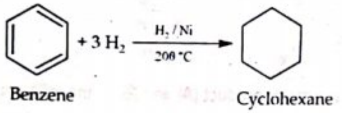


9. 2073 Set C Q.No. 8 **What happens when:** [1+1]
   - i. **Sodiumbenzoate is heated with soda-lime.**
   - ii. **Benzene is heated with hydrogen in presence of nickel powder.**

i. When sodium benzoate is heated with sodalime (NaOH + CaO), benzene is formed. This reaction is known as Decarboxylation reaction.

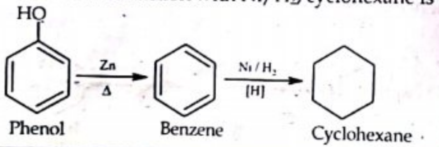


ii. When benzene is heated with hydrogen in the presence of Ni-powder, cyclohexane is obtained.



10. 2073 Set D Q.No. 8 **Starting from phenol how would you obtain cyclohexane.** [2]

Preparation of cyclohexane from phenol: When phenol is heated with zinc dust, benzene is obtained which on reduction with Ni/H_2, cyclohexane is obtained.

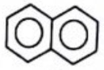


11. 2072 Supp. Q.No. 8 **What are aromatic compounds according to Huckel's rule?** [2]

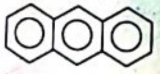
According to Huckel's rule, aromatic compounds contain (4n + 2) delocalized π electrons clouds, above and below the plane. Where 'n' is an integer and may be 0, 1, 2, 3, 4, ...

Examples:

Benzene (n = 1)
6π electron



Naphthalene (n = 2)
10π electron

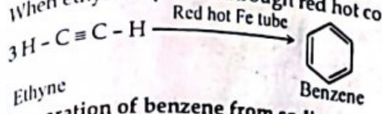


Anthracene (n = 3)
14π electron

12. 2072 Set C Q.No. 8 **How would you prepare benzene from:** [1+1]
   - i. **ethyne**
   - ii. **sodium benzoate**

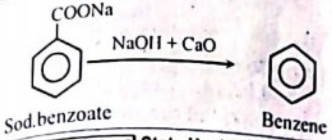
i. **Preparation of benzene from Ethyne:**

When ethyne is passed through red hot copper or iron tube, benzene is obtained.



ii. **Preparation of benzene from sodium benzoate:**

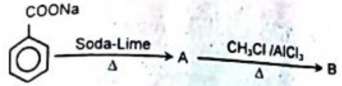
When sodium benzoate is heated with soda lime, benzene is obtained.



13. 2072 Set D Q.No. 8 **State Huckel's rule for aromaticity.** [2]

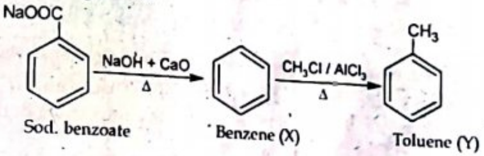
Huckel's rule: A cyclic conjugated system that consists of (4n+2)π electrons will show aromatic character, provided 'n' is a whole number of integer. Thus to be a aromatic, a molecules must have 2 ((n = 0), 6 (n = 1), 10 (n = 2)........ π electrons.

14. 2072 Set E Q.No. 8



Identify A and B of the above reaction. [1+1]

The reaction sequence is given as



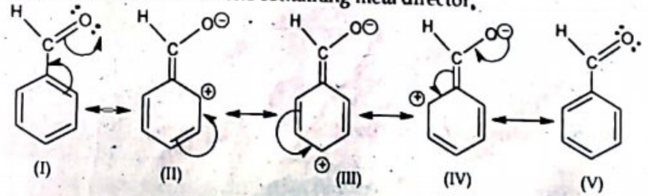
The compounds are
X = Benzene Y = Toluene

15. 2071 Supp. Q.No. 8 **What are aromatic compounds according to Huckel's rule?** [2]

Please refer to 2072 Supp. Q.No. 8

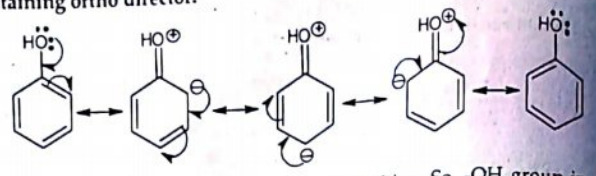
16. 2071 Set C Q.No. 8 **Write resonance hybrid structure of arene containing meta director and ortho director substituents of each.** [2]

Resonance hybrid structure of arene containing meta director.



Positive charges are developed on ortho and para position and no any charge is developed at meta position. The aldehydic functional group (–CHO) is electron withdrawing group and withdraw the electron form the benzene ring and electron rich carbon is meta position. So, aldehydic group in benzaldehyde is meta director in electrophilic substitution.

Arene containing ortho director:

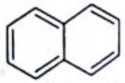


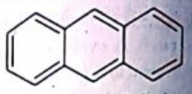
Negative charge is developed on ortho and para position. So, -OH group in phenol is ortho and para director in electrophilic substitution.

17. **2071 Set D Q.No. 8** **State Huckel's rule for aromaticity.** [2]

Huckel Rule: In 1931 Erich Huckel proposed this rule. According to this rule, cyclic planar compound containing (4n+2) delocalized π electron clouds above and below the plane of the ring.Where 'n' is an integer and may be 0,1,2,3,4......etc.Thus cyclic planer compound containing 2,6,10,14 etc. delocalized π electron cloud can show aromaticity.


Benzene n = 1, six pi electron (aromatic)


Naphthalene n = 2, ten pi electron (aromatic)


Anthracene n = 3, fourteen pi electron(aromatic)

The cyclic compound which does not follow the Huckel rule is known as non- aromatic
Example:


1,3-cyclobutadiene


Cyclopentadiene

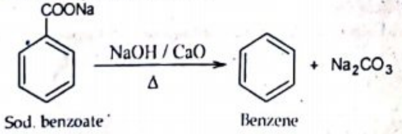

Cycloheptatriene

18. **2070 Supp. Q.No. 8** **Why is benzene called aromatic compound according to Huckel's rule?** [2]

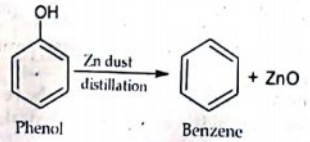
According to Huckel's rule, benzene contains (4n+2) delocalized π electorns clouds above and below the plane. So, benzene is aromatic compound. Benzene contains six π electrons.

19. **2070 Set C Q.No. 8** **What happens when**
   i. **Sodium benzoate is heated with soda-lime.**
   ii. **Phenol is heated with zinc dust.** [2]

i. When sodium benzoate is heated with sodalime (NaOH + CaO), benzene is formed. This reaction is known as **Decarboxylation reaction.**

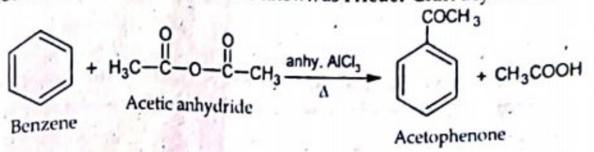


ii. When phenol is heated with zinc dust, benzene is obtained. This reaction is known as **Reduction.**

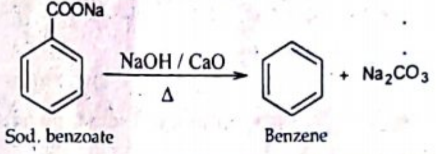


20. **2070 Set D Q.No. 8** **What happens when**
   i. **Benzene is heated with acetic anhydride in presence of anhydrous AlCl₃.** [2]
   ii. **Sodium benzoate is heated with sodalime.**

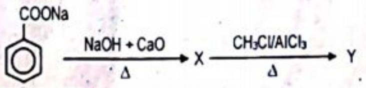
i. When benzene is heated with acetic anhydride in presence of anhydrous $AlCl_3$, acetophenone is formed. This reaction is known as **Friedel-Craft acylation reaction.**



ii. When sodium benzoate is heated with sodalime (NaOH + CaO), benzene is formed. This reaction is known as **Decarboxylation reaction.**



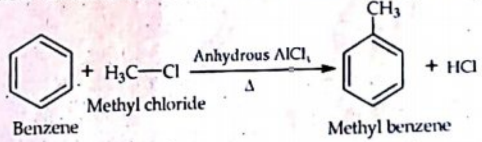
21. **2069 Supp. Set B Q.No. 8** **2069 (Set B) Q.No. 8** **Identify x and y in the following reactions and give their names.** [2]



Please refer to **2072 Set E Q.No. 8**

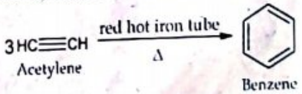
22. **2069 (Set A) Q.No. 32d** **Give the example of Friedel Craft's alkylation** [2]

Friedel-Craft alkylation: Benzene reacts with alkyl halide in the presence of $AlCl_3$, alkyl benzene is formed. This reaction is known as Friedel-Craft's Alkylation.



23. **2067 Q.No. 9** **Name the monomer which on polymerization can give benzene. What type of polymerization is this?** [2]

The monomer acetylene on polymerization gives benzene. When acetylene is passed through the red hot iron tube, benzene is obtained. This is an addition polymerization.

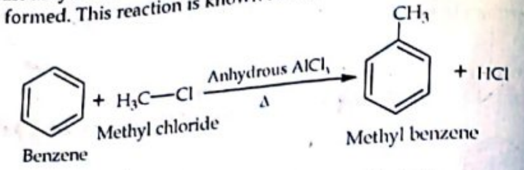


SHORT QUESTIONS ANSWERS [5 MARKS]

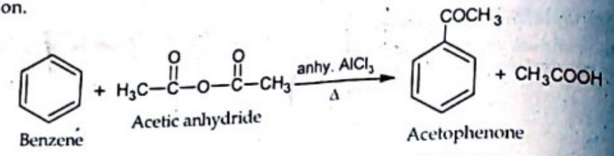
24. **2056 Q.No. 30 b (ii)** **Show your acquaintance with the following: Friedel Craft's reaction.** [5]

The substitution of an alkyl or acyl group into the benzene nucleus in the presence of anhydrous $AlCl_3$ by using alkyl halide or acyl halide is known as Friedel-Craft reaction. It is divided into two types:

i. **Friedel-Craft alkylation:** Benzene reacts with alkyl halide in the presence of AlCl$_3$, alky benzene is formed. This reaction is known as Friedel-Craft alkylation.



ii. **Friedel-Craft acylation:** Benzene reacts with acyl halide in the presence of AlCl$_3$, acy group is introduced in the benzene ring. This reaction is known as Friedel-Cra acylation.



25. 2053 Q.No. 28(a) 2062 Q.No. 319a) **Write short none on: Friedel-Crafts reaction** [5]

Please refer to 2056 Q No. 30 b (ii)

□□□

Unit **9**

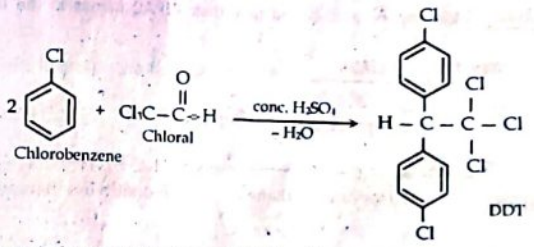
Haloalkanes and Haloarenes

9.1 Haloalkanes

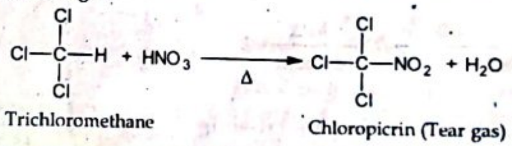
VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2074 Supp. Q.No. 9 **What happens when** **[2]**
   - i. **chlorobenzene is treated with chloral**
   - ii. **trichroromethane is heated with conc. Nitric acid**

i. When chlorobenzene is treated with chloral in acidic medium, dichlorodiphenyltrichloroethane (DDT) is formed.



ii. Trichloromethane is heated with Conc. HNO$_3$, chloropicrin is formed which is used as an insecticide and tear gas.



$$CHCl_3 + HNO_3 \xrightarrow{\Delta} CCl_3NO_2 + H_2O$$

2. 2074 Set A Q.No. 9 **What happens when chloroform is**
   - i. **exposed to atmospheric air?**
   - ii. **heated with silver powder?**

[1+1]

i. When Chloroform ($CHCl_3$) is left exposed to air and light, it slowly gets oxidized to phosgene gas or carbonyl chloride ($COCl_2$) which is a poisonous gas.

$2CHCl_3 + O_2 \longrightarrow 2\,COCl_2 + 2HCl$

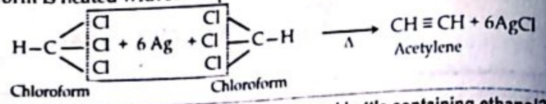
Chloroform   Carbonyl chloride

Chloroform ($CHCl_3$) is used for anesthetic purpose in surgery. Hence, anesthetic chloroform ($CHCl_3$) is kept in brown bottle to cut off light and the bottle is filled completely with chloroform to exclude air. A 1% solution of ethyl alcohol is also added to it to retard oxidation of chloroform. Ethanol converts phosgene to non-poisonous diethyl carbonate.

$$Cl-\overset{\overset{O}{\|}}{C}-Cl + 2H_3C-CH_2-OH \longrightarrow O=C\begin{matrix} O-C_2H_5 \\ O-C_2H_5 \end{matrix} + 2H-Cl$$

Phosgene gas Ethanol Diethyl carbonate

ii. When chloroform is heated with silver powder, acetylene gas is formed.



$$H-C\begin{matrix} Cl \\ Cl \\ Cl \end{matrix} + 6Ag + \begin{matrix} Cl \\ Cl \\ Cl \end{matrix}C-H \xrightarrow[\Delta]{} CH\equiv CH + 6AgCl$$

Chloroform Chloroform Acetylene

---

3. 2074 Set B Q.No. 9 **Why is chloroform stored in dark coloured bottle containing ethanol?** [2]

Please refer to 2074 Set A Q.No. 9

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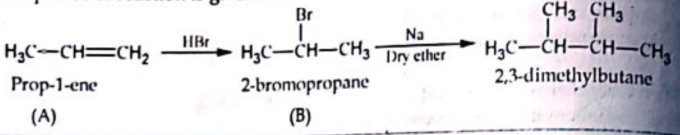
4. 2073 Supp Q.No. 9 **An alkene Ⓐ undergoes addition with HBr to give Ⓑ. When Ⓑ is heated with sodium in presence of dry ether give 2,3- dimethylbutane. Identify Ⓐ and Ⓑ.** [1+1]

The sequence of reaction is given as:



$$H_3C-CH=CH_2 \xrightarrow{HBr} H_3C-\overset{Br}{CH}-CH_3 \xrightarrow[\text{Dry ether}]{Na} H_3C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$$

Prop-1-ene (A) 2-bromopropane (B) 2,3-dimethylbutane

---

5. 2073 Set C Q.No. 9 **Identify Ⓐ and Ⓑ and give their IUPAC names in the following sequence of reaction** [1+1]

$$CH_3-Br \xrightarrow[\Delta]{AgCN(alc.)} Ⓐ \xrightarrow[\Delta]{LiAlH_4} Ⓑ$$

The sequence of reaction is given as

$$H_3C-Br \xrightarrow[\Delta]{AgCN\ (alc.)} H_3C-NC \xrightarrow[\Delta]{LiAlH_4} H_3C-NH-CH_3$$

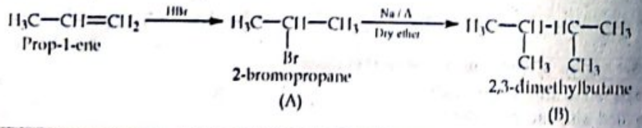
Bromomethane Isocyanomethane (A) *N*-methylmethanamine (B)

---

6. 2073 Set D Q.No. 9 **Identify Ⓐ and Ⓑ in the following sequence of the reaction and give their IUPAC name.** [2]

$$CH_3-CH=CH_2 \xrightarrow{HBr} Ⓐ \xrightarrow[\text{dry ether}]{Na/\Delta} Ⓑ$$

The sequence of reaction is given as:



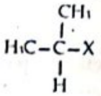
$$H_3C-CH=CH_2 \xrightarrow{HBr} H_3C-\underset{Br}{CH}-CH_3 \xrightarrow[\text{Dry ether}]{Na/\Delta} H_3C-\underset{CH_3}{CH}-\underset{CH_3}{HC}-CH_3$$

Prop-1-ene 2-bromopropane (A) 2,3-dimethylbutane (B)

---

7. 2072 Supp. Q.No. 9 **Write down the structure and IUPAC name of secondary haloalkane of C_3H_7X. What happens when the secondary haloalkane is heated with Na in presence of dry ether?** [1+1]

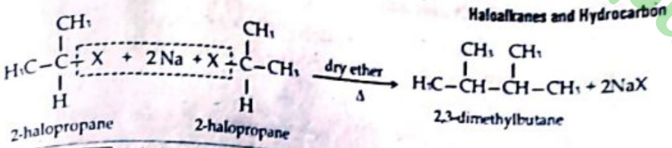
Structure of secondary haloalkane of C_3H_7X is



$$H_3C-\underset{H}{\overset{CH_3}{C}}-X$$

2-halopropane

When secondary haloalkane is heated with Sodium metal (Na) in presence of dry ether, 2,3-dimethylbutane is formed.



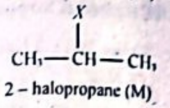
$$H_3C-\underset{H}{\overset{CH_3}{C}}-X + 2Na + X-\underset{H}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{\text{dry ether}} H_3C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3 + 2NaX$$

2-halopropane 2-halopropane 2,3-dimethylbutane

---

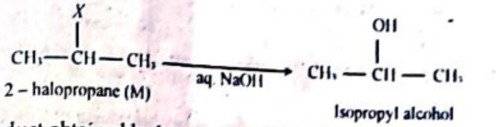
8. 2072 Set C Q.No. 9 **A haloalkane (M) reacts with aq. NaOH to give isopropyl alcohol. What major product would you get when (M) is heated with Na in presence of dry ether?** [2]

The structure of haloalkane (M) which reacts with aq. NaOH to give isopropyl alcohol is



$$CH_3-\overset{X}{CH}-CH_3$$

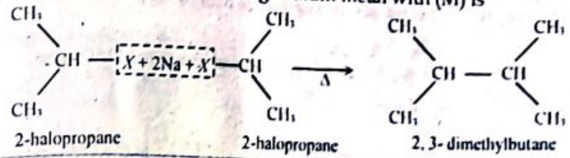
2 – halopropane (M)



$$CH_3-\overset{X}{CH}-CH_3 \xrightarrow{aq.\ NaOH} CH_3-\overset{OH}{CH}-CH_3$$

2 – halopropane (M) Isopropyl alcohol

The major product obtained by heating sodium metal with (M) is

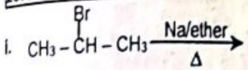


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}CH-X + 2Na + X-CH\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow{\Delta} \begin{matrix} CH_3 \\ CH_3 \end{matrix}CH-CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

2-halopropane 2-halopropane 2, 3- dimethylbutane

---

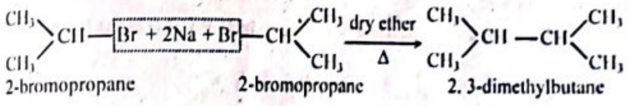
9. 2072 Set D Q.No. 9 **Give the major products in the following equations:** [1+1]

i. 

$$CH_3-\overset{Br}{CH}-CH_3 \xrightarrow[\Delta]{Na/ether}$$

ii. $CH_3-CH_2-Br \xrightarrow[\Delta]{LiAlH_4}$

The major product of

i. 

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}CH-\boxed{Br + 2Na + Br}-CH\begin{matrix} CH_3 \\ CH_3 \end{matrix} \xrightarrow[\Delta]{\text{dry ether}} \begin{matrix} CH_3 \\ CH_3 \end{matrix}CH-CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

2-bromopropane 2-bromopropane 2, 3-dimethylbutane

ii.

$$CH_3-CH_2-Br + 2[H] \xrightarrow[\Delta]{LiAlH_4} CH_3-CH_3 + H-Br$$

Bromoethane Ethane

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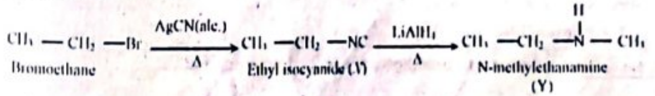
10. 2071 Supp. Q.No. 9 **Give the IUPAC name of X and Y in the following reaction sequence.** [1+1]

$$CH_3CH_2Br \xrightarrow[\Delta]{AgCN\ (alc)} X \xrightarrow[\Delta]{LiAlH_4} Y$$

The reaction sequence is



$$CH_3-CH_2-Br \xrightarrow[\Delta]{AgCN(alc.)} CH_3-CH_2-NC \xrightarrow[\Delta]{LiAlH_4} CH_3-CH_2-\overset{H}{N}-CH_3$$

Bromoethane Ethyl isocyanide (X) N-methylethanamine (Y)

The compounds are

X = Ethyl isocyanide

Y = N-methylethanamine

---

11. 2071 Set C Q.No. 9 **Starting from Iodomethane, how would you prepare:** [2]

i. Ethane ii. Ethene

i. **Ethane from iodomethane:** When iodomethane is heated with sodium metal in the presence of dry ether, ethane is formed.

$$\underset{\text{Iodomethane}}{CH_3-I} + 2Na + \underset{\text{Iodomethane}}{I-CH_3} \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

ii. **Ethene from iodomethane:** Iodomethane is heated with sodium metal in the presence of dry ether, ethane is formed. Ethane on chlorination with chlorine, chloroethane is formed which on dehydrohalogenation with alc. KOH, ethene is formed.

$$\underset{\text{Iodo methane}}{CH_3-I} + 2Na + I-CH_3 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

$$\underset{\text{Ethane}}{CH_3-CH_3} + Cl_2 \longrightarrow \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} + HCl$$

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} + \text{alc. KOH} \longrightarrow \underset{\text{Ethene}}{CH_2=CH_2} + KCl + H_2O$$

12. **2071 Set D Q.No. 9 Write down the structure of secondary haloalkane of C_3H_7X. What happen when the secondary haloalkane is heated with Na in presence of dry ether?** [2]

Please refer to 2072 Supp. Q.No. 9

13. **2070 Supp. Q.No. 9 Identify the major products A and B and give their IUPAC name.** [2]

$$CH_3CH_2I \xrightarrow{\text{AgCN(alc.)}} A \xrightarrow{\text{LiAlH}_4} B$$

The reaction sequence is

$$\underset{\text{Iodoethane}}{H_3C-CH_2-I} \xrightarrow{\text{AgCN(alc.)}} \underset{\substack{\text{Ethyl isocyanide}\\ \text{(A)}}}{H_3C-CH_2-NC} \xrightarrow{\text{LiAlH}_4} \underset{\substack{\text{N- methylethanamine}\\ \text{(B)}}}{H_3C-CH_2-NH-CH_3}$$

The compounds are

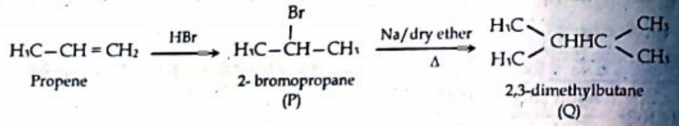
A = Ethylisocyanide

B = N-methylethanamine

14. **2070 Set C Q.No. 9 Write down the IUPAC name of major products P and Q in the following reaction sequence** [2]

$$CH_3-CH=CH_2 \xrightarrow{\text{HBr}} P \xrightarrow[\Delta]{\text{Na/ether}} Q$$

The reaction sequence is



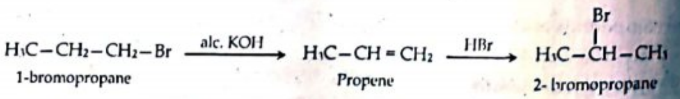
$$H_3C-CH=CH_2 \xrightarrow{\text{HBr}} H_3C-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3 \xrightarrow[\Delta]{\text{Na/dry ether}} (H_3C)_2CHHC(CH_3)_2$$

The compounds are

P = 2-bromopropane

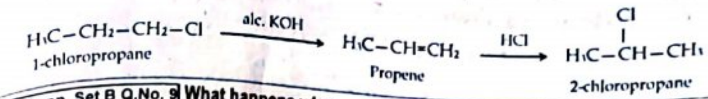
Q = 2, 3- dimethylbutane

15. **2070 Set D Q.No. 9 Convert 1 - bromopropane to 2 - bromopropane.** [2]



$$H_3C-CH_2-CH_2-Br \xrightarrow{\text{alc. KOH}} H_3C-CH=CH_2 \xrightarrow{\text{HBr}} H_3C-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3$$

16. **2069 (Set A) Q.No. 9 Convert 1-chloropropane into 2-chloropropane** [2]



$$H_3C-CH_2-CH_2-Cl \xrightarrow{\text{alc. KOH}} H_3C-CH=CH_2 \xrightarrow{\text{HCl}} H_3C-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3$$

17. **2069 Supp. Set B Q.No. 9 What happens when** [2]

i. **chlorobenzene is treated with chloral in acidic medium.**

ii. **chloroethane is heated with alcoholic KOH**

i. Please refer to 2074 Supp. Q.No. 9.

ii. When chloroethane is heated with alc. KOH, ethene is formed.

$$\underset{\text{Chloroethane}}{H_3C-CH_2-Cl} \xrightarrow{\text{alc. KOH}} \underset{\text{Ethene}}{H_2C=CH_2} + HCl$$

18. **2068 Q.No. 2 Identify the major products A and B in the following reaction.** [2]

$$C_2H_5Br \xrightarrow[\text{dry ether}]{\text{Mg}} A \xrightarrow{H_2O} B$$

The reaction sequence is

$$\underset{\text{Ethyl bromide}}{H_5C_2-Br} \xrightarrow[\text{dry ether}]{\text{Mg}} \underset{\substack{\text{Ethyl magnesium}\\ \text{bromide (A)}}}{C_2H_5MgBr} \xrightarrow{H_2O/H^+} \underset{\text{Ethane (B)}}{H_3C-CH_3} + Mg(OH)Br$$

The compounds are

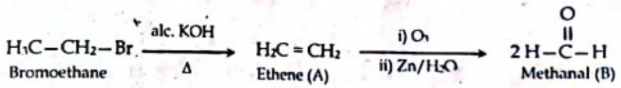
A = Ethyl magnesium bromide

B = Ethane

19. **2066 Q. No. 2 Identify A and B in the following reaction:** [2]

$$CH_3-CH_2-Br \xrightarrow[\Delta]{\text{alc KOH}} A \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} B$$

The reaction sequence is



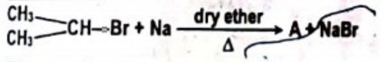
$$H_3C-CH_2-Br \xrightarrow[\Delta]{\text{alc. KOH}} H_2C=CH_2 \xrightarrow[\text{ii) Zn/H}_2\text{O}]{\text{i) O}_3} 2\,H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

The compounds are

A = Ethene

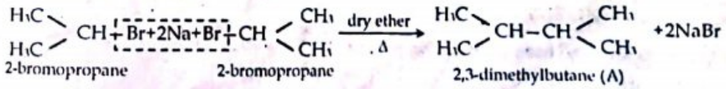
B = Methanal

20. **2065 Q.No. 2 Identify 'A' and write its IUPAC name in the following reaction** [2]



$$(CH_3)_2CH-Br + Na \xrightarrow[\Delta]{\text{dry ether}} A + NaBr$$

The reaction sequence is



$$(H_3C)_2CH-Br+2Na+Br-CH(CH_3)_2 \xrightarrow[\Delta]{\text{dry ether}} (H_3C)_2CH-CH(CH_3)_2 + 2NaBr$$

The above reaction is an example of Wurtz reaction. The IUPAC name of product 'A' is 2, 3-dimethylbutane.

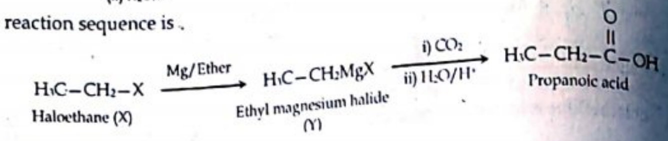
21. **2065 Q.No. 2 iii What happens when chloroform is heated with Silver powder?** [2]

Please refer to 2074 Set A Q.No. 9iii

22. **2063 Q.No. 2** **Identify (X) and (Y) in the following reaction:** [2]

$$(X) \xrightarrow{Mg/ether} (Y) \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CO_2} \text{Propanoic acid.}$$

The reaction sequence is .

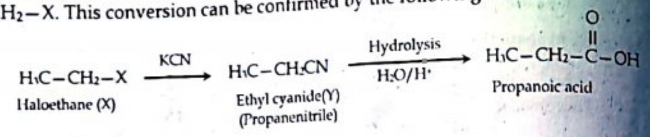


$$\underset{\text{Haloethane (X)}}{H_3C-CH_2-X} \xrightarrow{Mg/Ether} \underset{\text{Ethyl magnesium halide (Y)}}{H_3C-CH_2MgX} \xrightarrow[ii)\ H_2O/H^+]{i)\ CO_2} \underset{\text{Propanoic acid}}{H_3C-CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

The compounds are
X = Haloethane
Y = Ethyl magnesium halide

23. **2062 Q.No. 2** **A primary holoalkane (X), if allowed to react with KCN yields a compound (Y), which on acidic hydrolysis gave propanoic acid? Identify (X) and (Y).** [2]

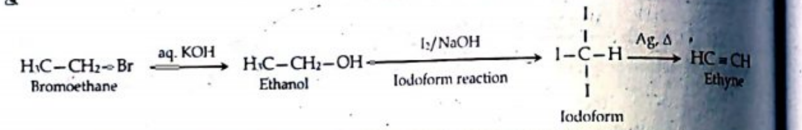
The compound (Y) is obtained from the compound (X) on treatment with KCN which on hydrolysis gives propanoic acid. The compound(Y) must be CH_3CH_2CN. The compound(Y) is obtained from (X) with KCN. So, the compound(X) must be CH_3CH_2-X. This conversion can be confirmed by the following reaction.



$$\underset{\text{Haloethane (X)}}{H_3C-CH_2-X} \xrightarrow{KCN} \underset{\substack{\text{Ethyl cyanide(Y)}\\ \text{(Propanenitrile)}}}{H_3C-CH_2CN} \xrightarrow[H_2O/H^+]{Hydrolysis} \underset{\text{Propanoic acid}}{H_3C-CH_2-\overset{\overset{O}{\|}}{C}-OH}$$

The compounds are
X = Haloethane
Y = Ethyl cyanide (Propanenitrile)

24. **2060 Q.No. 2** **Convert bromoethane to ethyne.** [2]



$$\underset{\text{Bromoethane}}{H_3C-CH_2-Br} \xrightarrow{aq.\ KOH} \underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow[\text{Iodoform reaction}]{I_2/NaOH} \underset{\text{Iodoform}}{I-\overset{\overset{I}{|}}{\underset{\underset{I}{|}}{C}}-H} \xrightarrow{Ag,\ \Delta} \underset{\text{Ethyne}}{HC\equiv CH}$$

25. **2058 Q.No. 2** **Why does chloroform not give white precipitate with aqueous silver nitrate?** [2]

Chloroform is non-polar covalent compound and does not ionize in aqueous solution. So, it does not give the white ppt. with silver nitrate solution. Only polar compound like HCl or NaCl give the white ppt with silver nitrate. If chloroform is impure, it may contain HCl as impurity and gives the test of silver nitrate solution.

$$\underset{\text{Silver nitrate}}{AgNO_3} + HCl \longrightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + HNO_3$$

26. **2056 Q.No. 15** **Why is chloroform stored in a dark brown bottle?** [2]

Please refer to 2074 Set A Q.No. 9

27. **2056 Q.No. 19** **Give the uses of chloroform.**

Following are the uses of chloroform:

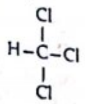
a. It is used as laboratory reagent.
b. It is used as preservative for biological specimens.
c. It is used as anesthetic in surgical operation.
d. It is used to prepare organic compound like chloropicrin, salicylic acid etc.

SHORT ANSWER QUESTIONS [5 MARKS]

28. **2076 Set B Q.No. 28** **How is trichloromethane prepared in the laboratory? Why is chloroform stored in a dark room air tied bottle containing a little ethyl alcohol?** [4+1]

Laboratory preparation of trichloromethane:

Chloroform or Trichloromethane($CHCl_3$)



Principle:

Chloroform is prepared in a laboratory by heating a paste of ethyl alcohol or acetone, bleaching powder and water. Bleaching powder acts as oxidizing, chlorinating and hydrolyzing agent.

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

From ethanol:

Oxidation: $$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

Chlorination: $$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral (Trichloroacetaldehyde)}}{CCl_3CHO} + 3HCl$$

Hydrolysis: $$\underset{\text{Chloral}}{2CCl_3CHO} + Ca(OH)_2 \xrightarrow[\Delta]{} \underset{\text{Chloroform}}{2CHCl_3} + Ca(HCOO)_2$$

From acetone:

Chlorination: $$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

Hydrolysis: $$\underset{\text{Trichloroacetone}}{2CCl_3COCH_3} + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$

Procedure: 100 g of bleaching powder, 200 mL water and 25 mL of ethyl alcohol or acetone are mixed to obtain a paste. This mixture is taken in the 1 litre round bottom flask. The flask is heated gently on a water bath until a mixture of chloroform and water distils over. The mixture from the receiver is transferred into a separating funnel and lower layer of chloroform is separated.

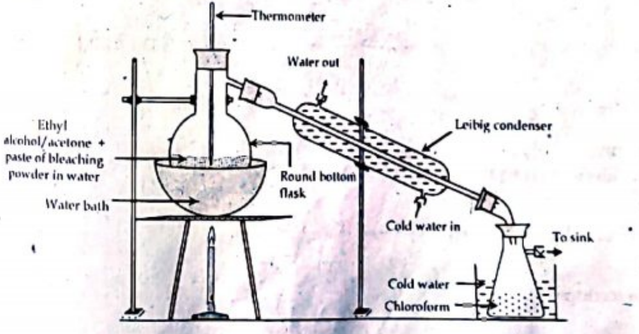


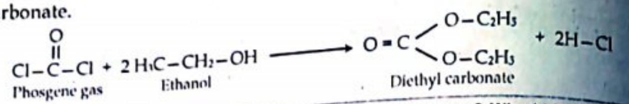
Figure: Laboratory preparation of chloroform

Purification: The impure chloroform is washed with dilute NaOH and water in separating funnel and it is dried over anhydrous $CaCl_2$ to absorb moisture. The distillate which is obtained at 61°C is pure chloroform.

When Chloroform ($CHCl_3$) is left exposed to air and light, it slowly gets oxidized to phosgene gas or carbonyl chloride ($COCl_2$) which is a poisonous gas.

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \longrightarrow \underset{\text{Carbonyl chloride}}{2COCl_2} + 2HCl$$

Chloroform ($CHCl_3$) is used for anesthetic purpose in surgery. Hence, anesthetic chloroform ($CHCl_3$) is kept in brown bottle to cut off light and the bottle is filled completely with chloroform to exclude air. A 1% solution of ethyl alcohol is also added to it to retard oxidation of chloroform. Ethanol converts phosgene to non-poisonous diethyl carbonate.



29. **2076 Set C Q.No. 28 How is trichloromethane prepared in the laboratory? Why is it discouraged to use chloroform as an anesthesia?** **[5]**

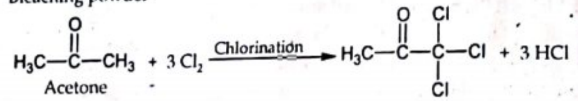
➢ **Laboratory preparation of trichloromethane:** Please refer to 2076 Set B Q.No. 28

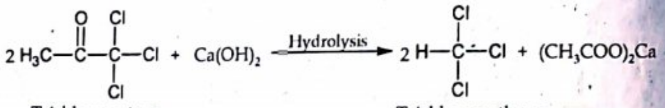
The anesthetic use of chloroform has been discouraged because it caused deaths due to respiratory failure and cardiac arrhythmias. Chloroform has induced liver tumors in mice and kidney tumors in mice and rats. The hepatotoxiciy and nephrotoxicity of chloroform is thought to be due to the formation of phosgene gas.

30. **2075 Set B Q.No. 27 Write down the chemical reaction for the preparation of trichloromethane from acetone. How would you convert trichloromethane into**
i. chloretone ii. methane iii. formic acid. **[2+1+1+1]**

➢ Trichloromethane is prepared by heating a paste of acetone, bleaching powder and water. Bleaching powder acts as oxidizing agent, chlorinating agent and hydrolyzing agent.

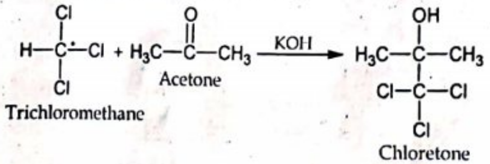
$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$



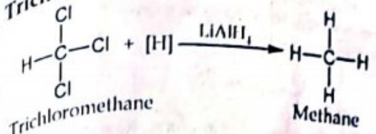


Conversion:

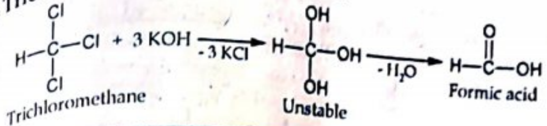
i. Trichloromethane into chloretone:



ii. Trichloromethane into methane:



iii. Trichloromethane into formic acid:



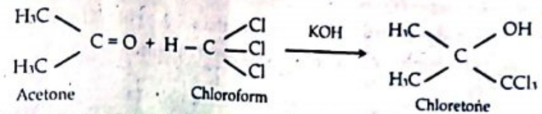
31. **2074 Supp. Q.No. 27 How is trichloromethane prepared in the laboratory from propanone? What product would you expect when trichloromethane is condensed with acetone? Give IUPAC name of the product.** **[4+1]**

➢ **Laboratory preparation of trichloromethane from propanone:**

Please refer to 2076 Set B Q.No. 28

Reaction of trichloromethane with acetone:

When chloroform is condensed with acetone i.e. propanone in the presence of a base KOH, chloretone.



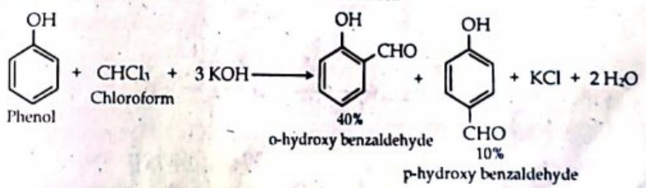
The IUPAC name of product is 1,1,1-trichloro-2-methylpropan-2-ol

32. **2073 Supp Q.No. 28 Write chemical reactions for the preparation of trichloromethane from propanone. How does trichloromethane react with**
i. Phenol ii. Silver powder iii. Conc. nitric acid **[2+1+1+1]**

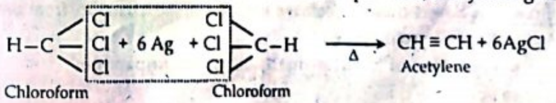
➢ Chemical reactions for the preparation of trichloromethane from propanone: Please refer to 2075 Set B Q.No. 27

Trichloromethane reacts with:

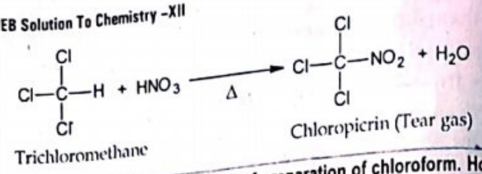
i. Phenol: When phenol is heated with chloroform in the presence of aqueous KOH at 70°C, a mixture of o-hydroxy benzaldehyde and p-hydroxy benzaldehyde is obtained. This reaction is known as Reimer-Tiemann reaction.



ii. Silver powder: When chloroform is heated with silver powder, acetylene gas is formed.



iii. Conc. Nitric acid: Trichloromethane is heated with Conc. HNO_3, chloropicrin is formed which is used as an insecticide and tear gas.

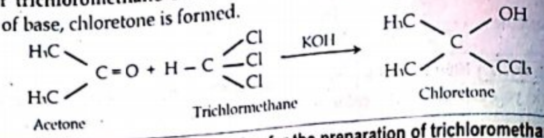


$$\underset{\text{Trichloromethane}}{CHCl_3} + HNO_3 \xrightarrow[\Delta]{} \underset{\text{Chloropicrin (Tear gas)}}{CCl_3NO_2} + H_2O$$

33. **2072 Set C Q.No. 27** **Describe laboratory method of preparation of chloroform. How does chloroform react with acetone?** **[4+1]**

Laboratory preparation of chloroform: Please refer to **2076 Set B Q.No. 28**

Action of trichloromethane on acetone: Trichloromethane reacts with acetone in the presence of base, chloretone is formed.



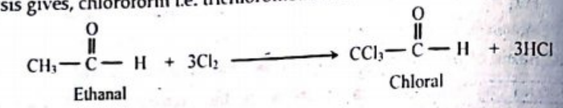
$$\underset{\text{Acetone}}{(CH_3)_2C=O} + \underset{\text{Trichlormethane}}{H-CCl_3} \xrightarrow{KOH} \underset{\text{Chloretone}}{(CH_3)_2C(OH)CCl_3}$$

34. **2072 Set D Q.No. 27** **Give the chemical reaction for the preparation of trichloromethane from ethanal. What happens when it is heated with silver powder? Identify the product Ⓐ and write its IUPAC name.** **[2+1+2]**

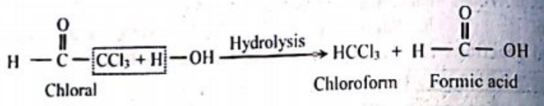
$$CHCl_3 \xrightarrow[\text{alkali}]{\text{acetone}} Ⓐ$$

Preparation of Trichloromethane from Ethanal

When ethanal is treated with chlorine, trichloroethanel i.e. chloral is obtained. Chloral on hydrolysis gives, chloroform i.e. trichloromethane is obtained.



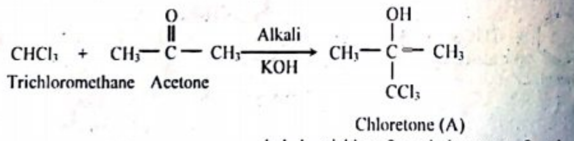
$$\underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3-\overset{O}{\overset{\|}{C}}-H} + 3HCl$$



$$\underset{\text{Chloral}}{H-\overset{O}{\overset{\|}{C}}-\boxed{CCl_3 + H}-OH} \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{HCCl_3} + \underset{\text{Formic acid}}{H-\overset{O}{\overset{\|}{C}}-OH}$$

When trichloromethane is heated with silver powder, ethyne i.e. acetylene gas is obtained.

$$\underset{\text{Chloroform}}{2\,CHCl_3 + 6\,Ag} \xrightarrow[\Delta]{} \underset{\text{Acetylene}}{H-C\equiv C-H} + 6\,AgCl$$



$$\underset{\text{Trichloromethane}}{CHCl_3} + \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[KOH]{\text{Alkali}} CH_3-\overset{OH}{\overset{|}{\underset{CCl_3}{\underset{|}{C}}}}-CH_3$$

Chloretone (A)

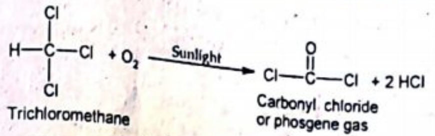
1, 1, 1 - trichloro-2-methyl propan - 2 - ol

35. **2072 Set E Q.No. 24** **How is trichloromethane prepared in the laboratory from propanone in pure and dry state? Write its action with oxygen.** **[4+1]**

Laboratory preparation of trichloromethane from propanone:

Please refer to **2075 Set B Q.No. 28**

Action of trichloromethane with oxygen: Trichloromethane reacts with oxygen in the presence of sunlight, carbonyl chloride is obtained which is commonly called phosgene gas. Phosgene gas is highly poisonous which attacks to the central nervous system and may cause death.



$$\underset{\text{Trichloromethane}}{H-CCl_3} + O_2 \xrightarrow{\text{Sunlight}} \underset{\text{Carbonyl chloride or phosgene gas}}{Cl-\overset{O}{\overset{\|}{C}}-Cl} + 2\,HCl$$

36. **2071 Supp. Q.No. 27** **How would you obtain** **[1+1+1+1+1+1]**

i. **ethane from bromoethane** ii. **ethylene from trichloromethane**

Identify the major product (A) and (B) in the following reaction sequence.

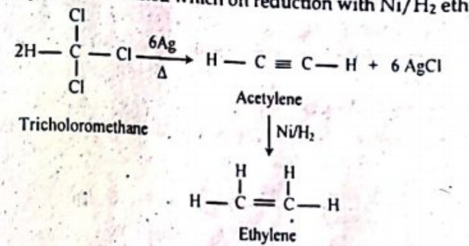
$$C_2H_5Br \xrightarrow[\Delta]{\text{Mg/ether}} (A) \xrightarrow{H_2O/H^+} (B)$$

Give reactions to convert (A) into ethanoic acid. Write down suitable chemical reaction for the preparation

i. **Preparation of ethane from bromoethane:** When bromoethane on reduction with Zn -Cu in the presence of methanol, ethane is obtained.

$$\underset{\text{Bromoethane}}{CH_3-CH_2-Br} + 2\,[H] \xrightarrow[CH_3-OH]{Zn-Cu} \underset{\text{Ethane}}{CH_3-CH_3} + H-Br$$

ii. **Preparation of ethylene from trichloromethane:** When trichloromethane is heated with silver powder acetylene is obtained which on reduction with Ni/H₂ ethylene is obtained.



$$\underset{\text{Tricholoromethane}}{2H-CCl_3} \xrightarrow[\Delta]{6Ag} \underset{\text{Acetylene}}{H-C\equiv C-H} + 6\,AgCl$$

$$\underset{\text{Acetylene}}{H-C\equiv C-H} \xrightarrow{Ni/H_2} \underset{\text{Ethylene}}{H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H}$$

The reaction sequence is

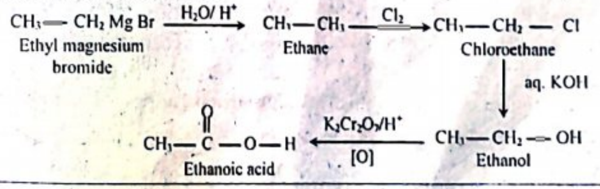
$$\underset{\text{Bromoethane}}{CH_3-CH_2-Br} \xrightarrow[\Delta]{\text{Mg/ether}} \underset{\text{Ethyl magnesium bromide (A)}}{CH_3-CH_2MgBr} \xrightarrow{H_2O/H^+} Mg(OH)Br + \underset{\text{Ethane (B)}}{CH_3-CH_3}$$

The compounds are

A = Ethyl magnesium bromide

B = Ethane

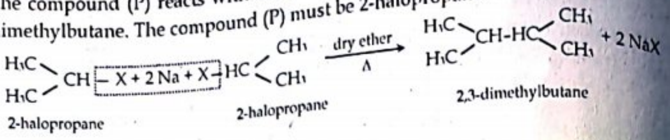
Conversion A to Ethanoic acid:



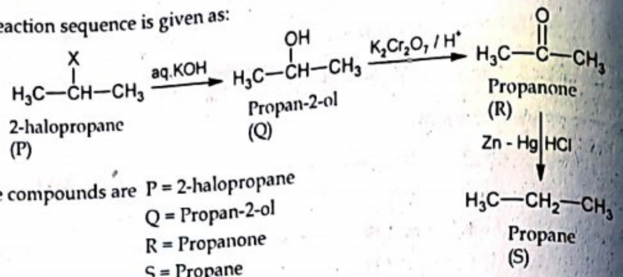
$$\underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2MgBr} \xrightarrow{H_2O/H^+} \underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow{Cl_2} \underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow{\text{aq. KOH}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-O-H}$$

37. **2071 Set C Q.No. 27** **A haloalkane Ⓟ reacts with aq. KOH to give Q. The compound Ⓠ on oxidation with $K_2Cr_2O_7 + H^+$ gives Ⓡ and Ⓡ undergoes Clemmensen reduction to produce Ⓢ. The compound Ⓟ react with sodium in presence of dry ether to form 2, 3- dimethylbutane, write chemical reactions involved and identify P, Q, R and S.**

The compound (P) reacts with sodium metal in the presence of dry ether to form 2,3-dimethylbutane. The compound (P) must be 2-halopropane.



The reaction sequence is given as:



The compounds are P = 2-halopropane
Q = Propan-2-ol
R = Propanone
S = Propane

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38. **2071 Set D Q.No. 27 How would you obtain:** **[5]**

a. **Ethane from bromoethane**
b. **Ethyne from trichloromethane**

Identify the major product Ⓐ and Ⓑ in the following reaction sequence:

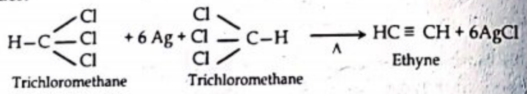
$$C_2H_5Br \xrightarrow[\Delta]{Mg/ether} Ⓐ \xrightarrow{H_2O/H^+} Ⓑ$$

Give reactions to convert Ⓐ into ethanoic acid.

a. **Ethane from bromoethane:** Ethane can be obtained by the reduction of bromoethane with Zn-Cu couple and ethyl alcohol.

$$\underset{\text{Bromoethane}}{H_3C—CH_2—Br} + 2[H] \xrightarrow[\text{Ethyl alcohol}]{\text{Zn - Cu couple}} \underset{\text{Ethane}}{H_3C—CH_3} + HBr$$

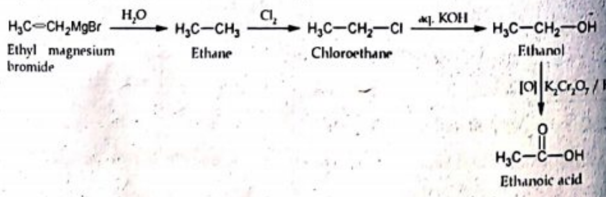
b. **Ethyne from trichloromethane:** Ethyne is prepared by heating trichloromethane with silver powder.



The reaction sequence is given as:

$$\underset{\text{Bromoethane}}{H_3C—CH_2—Br} \xrightarrow[\Delta]{Mg\ /\ Ether} \underset{\text{Ethyl magnesium bromide (A)}}{H_3C—CH_2—MgBr} \xrightarrow[\Delta]{H_2O\ /\ H^+} \underset{\text{Ethane (B)}}{H_3C—CH_3} + Mg(OH)Br$$

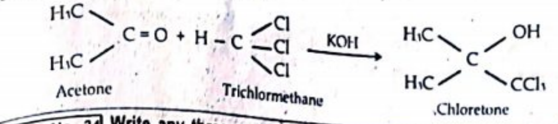
Conversion: Ethyl magnesium bromide (A) into ethanoic acid



39. **2070 Supp. Q.No. 26 How is trichloromethane prepared in the laboratory? Write its action on acetone.** **[5]**

Laboratory Preparation of Trichloromethane: Please refer to 2076 Set B Q No. 28

Action of trichloromethane on acetone: Trichloromethane reacts with acetone in the presence of base, chloretone is formed.



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40. **2070 Set D Q.No. 24 Write any three methods of preparation of Iodoethnae. What happens when Iodoethane is heated with** **[5]**

i. **Sodium in presence of dry ether**
ii. **alc. NaOH**

Three methods for the preparation of iodoethane:

a. **From ethene:** Ethene reacts with hydrogen iodide, iodoethane is formed.

$$\underset{\text{Ethene}}{H_2C═CH_2} + HI \longrightarrow \underset{\text{Iodoethane}}{H_3C—CH_2—I}$$

b. **From alcohol:** Ethanol is heated with iodine in the presence of red phosphorous, iodoethane is formed.

$$12\,\underset{\text{Ethanol}}{H_3C—CH_2—OH} + 6\,I_2 + P_4 \longrightarrow 12\,\underset{\text{Iodoethane}}{H_3C—CH_2—I} + 4\,H_3PO_3$$

c. **From ethane:** Ethane is heated with iodine in the presence of iodic acid, iodoethane is formed.

$$\underset{\text{Ethane}}{H_3C—CH_3} + I_2 \xrightarrow{HIO_3} \underset{\text{Iodoethane}}{H_3C—CH_2—I} + HI$$

i. When iodoethane is heated with sodium metal in the presence of dry ether, butane is formed.

$$\underset{\text{Iodoethane}}{H_3C—CH_2—}\boxed{I + 2\,Na + I}\underset{\text{Iodoethane}}{—CH_2—CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{H_3C—CH_2—CH_2—CH_3} + 2\,NaI$$

ii. When iodoethane reacts with alc. KOH, ethene is formed.

$$\underset{\text{Iodo ethane}}{H_3C—CH_2—I} \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{Ethene}}{H_2C═CH_2} + KI + H_2O$$

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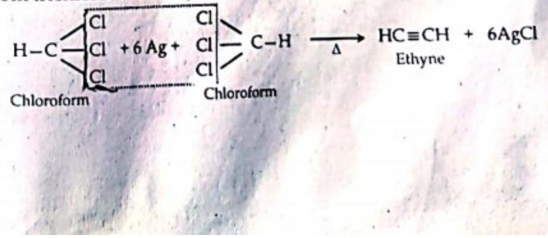
41. **2069 (Set B) Q.No. 23 Starting from trichoromethane, how would you prepare:** **[5]**

i. **Ethyne**
ii. **Methane**
iii. **Chloropicrin**
iv. **Carbonyl chloride**
v. **Chloretone**

Preparation of:

i. **Ethyne from trichloromethane (Chloroform):**

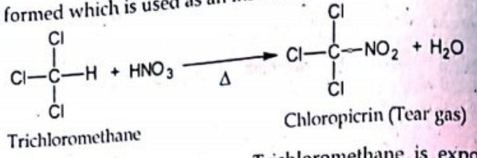


ii. Methane from trichloromethane: Trichloromethane is reduced with zinc dust and water, methane is formed.

$Zn + H_2O \longrightarrow ZnO + 2[H]$

$\underset{\text{Trichloromethane}}{CHCl_3} + 6[H] \longrightarrow \underset{\text{Methane}}{CH_4} + 3HCl$

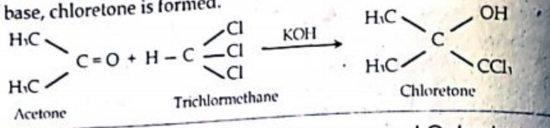
iii. Chloropicrin from trichloromethane: Trichloromethane is heated with Conc. HNO₃ chloropicrin is formed which is used as an insecticide and tear gas.



iv. Carbolyl chloride from trichloromethane: Trichloromethane is exposed in open air, carbonyl chloride is formed.

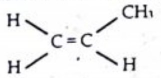
$\underset{\text{Trichloromethane}}{2CHCl_3} + O_2 \longrightarrow \underset{\text{Carbonyl chloride}}{2COCl_2} + 2HCl$

v. Chloretone from trichloromethane: Trichloromethane reacts with acetone in the presence of base, chloretone is formed.

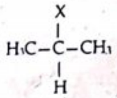


42. 2069 Supp. Set B Q.No. 23 **A secondary halolkane Ⓐ gives compound Ⓑ when heated with alc.KOH Ⓑ on ozonolysis produces ethanal and methanal as major products. Identify Ⓐ and Ⓑ; also write chemical reaction. What product would you expect when Ⓐ is heated with sodium in presence of dry ether?** [5]

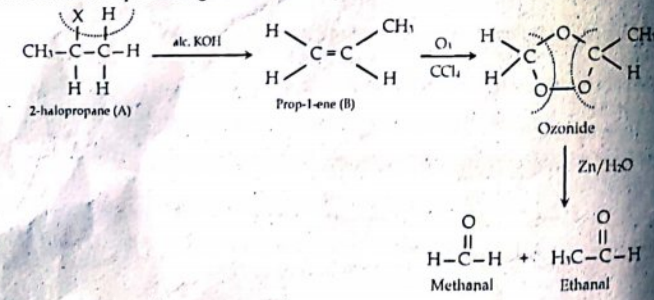
✍ The compound (B) undrgoes ozonolysis gives a mixture of ethanal and methanal. The compound (B) should have three carbons and having structure.



Secondary haloalkane (A) produce (B) when heated with alc. KOH. The compound (A) must have structure.

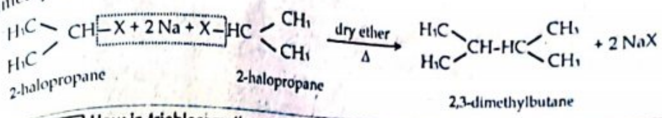


The reaction sequence is given as



Hence, the compounds are A = 2-halopropane
B = Prop-1-ene

When 2-halopropane is heated with sodium metal in the presence of dry ether, 2,3-dimethylbutane is formed.



43. 2068 Q.No. 22 **How is trichloromethane prepared in the laboratory? Give a chemical equation for the conversion of chloroform into ethyne.** [5]

✍ **Laboratory preparation of trichloromethane:** Please refer to 2076 Set B Q No. 28

Ethyne from trichloromethane: Please refer to 2069 (Set B) Q No. 23

44. 2066 Q. No. 22 (a) **Give the chemical reactions for the Laboratory Preparation of trichloromethane.** [2.5]

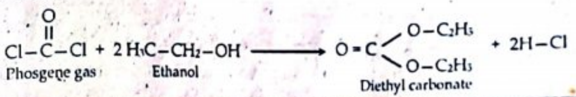
✍ Please refer to 2076 Set B Q.No. 28

45. 2066 Q. No. 22 (b) **Why is trichloromethane stored in dark-brown airtied bottle?** [2.5]

✍ When Chloroform ($CHCl_3$) is left exposed to air and light, it slowly gets oxidized to phosgene gas or carbonyl chloride ($COCl_2$) which is a poisonous gas.

$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \longrightarrow \underset{\text{Carbonyl chloride}}{2\,COCl_2} + 2HCl$

Chloroform ($CHCl_3$) is used for anesthetic purpose in surgery. Hence, anesthetic chloroform ($CHCl_3$) is kept in brown bottle to cut off light and the bottle is filled completely with chloroform to exclude air. A 1% solution of ethyl alcohol is also added to it to retard oxidation of chloroform. Ethanol converts phosgene to non-poisonous diethyl carbonate.

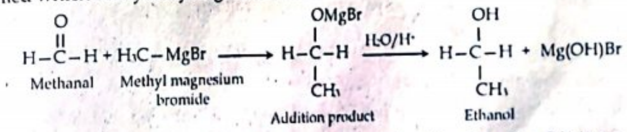


46. 2065 Q.No. 21 **Starting from Methyl magnesium bromide (CH_3MgBr) how would you prepare:** [5]

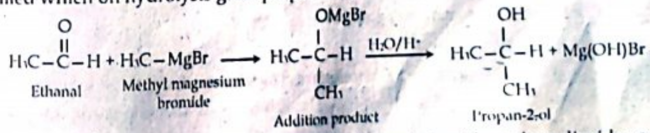
i. **Ethanol** ii. **Propan-2-ol** iii. **Ethanoic acid** iv. **2-methylpropan-2-ol**

✍

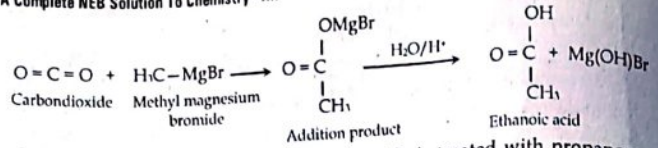
i. **Ethanol:** Methyl magnesium bromide is treated with methanal, addition product is formed which on hydrolysis gives ethanol.



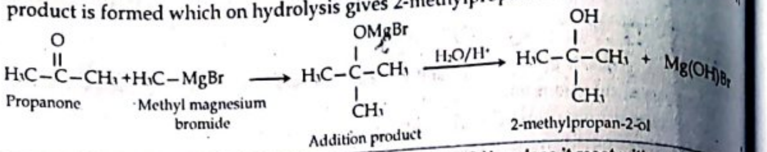
ii. **Propan-2-ol:** Methyl magnesium bromide is treated with ethanal, addition product is formed which on hydrolysis gives propan-2-ol.



iii. **Ethanoic acid:** Methyl magnesium bromide is treated with carbon dioxide, addition product is formed which on hydrolysis gives ethanoic acid.



iv. **2-methylpropan-2-ol:** Methyl magnesium bromide is treated with propanone, addition product is formed which on hydrolysis gives 2-methylpropan-2-ol.



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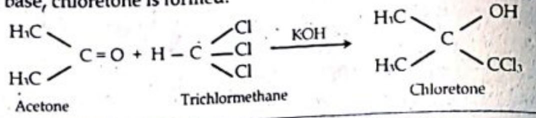
47. **2065 Q.No. 22** **How is trichloromethane prepared in laboratory? How does it react with propanone?** **[5]**

Laboratory preparation of chloroform: Please refer to 2076 Set B Q.No. 28

Reaction of trichloromethane with acetone: Trichloromethane reacts with acetone in the presence of base, chloretone is formed.



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48. **2064 Q.No. 31(ii)** **Write short notes on Laboratory preparation of chloroform.** **[5]**

Please refer to 2076 Set B Q.No. 28

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49. **2062 Q.No. 21** **Write the chemical reactions involved in the laboratory preparation of chloroform from ethanol. Why does chloroform not give white precipitate with aqueous $AgNO_3$? Write two important uses of chloroform.** **[5]**

Laboratory Preparation of chloroform: Please refer to 2076 Set B Q.No. 28

Chloroform does not give white precipitate with aqueous $AgNO_3$:

Chloroform is non-polar covalent compound and does not ionize in aqueous solution. So, it does not give the white ppt. with silver nitrate solution. Only polar compound like HCl or NaCl give the white ppt with silver nitrate. If chloroform is impure, it may contain HCl as impurity and gives the test of silver nitrate solution.

$$\underset{\text{Silver nitrate}}{AgNO_3} + HCl \longrightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + HNO_3$$

Uses of chloroform: Following are the uses of chloroform:

a. It is used as laboratory reagent.
b. It is used as preservative for biological specimens.
c. It is used as anesthetic in surgical operation.
d. It is used to prepare organic compound like chloropicrin, salicylic acid etc.

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50. **2055 Q.No. 27** **How is trichloromethane (chloroform) prepared in the laboratory?** **[5]**

Please refer to 2076 Set B Q.No. 28

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51. **2053 Q.No. 21** **Describe the laboratory preparation of chloroform.** **[5]**

Please refer to 2076 Set B Q.No. 28

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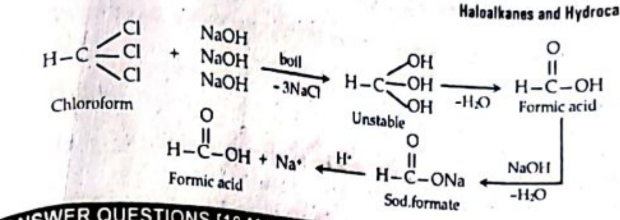
52. **2052 Q.No. 24(a)** **What happens when Chloroform is allowed to react with NaOH solution.** **[2.5]**

When chloroform is heated with aq.NaOH solution, sod. formate is obtained which on acidification yields formic acid.



LONG ANSWER QUESTIONS [10 MARKS]

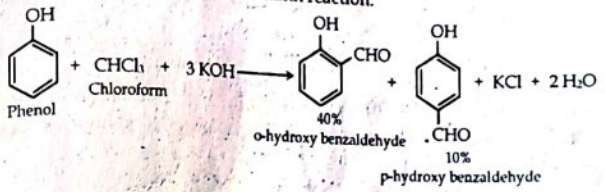
53. **2070 Set C Q.No. 31 b** **Give a suitable chemical reaction for the laboratory preparation of trichloromethane. What happen when chloromethane reacts with** **[10]**

i. **Phenol**
ii. **Nitric acid**
iii. **Silver powder**
iv. **Atmospheric air.**

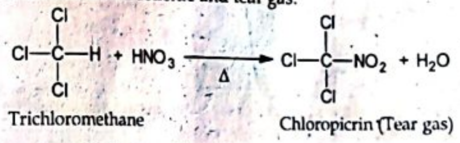
Laboratory preparation of trichloroform: Please refer to 2076 Set B Q.No. 28

Trichloromethane reacts with:

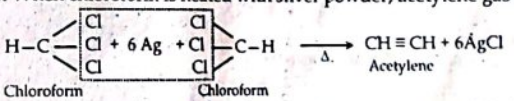
i. **Phenol:** When phenol is heated with chloroform in the presence of aqueous KOH at 70°C, a mixture of o-hydroxy benzaldehyde and p-hydroxy benzaldehyde is obtained. This reaction is known as Reimer-Tiemann reaction.



ii. **Nitric acid (Chloroform):** Trichloromethane is heated with Conc. HNO_3, chloropicrin is formed which is used as an insecticide and tear gas.



iii. **Silver powder:** When chloroform is heated with silver powder, acetylene gas is formed.



iv. **Atmospheric air:** When Chloroform ($CHCl_3$) is left exposed to air and light, it slowly gets oxidized to phosgene gas or carbonyl chloride ($COCl_2$) which is a poisonous gas.

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \longrightarrow \underset{\text{Carbonyl chloride}}{2\,COCl_2} + 2HCl$$

Chloroform ($CHCl_3$) is used for anesthetic purpose in surgery. Hence, anesthetic chloroform ($CHCl_3$) is kept in brown bottle to cut off light and the bottle is filled completely with chloroform to exclude air. A 1% solution of ethyl alcohol is also added to it to retard oxidation of chloroform. Ethanol converts phosgene to non-poisonous diethyl carbonate.

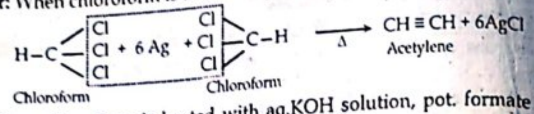
54. **2063 Q.No. 28** **Describe the preparation of pure and dry chloroform in the laboratory. Give its action upon:** **[10]**

a. Heated silver
b. Aqueous KOH
c. Aniline in presence of alc. KOH.

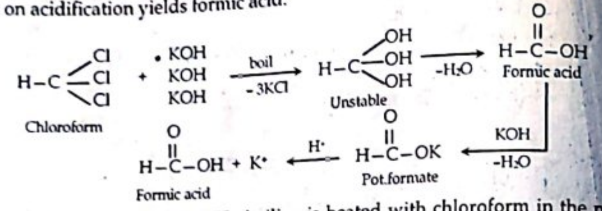
Laboratory preparation of chloroform: Please refer to 2076 Set B Q.No. 28

Action of chloroform on:

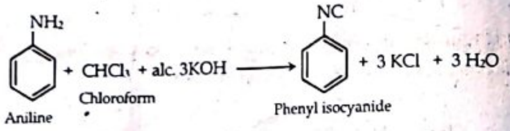
a. **Heated silver:** When chloroform is heated with silver powder, acetylene gas is formed.



b. **Aq. KOH:** When chloroform is heated with aq.KOH solution, pot. formate is obtained which on acidification yields formic acid.



c. **Aniline in presence of alc. KOH:** Aniline is heated with chloroform in the presence of alc. KOH, phenyl isocyanide is obtained. This reaction is known as Carbyl amine reaction.



Uses of chloroform: Please refer to 2062 Q.No. 21

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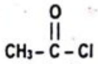
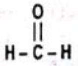
55. **2061 Q.No. 28** **How is Grignard reagent prepared? What precautions should be taken for preparation of Grignard reagents? How does CH_3CH_2MgBr react with** **[10]**

a.

$CH_3-\overset{\overset{O}{\|}}{C}-Cl$
b. H_2O
c.

$H-\overset{\overset{O}{\|}}{C}-H$
d. CO_2

Show the final product after aqueous work-up.

Grignard's reagent: Haloalkane i.e. alkyl halide is heated with magnesium metal in the presence of dry ether, alkyl magnesium halide is obtained. Alkyl magnesium halide is called Grignard's reagent.

$$\underset{\text{Ethyl halide}}{CH_3-CH_2-X} + Mg \xrightarrow{\text{dry ether}} \underset{\substack{\text{Ethyl magnesium halide}\\ \text{Grignard's reagent}}}{CH_3-CH_2-MgX}$$

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} + Mg \xrightarrow{\text{dry ether}} \underset{\text{Ethyl magnesium chloride}}{CH_3-CH_2-MgCl}$$

Precautions:

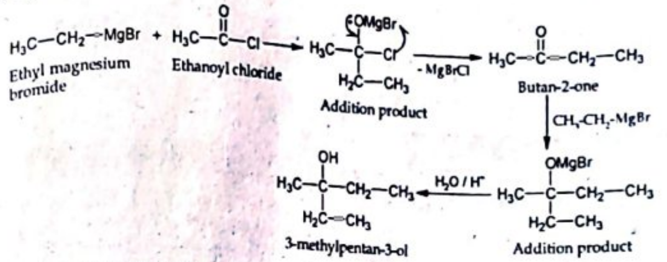
i. Grignard's reagent is more sensitive to water molecules. So, no any water molecules come in contact with Grignard's reagent during preparation. It reacts with water molecule to form alkane.

$$\underset{\text{Methyl magnesium bromide}}{CH_3-MgBr} + H_2O \longrightarrow \underset{\text{Methane}}{CH_4} + Mg(OH)Br$$

ii. There should be no naked flame near the apparatus, because ether is highly inflammable.

Reaction of CH_3-CH_2-MgBr with:

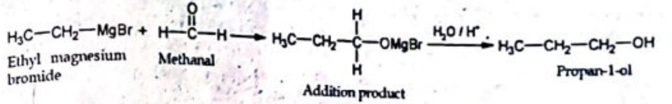
a. CH_3COCl: Ethyl magnesium bromide (CH_3CH_2MgBr) reacts with ethanoyl chloride (CH_3COCl), Butan-2-one is formed which further reacts with Grignard reagent to form 3-methylpentan-3-ol.



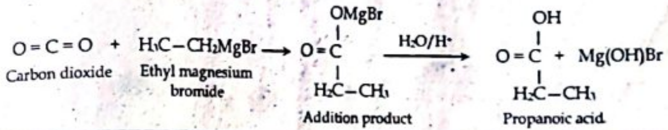
b. H_2O: Ethyl magnesium bromide reacts with water, ethane is formed.

$$\underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2-MgBr} + H_2O \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + Mg(OH)Br$$

c. HCHO: Ethyl magnesium bromide reacts with methanal, addition product is formed which on hydrolysis gives propan 1-ol.



d. CO_2: Ethyl magnesium bromide reacts with carbon dioxide, addition product is formed which on hydrolysis gives propanoic acid.



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56. **2053 Q.No. 27** **An organic compound A on catalytic reduction gives B, B on chlorination gives C, C on heating with sodium metal in presence of ether gives D, D on chlorination gives 2-chlorobutane as a major product. Give names for A, B, C and D.** **[5]**

The compound D on chlorination gives 2-chlorobutane as major product. The compound D must be butane.

$$\underset{\text{Butane (D)}}{CH_3-CH_2-CH_2-CH_3}$$

The compound D is obtained by heating C with sodium metal in presence of dry ether. The compound C must be chloroethane.

$$\underset{\text{Chloroethane (C)}}{CH_3-CH_2-Cl}$$

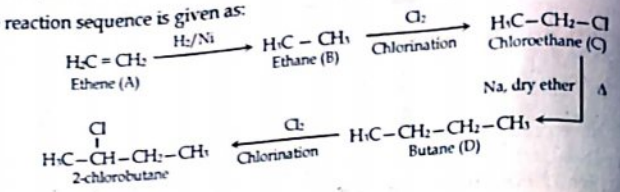
The compound C is obtained on chlorination of B. The compound B must be ethane.

$$\underset{\text{Ethane (B)}}{CH_3-CH_3}$$

The compound B is obtained by catalytic reduction of A. The compound A must be ethene.

$$\underset{\text{Ethene (A)}}{CH_2=CH_2}$$

The reaction sequence is given as:



The compounds are

A = Ethene B = Ethane

C = Chloroethane D = Butane

WRITE SHORT NOTES [5 MARKS]

57. 2072 Supp. Q.No. 33ii 2071 Supp. Q.No. 33b 2071 Set D Q.No. 33 b 2069 Supp. Set B Q.No. 33
Laboratory preparation of trichloromethane. [5]

Please refer to 2076 Set B Q No 28

58. 2071 Set C Q.No. 33 b Laboratory preparation of chloroform

Please refer to 2076 Set B Q No 28

59. 2053 Q.No. 28(c) 2055 Q.31(d) 2056 31(c) 2056 Q.31 (d) 2057 Q.31 (d) 2058 Q.31 (d)

a. Markovnikov's rule
b. Inductive effect
c. Inductive effect
d. Laboratory preparation of Chloroform [5]
e. Laboratory preparation of chloroform

a. **Markovnikov's rule:** When unsymmetrical alkene is treated with unsymmetrical reagent then positive part of unsymmetrical reagent goes to that double bonded carbon of alkene that have more hydrogen atom and negative part of unsymmetrical reagent goes to that carbon atom that have less number of hydrogen atom.

$$\underset{\text{1-propene}}{CH_3\text{-}CH=CH_2} + HBr \longrightarrow \underset{\text{2-bromopropane}}{CH_3-CHBr-CH_3}$$

Mechanism:

It completes in two steps.

Step- I Formation of carbocation

$$\underset{\text{1-propene}}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{\text{Carbocation}}{CH_3-C^{+}H-CH_3} + Br^{-}$$

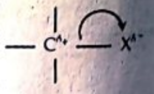
Step-II Addition of halide ion on carbocation

$$\underset{\text{Carbocation}}{CH_3-C^{+}H-CH_3} \xrightarrow{Br^{-}} \underset{\text{2-bromopropane}}{CH_3-CHBr-CH_3}$$

Anti-Markovnikov's rule or Peroxide effect or Kharash effect: In the presence of organic peroxide such as alkyl peroxide (R-O-O-R) or benzoyl peroxide ($C_6H_5CO\text{-}O\text{-}O\text{-}COC_6H_5$) unsymmetrical reagent adds to the unsymmetrical alkene in opposite of Markovnikov's rule.

$$\underset{\text{1-propene}}{CH_3-CH=CH_2} + HBr \xrightarrow{\text{Proxide}} \underset{\text{1-bromopropane}}{CH_3-CH_2-CH_2-Br}$$

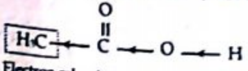
b. **Inductive effect:** The electron cloud in a sigma bond (σ) between two unlike atoms in not uniform. It is more dense towards the more electronegative of the two atoms i.e. the electron pair forming the sigma bond is slightly displaced towards X. This permanent state of polarization is called the inductive effect. It is represented by arrow (→). The atom X thus acquires a slight negative charge (δ^-) and the carbon atom acquires a slight positive charge (δ^+) i.e. the bond is polarized. If the electronegative atom is joined to a chain of carbon atoms, the positive charge on the carbon atom is related to the other carbon atoms.



$$C_4^{\delta+} \rightarrow\!\!\rightarrow\!\!\rightarrow C_3^{\delta+} \rightarrow\!\!\rightarrow C_2^{\delta+} \rightarrow\!\!\rightarrow C_1^{\delta+} \rightarrow\!\!\rightarrow X$$

Depending upon the nature of groups attached to the carbon chain, there are two types of inductive effect.

i. **Positive inductive effect or + I effect :** If the group attached to carbon atom in the carbon chain is less electronegative than carbon, the carbon atom gets partial negative charge and group gets partial positive charge because the bonding electrons are displaced towards carbon atom. Such inductive effect is known as positive inductive effect. Examples: $-CH_3$, $-COO^-$, $-CH_2R$, $-CR_3$ etc.



$$\boxed{H_3C} \leftarrow \overset{\overset{\large O}{\|}}{C} \leftarrow O \leftarrow H$$

Electron releasing group

ii. **Negative inductive effect or + I effect:** If the groups attached to carbon atom in carbon chain are more electronegative, the bonding pairs are mostly displaced towards more electronegative atom. Carbon atom acquires a partial positive charge and other atom acquires partial negative charge. Such inductive effect is called as negative inductive or – I effect. Examples: $-NO_2$, $-CN$, $-COOH$, $-F$, $-Cl$, $-I$, $-OR$, $-OH$ etc.

$$CH_3 \longrightarrow CH_2 \rightarrow\!\!\rightarrow CH_2 \rightarrow\!\!\rightarrow\!\!\rightarrow \boxed{Cl}$$ Electron withdrawing group

c. **Inductive effect:** Please refer to 2053 Q.No. 28

d. **Laboratory preparation of chloroform:** Please refer to 2076 Set B Q No 28

e. **Laboratory preparation of chloroform:** Please refer to 2076 Set B Q No 28

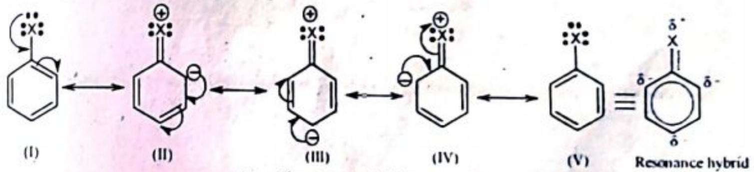
9.2 Haloarenes

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2076 Set B Q.No. 9 **Why is haloarene less reactive than benzene in electrophilic substitution reaction?** [2]

In haloarene, halo group is a weak ring deactivating group. This means haloarene is less reactive towards electrophiles than benzene. Due to the presence of non-bonding electron, halo group can donate electron density through the formation of π bond.

Resonance structure of haloarene



Resonating structures of haloarene

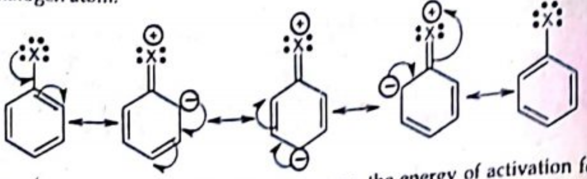
2. 2076 Set C Q.No. 9 **Explain, why is chlorobenzene less reactive than benzene in electrophilic substitution reaction?** [2]

Please refer to 2076 Set B Q.No.9

3. 2075 GIE Q.No. 9 2075 Set A Q.No. 9 **Why is haloarene less reactive towards nucleophilic substitution reaction than haloalkane?** [2]

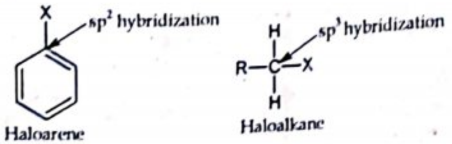
Haloarene is less reactive towards nucleophilic substitution reaction than haloalkane due to following reason:

i. **Resonance effect:** In haloarene, the lone pair of electron on halogen atom is delocalized on the benzene ring. Due to this partial double bond is developed between carbon and halogen atom.



Since haloarene is stabilized by resonance, the energy of activation for displacement of halogen from haloarene is much greater than haloalkane. Thus it does not undergo nucleophilic substitution reaction.

ii. **Difference of hybridization of carbon atom in C−X bond:**

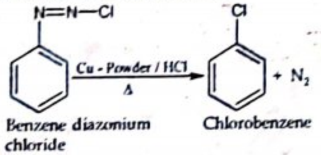


In haloarene the carbon atom to which the X-group is attached is sp^2 hybridized. Thus it is difficult to replace by nucleophile.

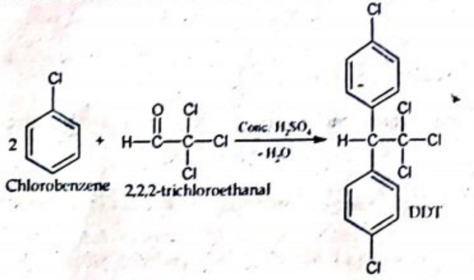
iii. **Electronic repulsion:** Since haloarene is electron rich molecule due to the presence of π-bond. It repels nucleophile attacking.

4. **2075 Set B Q.No. 9 What products would you expect when** **[1+1]**
   i. **Benzene diazonium chloride is heated with copper powder in presence of HCl.**
   ii. **Chlorobenzene is heated with 2,2,2-trichloroethanal.**

i. When benzene diazonium chloride is heated with copper powder in presence of HCl, chlorobenzene is obtained.

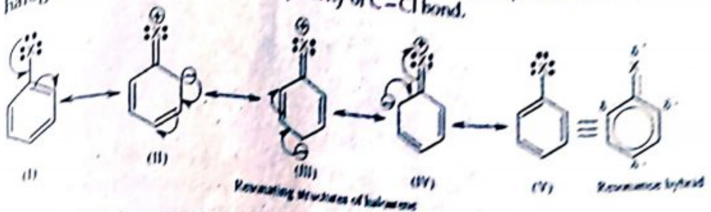


ii. When chlorobenzene is heated with 2,2,2-trichloroethanal, DDT is obtained.



5. **2072 Set E Q.No. 9 Why is nucleophilic substitution difficult in haloarenes?** **[2]**

In haloarene, the carbon attached with halogen is sp^2 hybridization and stabilized by resonance. Due to the resonance a double bond is developed between carbon and halogen atoms and having lesser polarity of C−Cl bond.

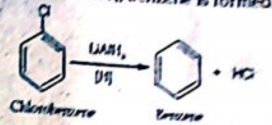


Resonating structures of haloarene

In case of haloarene, there is no resonance and no double bond is developed between carbon and halogen atom. Therefore, haloarene does not easily undergo nucleophilic substitution as compared to haloalkane.

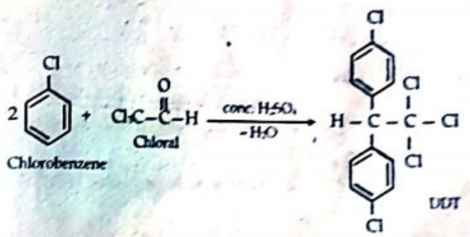
6. **2069 (Set A) Q.No. 8 (ii) How would you obtain benzene from chlorobenzene?**

Chlorobenzene on reduction with $LiAlH_4$, benzene is formed.

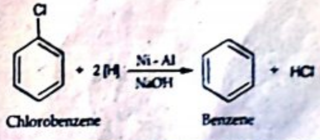


7. **2069 (Set B) Q.No. 9 What happens when chlorobenzene is**
   i. **treated with chloral in acidic medium.**
   ii. **heated with Ni-Al in alkaline medium.**

i. Chlorobenzene can be converted into DDT by reacting with chloral in the presence of conc. H_2SO_4.

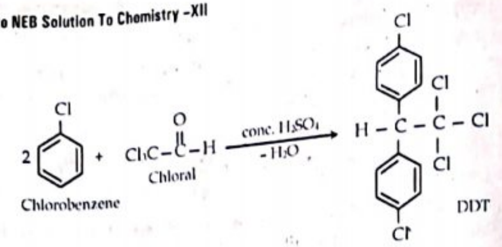


ii. Chlorobenzene on reduction with Ni-Al in the presence of alkaline medium, benzene is formed.

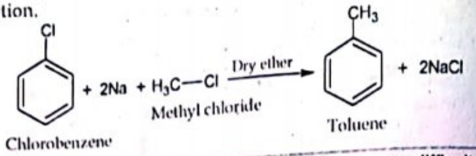


8. **2067 Q.No. 2 How would you convert chlorobenzene into:**
   i. **DDT** ii. **Toluene**

i. Chlorobenzene to DDT: Chlorobenzene can be converted into DDT by reacting with chloral in the presence of conc. H_2SO_4.



ii. **Chlorobenzene into Toluene:** When chlorobenzene and methyl chloride is heated with sodium metal in the presence of dry ether, toluene is formed. This reaction is known as Wurtz-Fittig reaction.

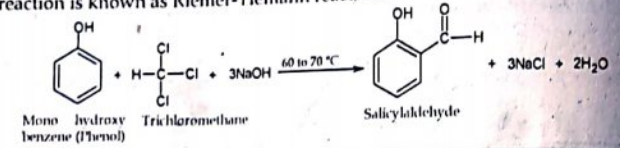


9. **2064 Q.No. 2 Why is nucleophilic substitution reaction in chlorobenzene difficult as compared to chloroethane?**

➣ Please refer to 2072 Set E Q.No 9

10. **2063 Q.No. 3(ii) Write the action of Monohydroxy benzene with trichloromethane in presence of aqueous NaOH.**

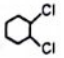
➣ When monohydroxy benzene i.e. phenol is heated with trichloromethane i.e. chloroform in the presence of aq. NaOH, ortho hyroxy benzaldehyde i.e. salicylaldehyde is formed. This reaction is known as Riemer-Tiemann reaction.



11. **2059 Q.No. 2 Why is it difficult to undergo nucleophilic substitution in haloarene?**

➣ Please refer to 2072 Set E Q.No. 9

12. **2056 Q.No. 18a Write the name of the following components according to the IUPAC rule.** [1]



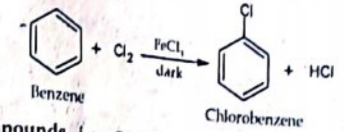
➣ IUPAC name = 1, 2- dichlorocyclohexane

SHORT ANSWER QUESTIONS [5 MARKS]

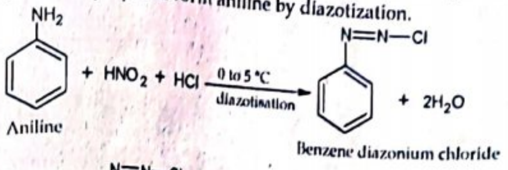
13. **2069 Set A Q.No. 27 Write any two methods of preparation of chlorobenzene. How does it react with?**
    a. **Chloral and**
    b. **Methyl chloride in the presence of dry ether.**

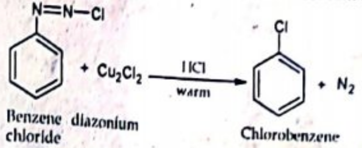
➣ Two method of preparation of chlorobenzene:

1. **By direct halogenations:** When benzene is treated with chlorine in the presence of Lewis acid like $FeCl_3$,$AlCl_3$ etc, chlorobenzene is obtained. This reaction is known as halogenations.

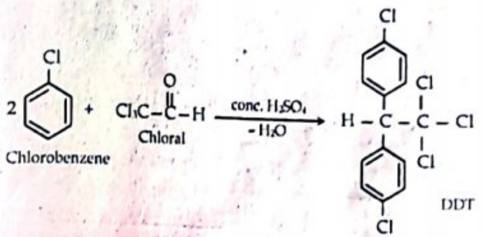


2. **From diazonium compounds i.e. Sandmeyer reaction:** When benzene diazonium chloride is warmed with cuprous chloride in the presence of halogen acids, chlorobenzene is obtained. This reaction is known as Sandmeyer reaction. Benzene diazonium chloride is prepared form aniline by diazotization.

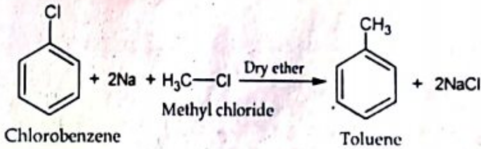




a. **Reaction of chlorobenzene with chloral:** Chlorobenzene can be converted into DDT by reacting with chloral in the presence of conc. H_2SO_4.



b. **Reaction of chlorobenzene with methyl chloride:** Chlorobenzene reacts with methyl chloride in the presence of dry ether, toluene is formed. This reaction is called Wurtz-Fittig reaction.

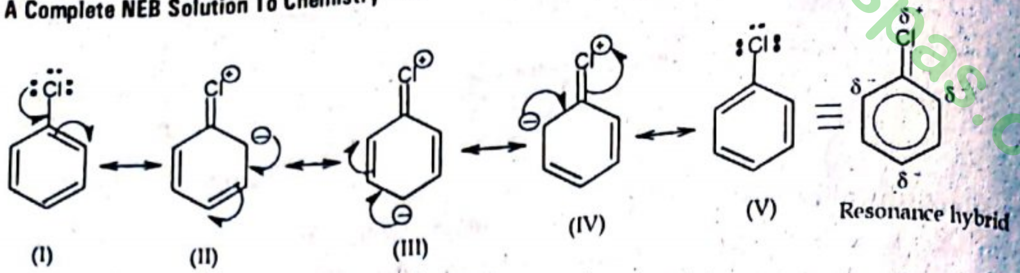


14. **2060 Q.No. 23 Write two chemical reactions for the preparation of chlorobenzene. Why does it give ortho and para products during electrophilic substitution reaction? Give its action on chloral.**

➣ Two method of preparation of chlorobenzene: Please refer to 2069 Set A Q.No. 27

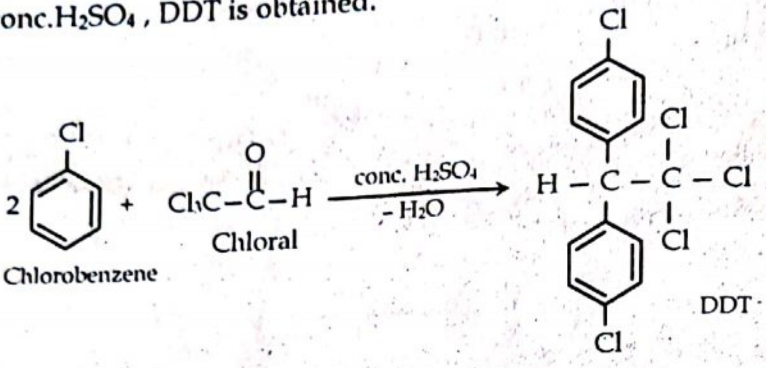
Ortho and para director in the electrophilic substitution:

In the resonance of chlorobenzene, negative charge is developed on the ortho and para position. So, the electrophile is attracted towards the negative charge and chlorobenzene is ortho and para director in electrophilic substitution.



Resonance of chlorobenzene

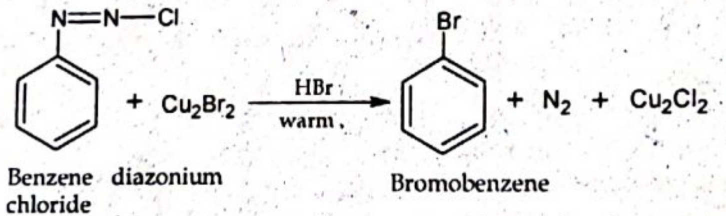
Action of chlorobenzene on chloral: When chlorobenzene is heated with chloral in the presence of conc.H_2SO_4, DDT is obtained.



LONG ANSWER QUESTIONS [10 MARKS]

15. 2059 Q.No. 29 b(a) **Predict the major products of the following reactions:**

$ArN_2Cl \xrightarrow[\Delta]{Cu_2Br_2 / HBr} ....$



□□□

Unit 10

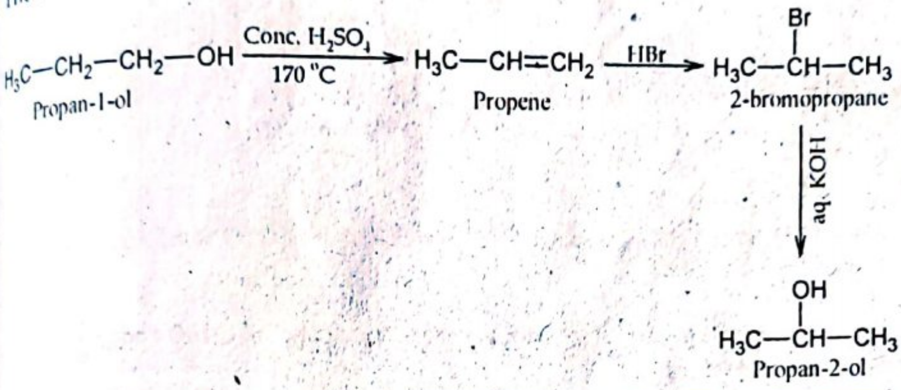
Alcohols and Phenols

0.1 Alcohols

ERY SHORT ANSWER QUESTIONS [2 MARKS]

2075 GIE Q.No. 10 Give reactions for the conversion of propan-1-ol into propan-2-ol. **[2]**

The conversion is



2075 Set A Q.No. 10 Give reactions for the conversion of cane sugar into ethyl alcohol. **[2]**

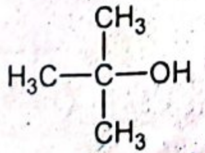
Cane sugar is converted into ethyl alcohol by using enzyme invertase and zymase.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH} + 2\,CO_2$$

2075 Set B Q.No. 10 Write a structural formula of 3° alcohol of $C_4H_{10}O$. How is this alcohol prepared by using Grignard reagent. **[1+1]**

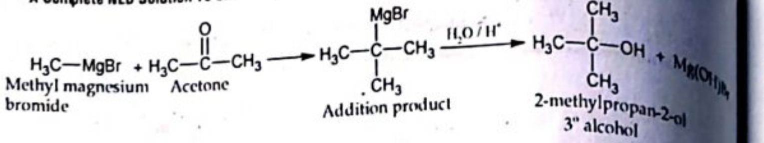
The structural formula of 3° alcohol of $C_4H_{10}O$ is



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$

2-methylpropan-2-ol
3° alcohol

When methyl magnesium bromide (CH_3MgBr) is treated with acetone, addition product is obtained which on hydrolysis in the presence of acid to give 2-methylpropan-2-ol.



$$\underset{\text{Methyl magnesium bromide}}{H_3C-MgBr} + \underset{\text{Acetone}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} \longrightarrow \underset{\text{Addition product}}{H_3C-\overset{MgBr}{\underset{CH_3}{C}}-CH_3} \xrightarrow{H_2O/H^+} \underset{\text{2-methylpropan-2-ol, 3° alcohol}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH} + Mg(OH)Br$$

4. **2074 Supp. Q.No. 10 Starting from cane sugar, how would you obtain ethyl alcohol?**

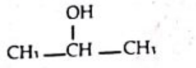
Cane sugar i.e. sucrose is converted into glucose and fructose with the help of enzyme invertase. Glucose is converted into ethyl alcohol with the help of enzyme zymase.

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

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH} + 2\,CO_2$$

5. **2072 Supp. Q.No. 10 What is the structure of isomeric alcohol of C_3H_8O that gives Iodoform tes Write the test reaction.** [1+1]

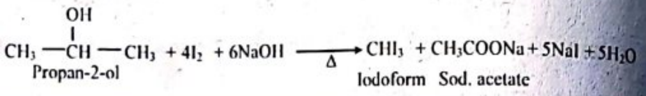
The secondary alcohol which gives iodoform test is



$$CH_3-\overset{OH}{CH}-CH_3$$

Propan -2 – ol (2° alcohol)

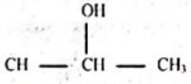
The chemical reaction is



$$\underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. acetate}}{CH_3COONa} + 5NaI + 5H_2O$$

6. **2072 Set C Q.No. 10 Write a structural formula of secondary alcohol of C_3H_8O and give its method of preparation using Grignard reagent.** [1+1]

The structural formula of secondary alcohol of C_3H_8O is

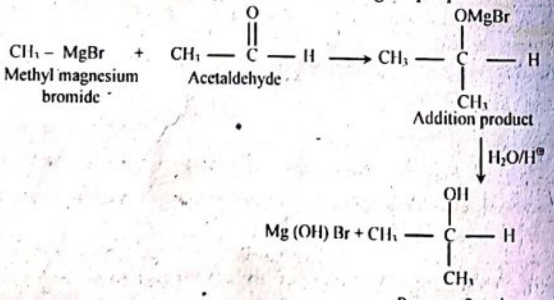


$$CH_3-\overset{OH}{CH}-CH_3$$

Propan – 2 – ol

Preparation of propan – 2 – ol by using Grignard reagent:

When methyl magnesium bromide is treated with acetaldehyde, addition product is formed which on hydrolysis in the presence of acid to give propan – 2 – ol

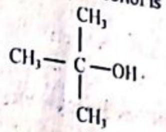


$$\underset{\text{Methyl magnesium bromide}}{CH_3-MgBr} + \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \longrightarrow \underset{\text{Addition product}}{CH_3-\overset{OMgBr}{\underset{CH_3}{C}}-H} \xrightarrow{H_2O/H^+} Mg(OH)Br + CH_3-\overset{OH}{\underset{CH_3}{C}}-H$$

Propan – 2 – ol

7. **2072 Set D Q.No. 10 Write down the structural formula and IUPAC name of tert-butyl alcohol.** [1+1]

The structure formula of tert-butyl alcohol is



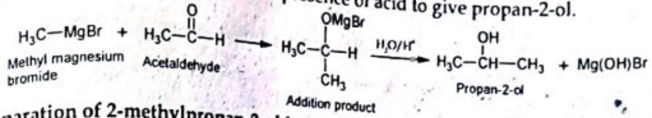
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

IUPAC name = 2-methylpropan -2 -ol

8. **2072 Set E Q.No. 10 Prepare butan -2-ol and 2-methylpropan -2-ol by using CH_3MgBr.** [1+1]

Preparation of butan-2-ol by using CH_3MgBr:

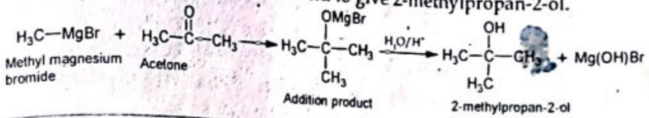
When methyl magnesium bromide is treated with acetaldedyde, addition product is obtained which on hydrolysis in the presence of acid to give propan-2-ol.



$$\underset{\text{Methyl magnesium bromide}}{H_3C-MgBr} + \underset{\text{Acetaldehyde}}{H_3C-\overset{\overset{O}{\|}}{C}-H} \longrightarrow \underset{\text{Addition product}}{H_3C-\overset{OMgBr}{\underset{CH_3}{C}}-H} \xrightarrow{H_2O/H^+} \underset{\text{Propan-2-ol}}{H_3C-\overset{OH}{CH}-CH_3} + Mg(OH)Br$$

Preparation of 2-methylpropan-2-ol by using CH_3MgBr:

When methyl magnesium bromide is treated with acetone, addition product is obtained which on hydrolysis in the presence of acid to give 2-methylpropan-2-ol.



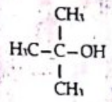
$$\underset{\text{Methyl magnesium bromide}}{H_3C-MgBr} + \underset{\text{Acetone}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} \longrightarrow \underset{\text{Addition product}}{H_3C-\overset{OMgBr}{\underset{CH_3}{C}}-CH_3} \xrightarrow{H_2O/H^+} \underset{\text{2-methylpropan-2-ol}}{H_3C-\overset{OH}{\underset{H_3C}{C}}-CH_3} + Mg(OH)Br$$

9. **2071 Supp. Q.No. 10 Name any suitable secondary alcohol that gives iodoform test and write the test reaction.** [1+1]

Please refer to 2072 Supp. Q.No. 10.

10. **2071 Set C Q.No. 10 Write structure of tertiary alcohol of $C_4H_{10}O$ and give its IUPAC name.** [2]

The structure of tertiary alcohol of molecular formula $C_4H_{10}O$ is

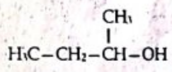


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

2-methylpropan-2-ol

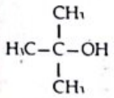
11. **2070 Supp. Q.No. 10 Write down the secondary and tertiary alcohol of $C_4H_{10}O$ and give their IUPAC name.** [2]

The structure of secondary and tertiary alcohol of molecular formula $C_4H_{10}O$ are



$$H_3C-CH_2-\overset{CH_3}{CH}-OH$$

Butan-2-ol

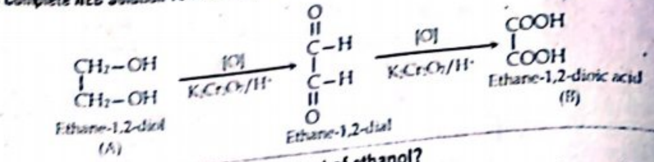


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

2-methylpropan-2-ol

12. **2070 Set C Q.No. 10 A dihydric alcohol $C_2H_6O_2$ Ⓐ undergoes step wise oxidation with $K_2Cr_2O_7/H^+$ to give a dicarboxylic acid $C_2H_2O_4$ Ⓑ as final product. Identify Ⓐ and Ⓑ with reactions and give their IUPAC name.** [2]

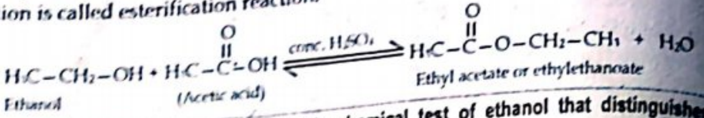
Dihydric alcohol (A) should be ethane-1,2-diol which undergoes stepwise oxidation with $K_2Cr_2O_7$ / H^+ to give dicarboxylic acid (B) and (B) should be oxalic acid i.e. ethane-1,2-dioic acid.



$$\underset{\substack{\text{Ethane-1,2-diol}\\ \text{(A)}}}{\begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array}} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Ethane-1,2-dial}}{\begin{array}{c}O\\ \|\\ C-H\\ |\\ C-H\\ \|\\ O\end{array}} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\substack{\text{Ethane-1,2-dioic acid}\\ \text{(B)}}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}}$$

13. **2070 Set D Q.No. 10 What is the laboratory test of ethanol?** [2]

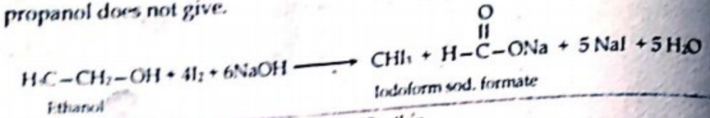
» Ethanol is tested by esterification reaction. Few mL of ethanol is heated with acetic acid in the presence of conc. H_2SO_4, a fruity smell of ester i.e ethyl acetate is formed. This reaction is called esterification reaction.



$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + \underset{\text{(Acetic acid)}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} \xrightleftharpoons{\text{conc. }H_2SO_4} \underset{\text{Ethyl acetate or ethylethanoate}}{H_3C-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3} + H_2O$$

14. **2069 Supp. Set B Q.No. 10 Give a suitable chemical test of ethanol that distinguishes it from propanol.** [2]

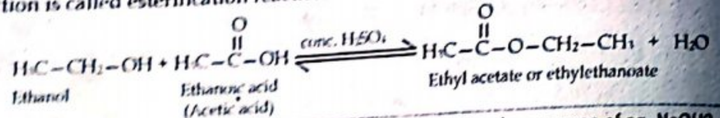
» Iodoform test distinguishes ethanol from propanol, ethanol gives positive iodoform test but propanol does not give.



$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. formate}}{H-\overset{\overset{O}{\|}}{C}-ONa} + 5\,NaI + 5\,H_2O$$

15. **2069 (Set A) Q.No. 22b Give the example of Esterification** [1]

» Alcohols react with carboxylic acid in the presence of conc. H_2SO_4, ester is formed. This reaction is called esterification reaction.



$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + \underset{\substack{\text{Ethanoic acid}\\ \text{(Acetic acid)}}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} \xrightleftharpoons{\text{conc. }H_2SO_4} \underset{\text{Ethyl acetate or ethylethanoate}}{H_3C-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3} + H_2O$$

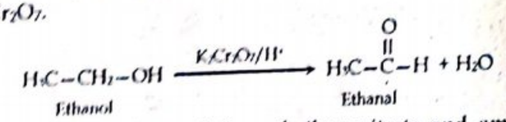
16. **2065 Q.No. 3 What happens when: Ethanol is heated with iodine in presence of aq. NaOH?** [2]

» When ethanol is heated with iodine in the presence of aq. NaOH, iodoform is obtained.

$$\underset{\text{Ethanol}}{CH_3CH_2-OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sod. formate}}{HCOONa} + 5\,NaI + 5\,H_2O$$

17. **2064 Q.No. 3 What happens when the product obtained by dehydrogenation of ethanol is allowed to react with Tollen's reagent?** [2]

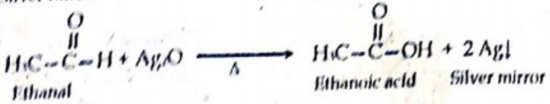
» Ethanal is obtained by the dehydrogenation of ethanol in the presence of acidified solution of $K_2Cr_2O_7$.



$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Ethanal}}{H_3C-\overset{\overset{O}{\|}}{C}-H} + H_2O$$

Tollen's reagent is a colourless solution of silver nitrate and ammonium hydroxide (NH_4OH). When a few mL of Tollen's reagent is warmed with a few drops of an ethanal, a shining mirror of silver is formed on the inner walls of the test tube.

$$\underset{\text{Silver nitrate}}{2AgNO_3} + 2NH_4OH \longrightarrow \underset{\text{Silver oxide}}{Ag_2O} + 2NH_4NO_3 + H_2O$$



$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{O}{\|}}{C}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Silver mirror}}{2\,Ag\downarrow}$$

18. **2064 Q.No. 4 Convert ethanol to propanoic acid.**

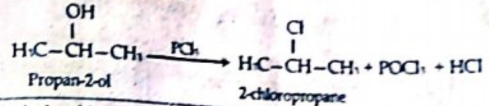
» Conversion ethanol.to propanoic acid:

$$\underset{\text{Ethanol}}{3CH_3CH_2-OH} + PI_3 \longrightarrow \underset{\text{Ethyl iodide}}{3CH_3CH_2I} + H_3PO_3$$

$$\underset{\text{Ethyl iodide}}{CH_3CH_2-I} + \underset{\text{Pot.cyanide}}{KCN} \longrightarrow \underset{\text{Ethyl cyanide}}{CH_3CH_2-CN} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3CH_2-COOH}$$

19. **2062 Q.No. 3(i) Write the action of: Propan-2-ol with PCl_5** [1]

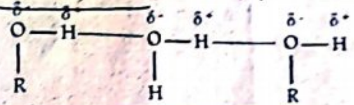
» Action of Propan-2-ol with PCl_5: Propan-2-ol reacts with phosphorous pentachloride (PCl_5), 2-chloropropane is obtained.



$$\underset{\text{Propan-2-ol}}{H_3C-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow{PCl_5} \underset{\text{2-chloropropane}}{H_3C-\overset{\overset{Cl}{|}}{C}H-CH_3} + POCl_3 + HCl$$

20. **2061 Q.No. 3 Alcohols of low molecular weight are moderately soluble in water, whereas ethers of about the same molecular weight are not. Explain.** [2]

» Alcohols having the –OH polar group and forms hydrogen bond with other molecules of water but ether does have polar group and does not form hydrogen bond. Due to this alcohols of low molecular wteight are moderately soluble in water, whereas ether is not.



$$\begin{array}{ccccc}\overset{\delta^-}{O}-\overset{\delta^+}{H}\cdots & \overset{\delta^-}{O}-\overset{\delta^+}{H}\cdots & \overset{\delta^-}{O}-\overset{\delta^+}{H}\\ | & | & |\\ R & H & R\end{array}$$

21. **2060 Q.No. 3 Identify the organic compounds A, B, C and D.** [2]

$$(CH_3)_2\,CHOH \xrightarrow{PCl_5} A \xrightarrow{\text{alc. KOH}} B \xrightarrow{\text{ozonolysis}} C + D$$

» The reaction sequence is given as:

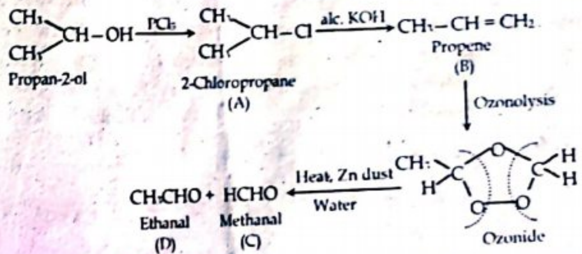
The compounds are

A = 2-chloropropane

B = Propene

C = Methanal

D = Ethanal



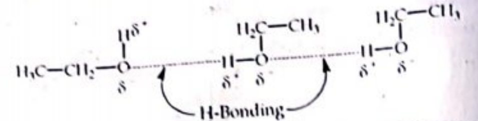
22. **2059 Q.No. 3 Write a chemical reaction for the preparation of primary alcohol by Oxo process.** [2]

» Oxo Process: When alkene is heated with water gas i.e. CO + H_2 under pressure in presence of cobalt carbonyl as catalyst, aldehyde is formed which on reduction gives alcohol.

$$\underset{\text{Ethene}}{CH_2=CH_2} + CO + H_2 \xrightarrow{[Co(CO)_4]_2} \underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow{H_2/Ni} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

23. **2059 Q.No. 4 Why is the boiling point of ethanol higher than its isomer methoxymethane?** [2]

» Ethanol forms hydrogen bond with its molecule whereas methoxymethane does not form hydrogen bond. So, the ethanol has higher boiling point than methoxymethane. We know that hydrogen bonded compound having higher boiling point than hydrogen non-bonded compound.



24. **2058 Q.No. 3** **Write a chemical reaction for the preparation of a primary alcohol by 'Oxo' process.** [2]

➢ Please refer to 2059 Q No. 3

25. **2058 Q.No. 4** **What action takes place when excess of ethanol is heated with conc. Sulphuric acid at about 140°C?** [2]

➢ When excess of ethyl alcohol i.e. ethanol is heated with conc. H_2SO_4 at 140°C, diethyl ether is obtained.

$$\underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH} + H_2SO_4 \xrightarrow{100^\circ C} \underset{\text{Ethyl hydrogen sulphate}}{H_3C-CH_2-HSO_4} + H_2O$$

$$\underset{\text{Ethyl hydrogen sulphate}}{H_3C-CH_2-HSO_4} + \underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH} \xrightarrow{140^\circ C} \underset{\text{Diethyl ether}}{H_3C-CH_2-O-CH_2-CH_3} + H_2SO_4$$

26. **2056 Q.No. 16** **What is fermentation?** [2]

➢ The chemical process by which a bigger organic molecule is converted into simpler organic molecules in presence of an enzyme is called 'Fermentation'. By this process cane sugar, fructose and starchy material are converted into ethyl alcohol.

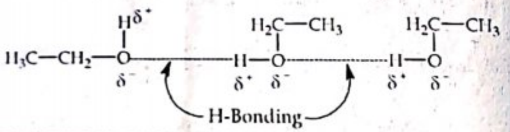
Example:

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

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH} + 2\,CO_2$$

27. **2055 Q.No. 16** **Why is boiling point of ethanol greater than that of ethoxyethane?** [2]

➢ Ethanol forms hydrogen bond with its molecule whereas ethoxyethane does not form hydrogen bond. So, the ethanol has higher boiling point than ethoxyethane. We know that hydrogen bonded compound having higher boiling point than hydrogen non-bonded compound.



28. **2054 Q.No. 11(b)** **Give the IUPAC name of the following compounds.** [2]
$CH_2=CH\,CH_2\,OH$

➢ The IUPAC name of $CH_2=CH-CH_2-OH$ is prop-2-en-1-ol.

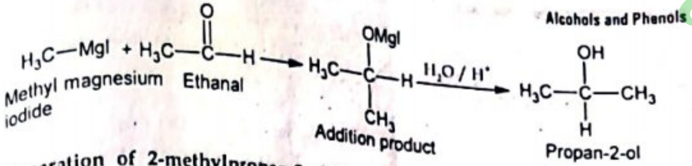
SHORT ANSWER QUESTIONS [5 MARKS]

29. **2076 Set B Q.No. 27** **Starting from CH_3MgI how would you prepare**
   i. **propan-2-ol**
   ii. **2-methylpropan-2-ol**

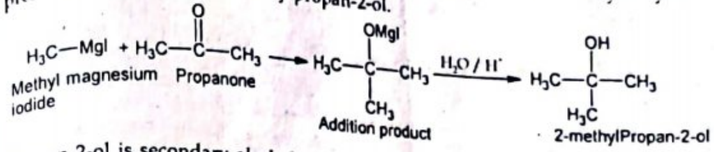
Give the chemical test to distinguish them. Why are lower member of alcohol highly soluble in water? [2+2+1]

➢

i. **Preparation of propan-2-ol from CH_3MgI:** When CH_3MgI is treated with ethanal (CH_3CHO), addition product is obtained which on hydrolysis in the presence of acid to form propan-2-ol.

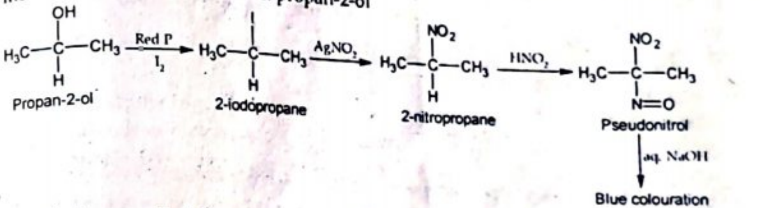


ii. **Preparation of 2-methylpropan-2-ol from CH_3MgI:** When CH_3MgI is treated with propanone (CH_3COCH_3), addition product is obtained which on hydrolysis in the presence of acid to form 2-methylpropan-2-ol.

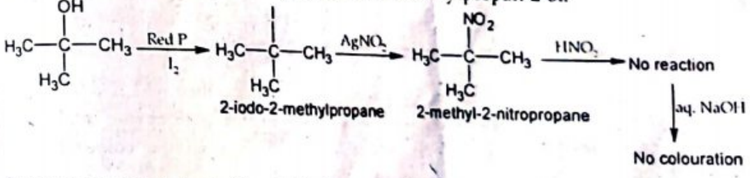


Propan-2-ol is secondary alcohol and 2-methylpropan-2-ol is tertiary alcohol, these can be distinguished by Victor Meyer's method.

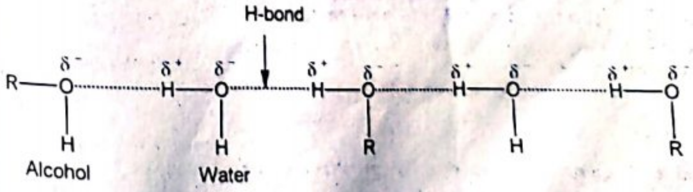
Propan-2-ol is treated with red P and I_2, 2-iodopropane is obtained which is treated with $AgNO_2$, 2-nitropropane is obtained. 2-nitropropane is treated with nitrous acid (HNO_2), pseudonitrol is obtained which on treatment with alkali to give blue colouration. This indicates secondary alcohol i.e. propan-2-ol



2-methylpropan-2-ol is treated with red P and I_2, 2-iodo-2-methylpropane is obtained which is treated with $AgNO_2$, 2-methyl-2-nitropropane is obtained. 2-methyl-2-nitropropane is treated with nitrous acid (HNO_2), no reaction and no colouration occur with alkali. This indicates tertiary alcohol i.e. 2-methylpropan-2-ol.

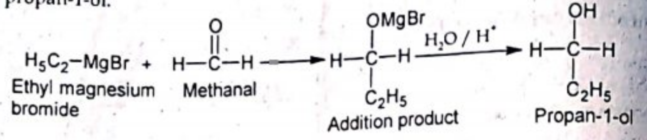


Lower member of alcohol is soluble in water, this is due to the formation of H-bond with water molecule. Higher the molecular mass lower the formation of H-bond.

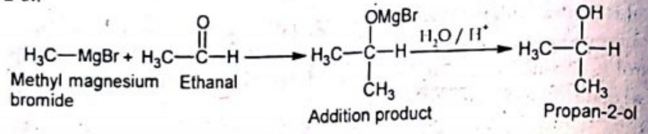


30. **2076 Set C Q.No. 27** **Starting from Grignard's reagent, how would you prepare (i) propan-1-ol (ii) propan-2-ol. Mention the chemical test to distinguish them. Write down the structural formula of neo-pentyl alcohol and its IUPAC name.** **[1+1+2+1]**

i. **Preparation of propan-1-ol from Grignard's reagent:** When ethyl magnesium bromide is treated with methanal, addition product is obtained which on hydrolysis to give propan-1-ol.

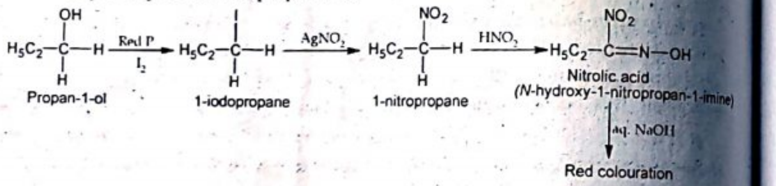


ii. **Preparation of propan-2-ol from Grignard's reagent:** When methyl magnesium bromide is treated with ethanal, addition product is obtained which on hydrolysis to give propan-2-ol.

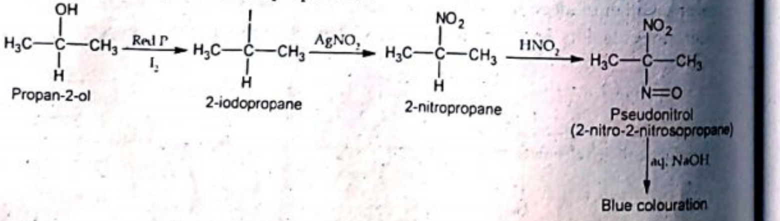


Propan-1-ol is primary alcohol and propan-2-ol is secondary alcohol, these can be distinguished by Victor Meyer's method.

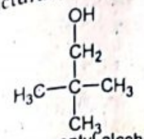
Propan-1-ol is treated with red P and I_2, 1-iodopropane is obtained which is treated with $AgNO_2$, 1-nitropropane is obtained. 1-nitropropane is treated with nitrous acid (HNO_2), nitrolic acid is obtained which on treatment with alkali to give red colouration. This indicates primary alcohol i.e. propan-1-ol.



Propan-2-ol is treated with red P and I_2, 2-iodopropane is obtained which is treated with $AgNO_2$, 2-nitropropane is obtained. 2-nitropropane is treated with nitrous acid (HNO_2), pseudonitrol is obtained which on treatment with alkali to give blue colouration. This indicates secondary alcohol i.e. propan-2-ol



Structural formula of neo-pentyl alcohol is

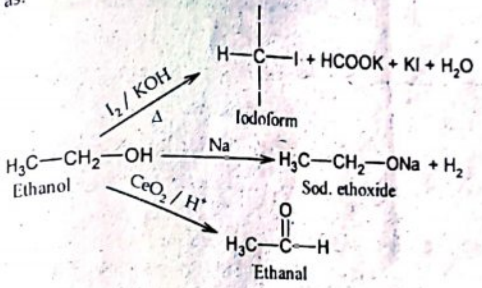


Neo-pentyl alcohol

IUPAC = 2,2-dimethylpropan-1-ol

31. **2075 GIE Q.No. 29** **An organic compound gives H_2 gas with Sodium metal. On treatment with alkaline iodine gives yellow ppt and on oxidation with CeO_2/H^+ form an aldehyde (C_2H_4O). Name the compound and write reactions involved. How would you convert the compound into ethene?** **[4+1]**

The organic compound which gives H_2 gas with sodium metal should be alcohol. The alcohol mulst have two carbon atoms i.e. ethanol. When alcohol is treated with alkaline iodine, yellow ppt of iodoform is formed. When alcohol is oxidized with CeO_2/H^+, aldehyde is obtained having molecular formula (C_2H_4O). The reaction sequence is given as:



When ethanol is heated with conc. H_2SO_4 at 170°C, ethene is obtained.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow[170\,^\circ C]{Conc.\ H_2SO_4} \underset{\text{Ethene}}{H_2C=CH_2}$$

32. **2075 Set A Q.No. 29** **An organic compound Ⓜ gives H_2 gas with sodium metal. On treatment with alkaline iodine gives yellow ppt and on oxidation with CeO_2/H^+ forms an aldehyde (C_2H_4O). Name the compound Ⓜ and write reactions involved. What happens when Ⓜ is heated with P_2O_5?** **[4+1]**

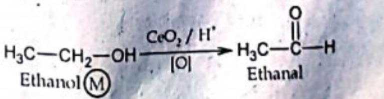
The compound Ⓜ gives H_2 gas with sodium metal, yellow ppt with alkaline iodine and aldehyde having molecular formula C_2H_4O on oxidation. The compound Ⓜ must be alcohol containing two carbon atoms.

CH_3-CH_2-OH (Ethanol) Ⓜ

The reaction is given as:

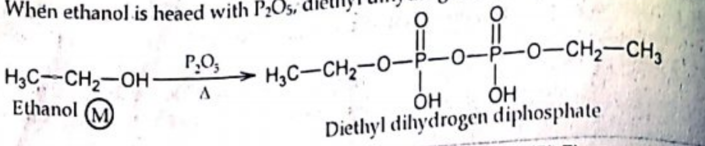
$$\underset{\text{Ethanol Ⓜ}}{H_3C-CH_2-OH} \xrightarrow{Na} \underset{\text{Sod.ethoxide}}{H_3C-CH_2-ONa} + H_2$$

$$\underset{\text{Ethanol Ⓜ}}{H_3C-CH_2-OH} \xrightarrow[\Delta]{I_2 + NaOH} \underset{\text{Iodoform Yellow ppt}}{CHI_3}$$



$$\underset{\text{Ethanol Ⓜ}}{H_3C-CH_2-OH} \xrightarrow[{[O]}]{CeO_2 / H^+} \underset{\text{Ethanal}}{H_3C-\overset{O}{\overset{\|}{C}}-H}$$

When ethanol is heaed with P_2O_5, diethyl dihydrogen diphosphate is obtained.



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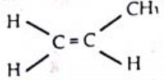
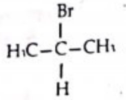
33. **2072 Set E Q.No. 23** **A monohydric alcohol reacts with PBr_3 to give 'B'. The compound B, If heated with alc. KOH gives 'C'. C on ozonolysis produces ethanal and methanal as major products.The compound 'A" responses iodoform test. Identify A, B and C with reactions involved. What happens when 'B' is heated with sodium in presence of dry ether?** [5]

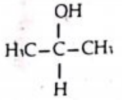
First part: The compound (C) undrgoes ozonolysis gives a mixture of ethanal and methanal.The compound (C) should have three carbons and having structure.



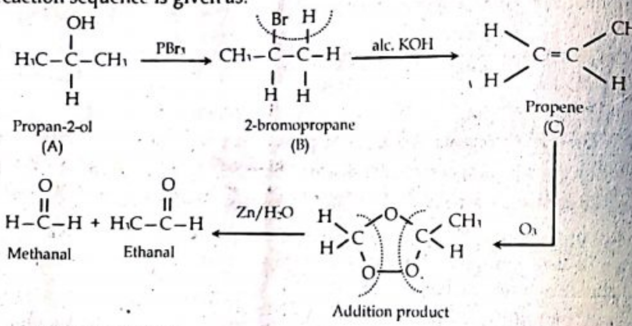
The compound (B) produce (C) when heated with with alc. KOH. The compound (B) must have structure.



The compound (A) reacts with PBr_3 to give compound (B).The compound (A) must have structure.

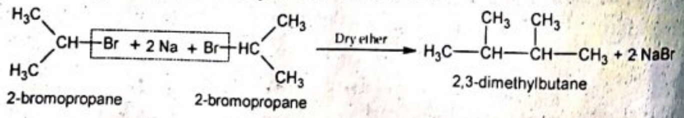


The reaction sequence is given as:



Hence, the compounds are
A = Propan-2-ol B = 2-bromopropane C = Propene
The compound (A) is secondary alcohol propan-2-ol which responses the positive iodoform test.

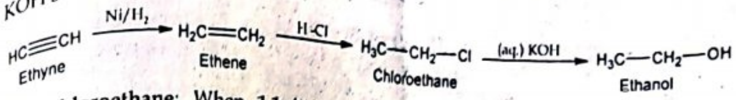
Second part: The compound (B) is 2-bromopropane which is heated sodium metal in presence of dry ether, 2,3-dimethylbutane is obtained.



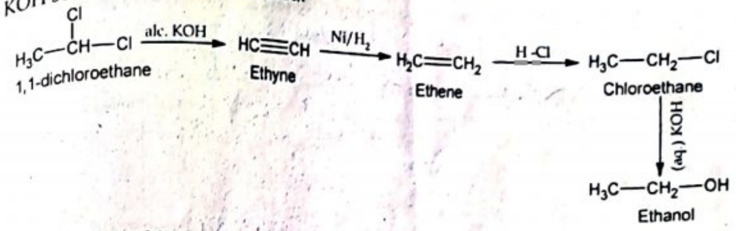
34. **2072 Set E Q.No. 25** **How is ethanol prepared from: i. ethyne ii. 1, 1 – dichloroethane? Convert ethanol to propanone. What is the laboratory test of carbonyl compounds?** **[1+1+2+1]**

Preparation of ethanol from:

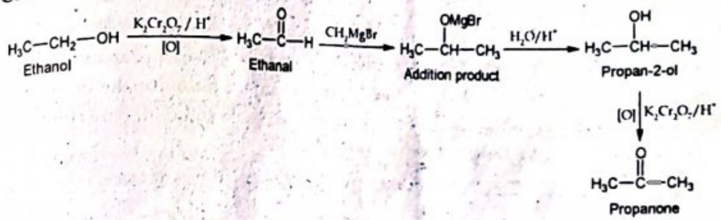
i. **Ethyne:** When ethyne on reduction with Ni/H_2, ethene is obtained. Ethene is treated with hydrogen chloride, chloroethane is obtained which on treatment with aqueous KOH solution, ethanol is obtained.



ii. **1,1-dichloroethane:** When 1,1-dichloroethane is treated with alc. KOH, ethyne is obtained. When ethyne on reduction with Ni/H_2, ethene is obtained. Ethene is treated with hydrogen chloride, chloroethane is obtained which on treatment with aqueous KOH solution, ethanol is obtained.



Convert ethanol into propanone:



Laboratory test of carbonyl compound: Silver mirror test and Fehling solution test are test of carbonyl compound.

Silver mirror test: The ammoniacal solution silver nitrate in presence of NaOH is called Tollen's reagent. Aldehyde reduce Tollen's reagent to metallic silver mirror in inner wall of test tube. Ketone does not give silver mirror test.

$$AgNO_3 + NaOH \longrightarrow \underset{\text{Grey ppt}}{AgOH} + NaNO_3$$

$$AgOH + 2\,NH_4OH \longrightarrow \underset{\text{Tollen's reagent}}{[Ag(NH_3)_2]OH} + 2\,H_2O$$

$$\underset{\text{Aldehyde Tollen's reagent}}{RCHO + 2\,[Ag(NH_3)_2]OH} \longrightarrow RCOONH_4 + \underset{\text{Silver mirror}}{2\,Ag\downarrow} + H_2O + 3\,NH_3$$

Fehling solution test: Fehling solution is a mixture of Fehling solution A (Copper sulphate and NaOH) and Fehling solution B (Alkaline solution of sod. Pot. Tartarate, Rochell's salt). Aldehyde gives brick red ppt of cuprous oxide. Ketone does not give this test.

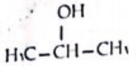
$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{From Fehling solution}}{2\,Cu(OH)_2} \longrightarrow \underset{\text{Brick red ppt}}{Cu_2O\downarrow} + RCOOH + 2H_2O$$

35. **2070 Set C Q.No. 28** **Write down the Isomeric alcohols of C_3H_8O and IUPAC name. Explain Victor Meyer's method to distinguish them.** [5]

The possible isomers of C_3H_8O are

$H_3C-CH_2-CH_2-OH$

1-propanol
1° alcohol



$H_3C-\overset{OH}{\overset{|}{C}H}-CH_3$

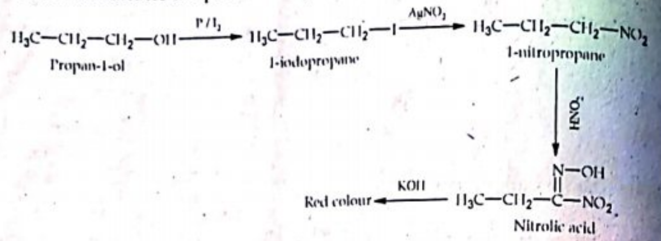
2-propanol
2° alcohol

$H_3C-CH_2-O-CH_3$

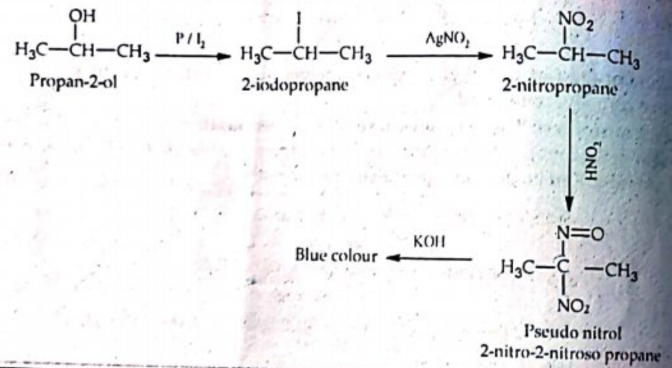
Methoxyethane

Distinction of primary (1°) and secondary (2°) alcohols:

Propan-1-ol: When propan-1-ol is treated with red P/I_2, 1-iodopropane is obtained which on treatment with $AgNO_2$ to give 1-nitropropane. 1-nitropropane is treated with HNO_2 to give nitrolic acid which on treatment with KOH solution, red colouration is obtained. This indicates the presence of propan-1-ol.



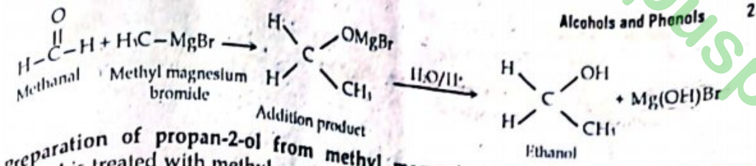
Propan-2-ol: When propan-2-ol is treated with red P/I_2, 2-iodopropane is obtained which on treatment with $AgNO_2$ to give 2-nitropropane. 2-nitropropane is treated with HNO_2 to give pseudo nitrol which on treatment with KOH solution, blue colouration is obtained. This indicates the presence of propan-2-ol.



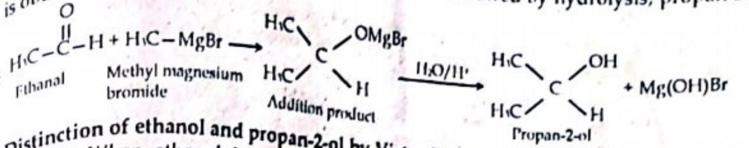
36. **2069 Supp. Set B Q.No. 25** **Write chemical reaction for the preparation of** [5]

i. **ethanol**
ii. **propan-2-ol from methyl magnesium bromide. How would you distinguish them by Victor Meyer's method?**

i. **Preparation of ethanol from methyl magnesium bromide:** When methanal is treated with methyl magnesium bromide, addition product is formed which on hydrolysis in the presence of acid to give ethanol.

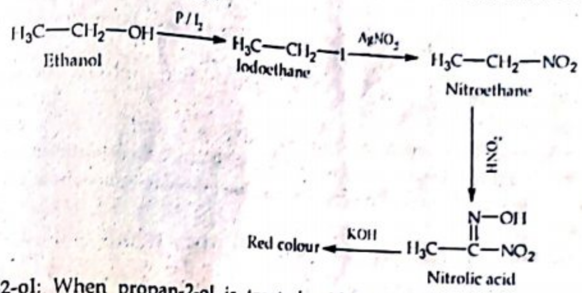


ii. **Preparation of propan-2-ol from methyl magnesium bromide (CH_3MgBr):** When ethanal is treated with methyl magnesium bromide followed by hydrolysis, propan-2-ol is obtained.

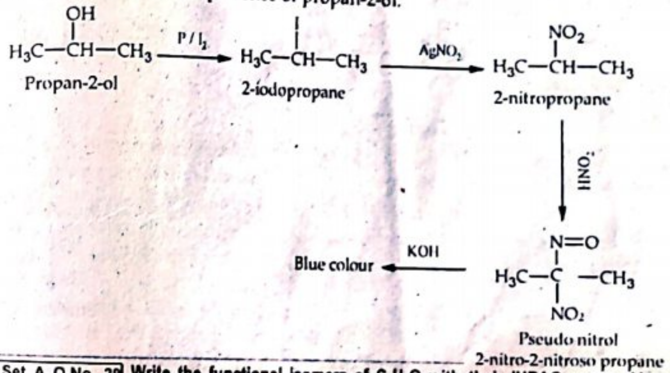


Distinction of ethanol and propan-2-ol by Victor Meyer's method:

i. **Ethanol:** When ethanol is treated with red P/I_2, Iodoethane is obtained which on treatment with $AgNO_2$ to give Nitroethane. Nitroethane is treated with HNO_2 to give nitrolic acid which on treatment with KOH solution, red colouration is obtained. This indicates the presence of ethanol.

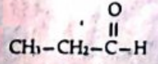


ii. **Propan-2-ol:** When propan-2-ol is treated with red P/I_2, 2-iodopropane is obtained which on treatment with $AgNO_2$ to give 2-nitropropane. 2-nitropropane is treated with HNO_2 to give pseudo nitrol which on treatment with KOH solution, blue colouration is obtained. This indicates the presence of propan-2-ol.



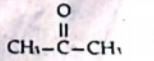
37. **2069 Set A Q.No. 29** **Write the functional Isomers of C_3H_6O with their IUPAC name. Also, give a chemical test to distinguish them which one gives Iodoform test and why?** [5]

The functional isomer of C_3H_6O is



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

Propanal

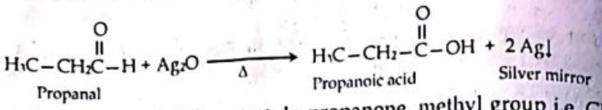


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Propanone

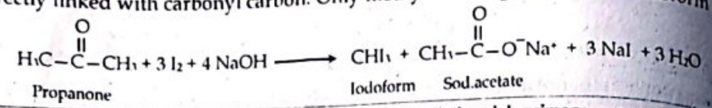
Propanal and propanone are distinguished by Tollen's reagent test. Propanal gives Tollen's reagent test but propanone does not give.

$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$



$$\underset{\text{Propanal}}{H_3C-CH_2-\overset{\overset{\large O}{\|}}{C}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Propanoic acid}}{H_3C-CH_2-\overset{\overset{\large O}{\|}}{C}-OH} + \underset{\text{Silver mirror}}{2\,Ag\downarrow}$$

Propanone gives positive iodofrom test. In propanone, methyl group i.e. CH_3- group is directly linked with carbonyl carbon. Only methyl ketone gives positive iodoform test.



$$\underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{\|}}{C}-CH_3} + 3\,I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod.acetate}}{CH_3-\overset{\overset{\large O}{\|}}{C}-O^-Na^+} + 3\,NaI + 3\,H_2O$$

---

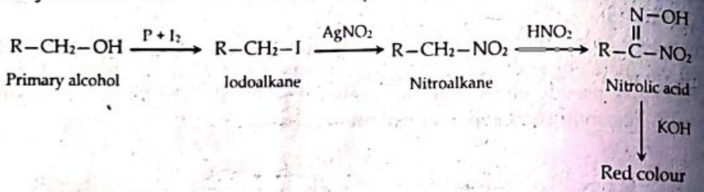
38. **2069 Set A Q.No. 32 Describe Victor Meyer's method to distinguish primary, secondary and tertiary alcohols.** [5]

Victor Meyer's method for the distinction of primary, secondary, tertiary alcohols: It involves different steps.

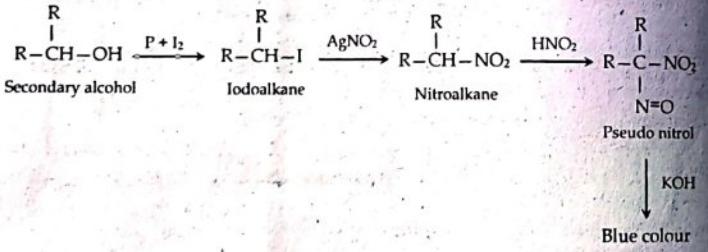
i. The given alcohol is treated with a mixture of red phosphorous and iodine, corresponding iodoalkane is obtained.
ii. The iodoalkane is then treated with siver nitrite solution ($AgNO_2$), the corresponding nitroalkane is obtained.
iii. The **nitroalkane** is then treated with nitrous acid (HNO_2).
iv. The **resulting** solution is made alkaline with aq. KOH or NaOH solution.

The colour of the final solution gives the idea about the class of alcohols i.e. 1°, 2° and 3° alcohols.

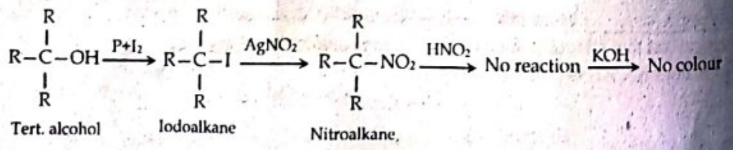
Primary alcohol



Secondary alcohol



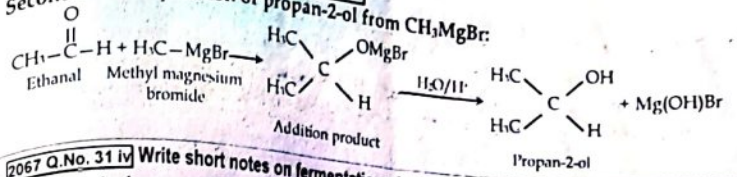
Tertiary alcohol



39. **2069 Set B Q.No. 25 An Organic Compound (A) reacts with PBr_3 to give (B). Compound B produces (C) when heated with alc. KOH. The compound (C) undergoes ozonolysis to yield ethanal and methanal as major products. The compound 'A' responses Iodoform test. Identify A, B, C, and write reactions involved. How is (A) obtained from CH_3MgBr?** [5]

First Part: Please refer to 2072 Set E Q.No. 23

Second Part: Preparation of propan-2-ol from CH_3MgBr:



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40. **2067 Q.No. 31 iv Write short notes on fermentation of ethyl alcohol.** [5]

The chemical process by which a bigger organic molecule is converted into simpler organic molecules in presence of an enzyme is called 'Fermentation'. By this process cane sugar, fructose and starchy material are converted into ethyl alcohol.

i. From sugars: Molasses is a very rich source of sugar i.e. sucrose, glucose, fructose. It is dark colored mother liquor obtained after crystallization of cane sugar from concentrated cane juice. Yeast is unicellular living plant which contains various enzyme like invertase, zymase etc.

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

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH} + 2\,CO_2$$

ii. From Starches: The starch containing raw materials are rice, wheat, maize, potatoes, barley etc. These food materials are first cooked with water so as to release the granules of starch. The resulting solution is called 'Mash'.

The mash is then mixed with malt (which is the dried germinated barley containing various enzyme like diastase, maltase, zymase etc.)

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

---

41. **2066 Q. No. 21 Write down the oxidation of Primary, Secondary and Tertiary alcohols. How would you convert Propan-1- ol into Propon-2- ol ?** [5]

Oxidation of primary, secondary and tertiary alcohols:

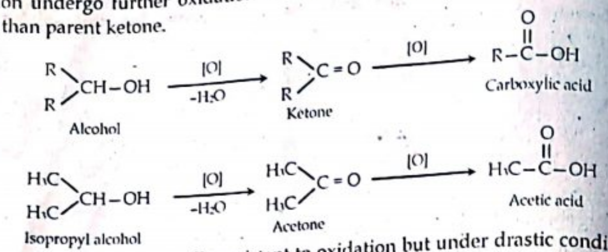
Alcohol can be easily oxidized by acidic or alkaline $KMnO_4$ or acidified $Na_2Cr_2O_7$ or $K_2Cr_2O_7$. The ease of oxidation and the nature of product formed depend on the type of alcohol used.

a. **Primary alcohols** are easily oxidized first to corresponding aldehydes and then to corresponding carboxylic acids.

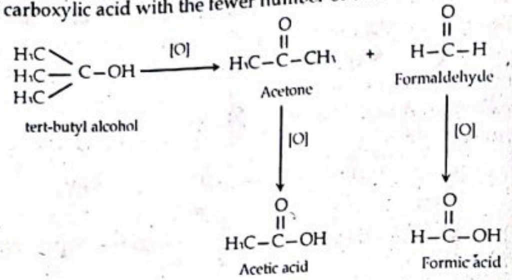
$$\underset{\text{Alcohol}}{RCH_2OH} \xrightarrow[-H_2O]{[O]} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

b. **Secondary alcohol** on oxidation yield the corresponding ketone which on drastic reaction undergo further oxidation to form a carboxylic acid containing lesser carbon atom than parent ketone.

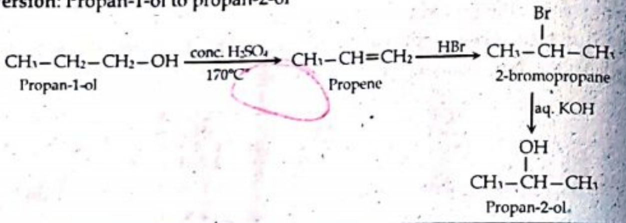


c. **Tertiary alcohols** are generally resistant to oxidation but under drastic condition yield a mixture of carboxylic acid with the fewer number of carbon atoms.



This different behaviour of the three types of alcohols may be used for their distinction.

Conversion: Propan-1-ol to propan-2-ol



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42. 2065 Q.No. 29 b **Write the Victor Meyer's test of distinction of primary, secondary and tertiary alcohols.** [5]

Please refer to 2069 Set A Q.No. 32

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43. 2064 Q.No. 21 **What is meant by Grignard's reagent? How could you convert a primary alcohol to Grignard's reagent? By using a suitable Grignard's reagent how would you synthesise:** [5]

i. 2-methylpropan -2- ol **ii. ethanoic acid?**

When haloalkane is treated with magnesium metal in the presence of dry ether, alkyl magnesium halide is formed which is known as Grignard's reagent.

$$R-X + Mg \xrightarrow{\text{Dry ether}} RMgX$$

$$\underset{\text{Methyl bromide}}{CH_3-Br} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Methyl magnesium bromide}}{CH_3MgBr}$$

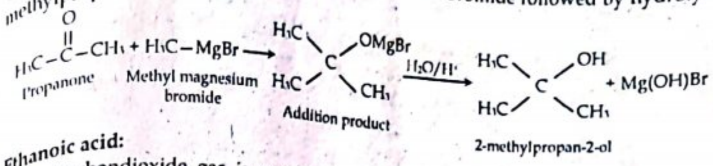
Coversion of primary alcohol to Grignard's reagent:

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow{SOCl_2} \underset{\text{Ethyl chloride}}{H_3C-CH_2-Cl} + Mg \xrightarrow[\Delta]{\text{Dry ether}} \underset{\substack{\text{Ethyl magnesium chloride}\\ \text{Grignard reagent}}}{H_3C-CH_2-MgCl}$$

Synthesis of

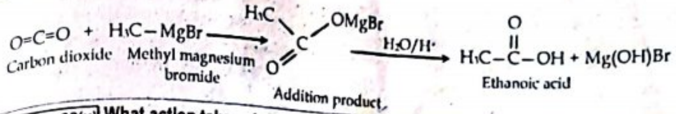
i. 2-methylpropan-2-ol

When propanone is treated with methyl magnesium bromide followed by hydrolysis, 2-methylpropan-2-ol is obtained.



ii. Ethanoic acid:

When carbondioxide gas is passed through ethereal solution of methyl magnesium bromide, ethanoic acid is obtained.



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44. 2063 Q.No. 22(v) **What action takes place when:** [5]

i. Ethanol is heated with conc. H_2SO_4 at about 160-170° C?

When ethanol is heated with conc. H_2SO_4 at about 160 - 170°C, ethene is obtained.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow[\text{conc. } H_2SO_4]{160\text{-}170^\circ C} \underset{\text{Ethene}}{H_2C=CH_2} + H_2O$$

---

45. 2061 Q.No. 21 **Write down the oxidation products of primary, secondary and tertiary alcohols.**

Please refer to 2066 Q. No. 21

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46. 2060 Q.No. 21 **Describe Victor Meyer's method for the distinction, between 1°, 2° and 3° alcohols.** [5]

Please refer to 2069 Set A Q.No. 32

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47. 2060 Q.No. 22

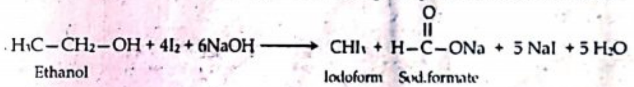
i. Consider a reaction.

$$A \xrightarrow[\Delta]{PBr_3} B \xrightarrow{KCN} C \xrightarrow[\Delta]{H_2O/H^+} D \xrightarrow[\Delta]{P_2O_5} E$$

The compound A is a primary alcohol which gives positive iodoform test. Identify the organic compounds A, B, C, D and E.

ii. Convert the above compound D into ethanoic acid.

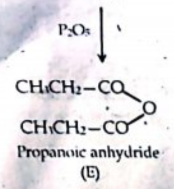
i. The compound A is primary alcohol and it gives positive iodoform test. The compound A must be ethanol which is primary alcohol and gives positive iodoform test.



$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod.formate}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + 5\,NaI + 5\,H_2O$$

The reaction sequences are given as:

$$\underset{\substack{\text{Ethanol}\\ (A)}}{H_3C-CH_2-OH} \xrightarrow{PBr_3} \underset{\substack{\text{Bromoethane}\\ (B)}}{H_3C-CH_2-Br} \xrightarrow{KCN} \underset{\substack{\text{Ethyl cyanide}\\ (C)}}{H_3C-CH_2-CN} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Propanoic acid}\\ (D)}}{H_3C-CH_2-COOH}$$



Propanoic anhydride

(E)

The compounds are

A = Ethanol

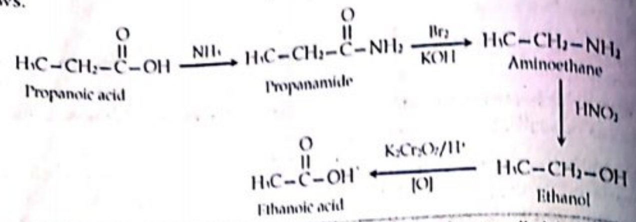
B = Bromoethane

C = Ethyl cyanide

D = Propanoic acid

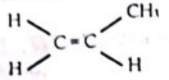
E = Propanoic anhydride

ii. **Conversion:** The compound D is propanoic acid. It is converted into ethanoic acid as follows.

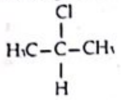


48. **2059 Q.No. 21 A secondary alcohol (X) reacts with PCl_5 to give an alkyl halide (Y), which on dyhydrohalogenation yields an alkene (Z). The alkene (Z) upon ozonolysis gives the mixture of ethanal and methanal. Identify X, Y and Z. Suggests your answer with chemical reaction.**

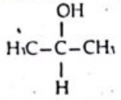
Alkene (Z) up on ozonolysis gives a mixture of ethanal and methanal. Alkene should have three carbons and having structure.



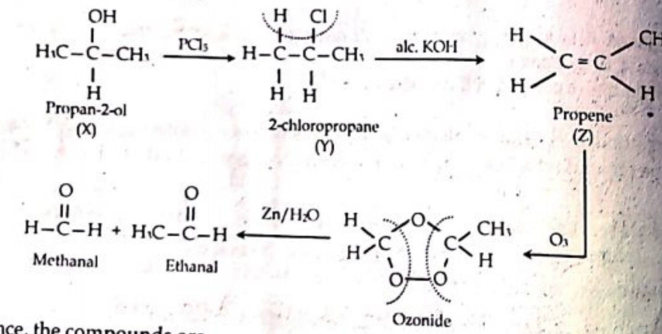
Alkyl halide (Y) on dehydrohalogenation gives alkene, (Y) must have structure.



Secondary alcohol (X) reacts with PCl_5 to give alkylhalide, X must have structure.



The reaction sequence is given as:



Hence, the compounds are

X = Propan-2-ol

Y = 2-chloropropane

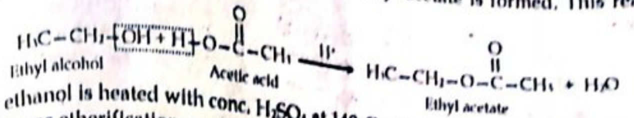
Z = propene

49. **2052 Q.No. 24(b); 2053 Q.No. 23(c) What happens when:** [5]

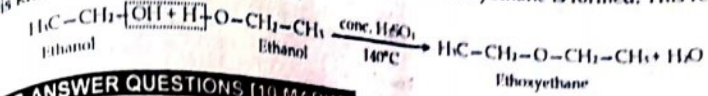
b. Ethyl alcohol is treated with acetic acid

c. Ethanol is heated with conc. H_2SO_4

→ When ethyl alcohol is treated with acetic acid, ethyl acetate is formed. This reaction is known as esterification reaction.



c. When ethanol is heated with conc. H_2SO_4 at 140°C, ethoxyethane is formed. This reaction is known as etherification reaction.



LONG ANSWER QUESTIONS [10 MARKS]

50. **2075 GIE Q.No. 30 Explain Victor-Meyer's test for the distinction of 1°, 2° and 3° alcohol. How is 2-bromopropane converted into 1-bromopropane? Write an example of each of:**

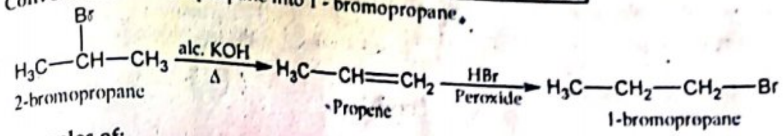
i. **Reimer-Tiemann reaction**

ii. **Wurtz reaction**

iii. **Iodoform reaction** [5+2+3]

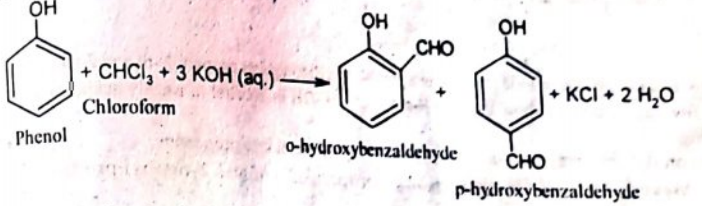
→ **Distinction of 1°, 2° and 3° alcohol:** Please refer to 2069 Set A Q No. 32

Conversion: 2-bromopropane into 1-bromopropane.

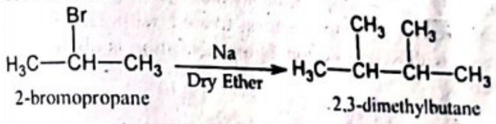


Examples of:

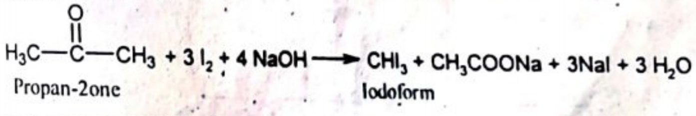
i. **Reimer-Tiemann reaction:**



ii. **Wurtz reaction:**



iii. **Iodoform reaction:**



51. **2075 Set A Q.No. 30 Explain Victor-Mayer's test for the distinction of primary, secondary and tertiary alcohol. How is 1-chloropropane converted into 2-chloropropane? Write an example of each.** [5+2+3]

i. **Carbylamine reaction**

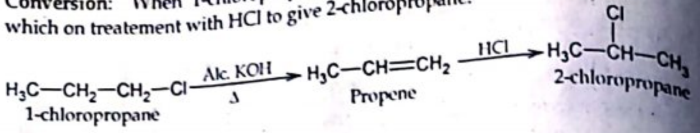
ii. **Reimer-Tiemann reaction**

iii. **Cannizzaro's reaction** [10]

→ **Distinction of primary, secondary and tertiary alcohol Victor-Meyer's test:**

Please refer to 2069 Set A Q.No. 32

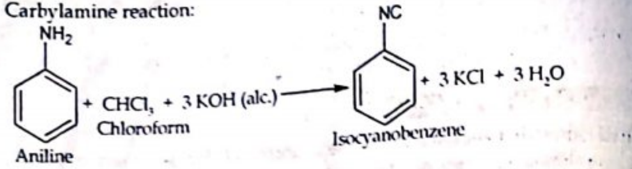
Conversion: When 1-chloropropane is treated with alc. KOH, propene is obtained which on treatement with HCl to give 2-chloropropane.



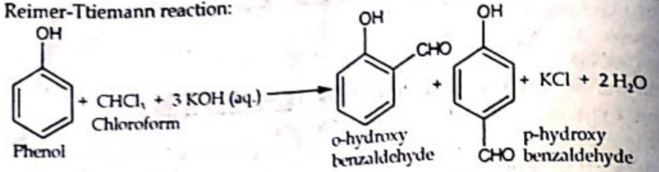
$$H_3C-CH_2-CH_2-Cl \xrightarrow[\Delta]{Alc.\ KOH} H_3C-CH=CH_2 \xrightarrow{HCl} H_3C-\overset{Cl}{CH}-CH_3$$

Example of:

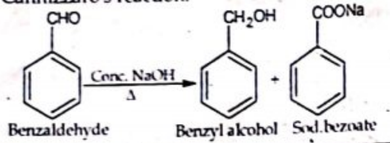
i. Carbylamine reaction:



ii. Reimer-Ttiemann reaction:



iii. Cannizzaro's reaction:

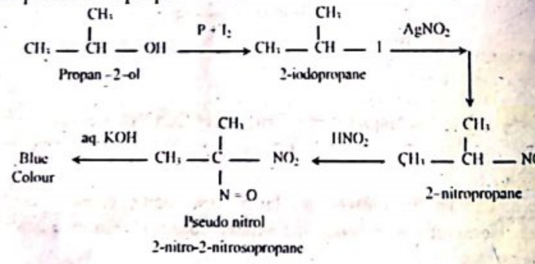


52. **2075 Set B Q.No. 32 Describe Victor Meyer's method to distinguish propan -2 -ol and 2-methyl propan -2 -ol. Give a reaction to show that the H-atom of the -OH in alcohol is weakly acidic. Convert the followings.**
   i. propan -1-ol into propan -2-ol **ii. ethanal into propanone** **[5+1+2+2]**

✍ Victor Meyer's Method for distinction of propan – 2 – ol and 2–methyl propan – 2 – ol:

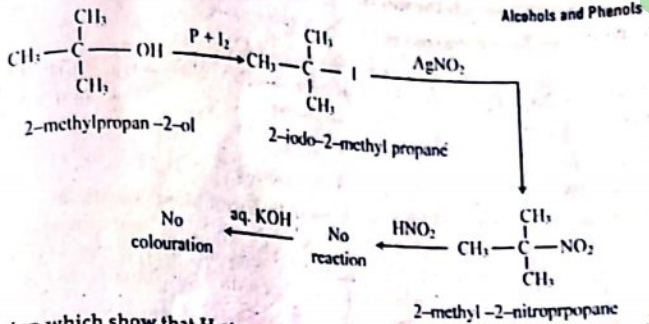
Propan – 2 – ol:

Propan –2 – ol is treated with red P/I_2, 2 –iodopropane is obtained which on treatment with $AgNO_2$ to give 2-nitropropane. 2- nitropropane is treated with HNO_2 to give pseudo nitrol which on treatment with KOH solution, blue colouration is obtained. This indicates the presence of propan –2 – ol



2-methylpropan –2 –ol:

Alcohol is treated with red P/I_2, iodoalkane is obtained which on treatment with $AgNO_2$ to give nitroalkane. Nitroalkane does not react with HNO_2 and give no colouration with KOH. It indicates the presence of 2-methylpropan -2-ol.



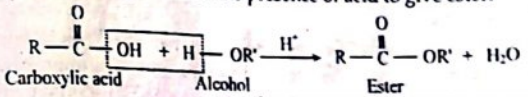
Reaction which show that H-atom of the -OH group in alcohol is weakly acidic.

a. Alcohols react with metal like Na, K, Mg etc. to form hydrogen gas.

$$\underset{Alcohol}{2ROH} + 2Na \longrightarrow \underset{Sod.\ alkoxide}{2RONa} + H_2\uparrow$$

$$2C_2H_5OH + 2Na \longrightarrow \underset{Sod.\ ethoxide}{2C_2H_5ONa} + H_2\uparrow$$

b. Alcohol reacts with carboxylic acid in the presence of acid to give ester.



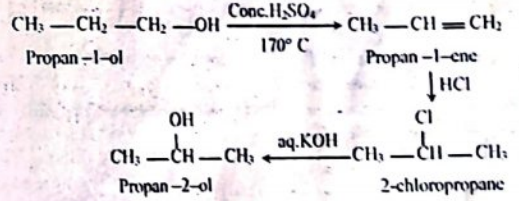
$$\underset{Carboxylic\ acid}{R-\overset{O}{\overset{\|}{C}}-}\boxed{OH + H}\underset{Alcohol}{-OR'} \xrightarrow{H^+} \underset{Ester}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$$

c. Alcohol reacts with Grignard reagent to form alkane

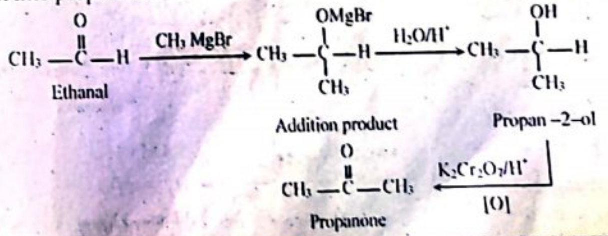
$$\underset{Methanol}{CH_3O}\boxed{-H + C_2H_5}\underset{Ethyl\ magnesium\ bromide}{MgBr} \longrightarrow \underset{Ethane}{C_2H_6} + CH_3OMgBr$$

Conversion

i. Propan –1–ol into propan –2–ol:



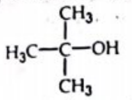
ii. Ethanal into propanone:



53. **2074 Supp. Q.No. 31 Write down a structural formula and its IUPAC name of $C_4H_{10}O$. How would you apply Victor Meyer's method for the distinction of propan-1-ol from propan-2-ol? Write an example of:**
   i. Oxo-Process **ii. Baeyer's test**

Convert propan-2-ol into propan-1-ol. [2+4+2+2]

✎ The structural formula of tertiary alcohol of $C_4H_{10}O$

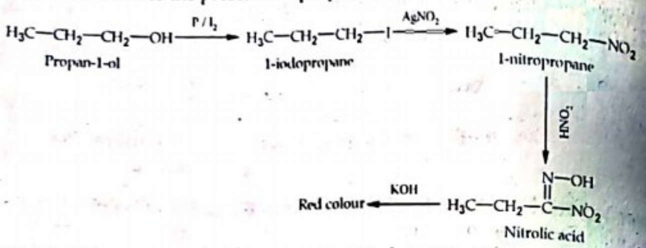


$H_3C-C(CH_3)_2-OH$

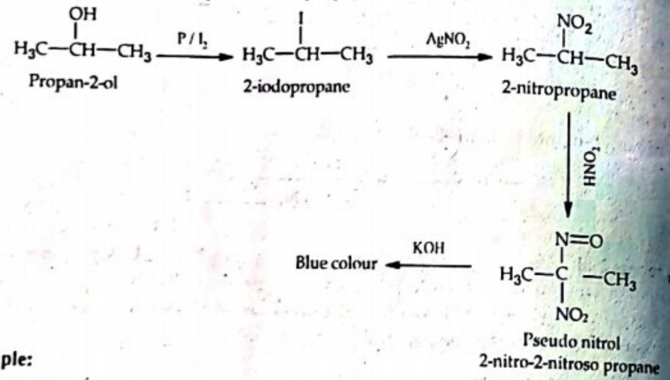
2-methylpropan-2-ol

Distinction of propan-1-ol from propan-2-ol by Victor Meyer's method:

Propan-1-ol: When propan-1-ol is treated with red P/I_2, 1-iodopropane is obtained which on treatment with $AgNO_2$ to give 1-nitropropane. 1-nitropropane is treated with HNO_2 to give nitrolic acid which on treatment with KOH solution, red colouration is obtained. This indicates the presence of propan-1-ol.

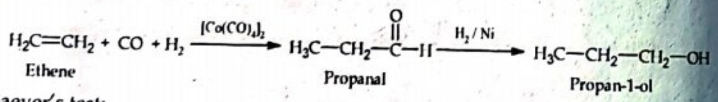


Propan-2-ol: When propan-2-ol is treated with red P/I_2, 2-iodopropane is obtained which on treatment with $AgNO_2$ to give 2-nitropropane. 2-nitropropane is treated with HNO_2 to give pseudo nitrol which on treatment with KOH solution, blue colouration is obtained. This indicates the presence of propan-2-ol.

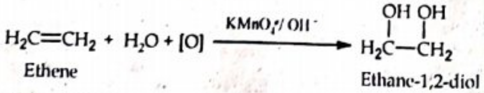


Example:

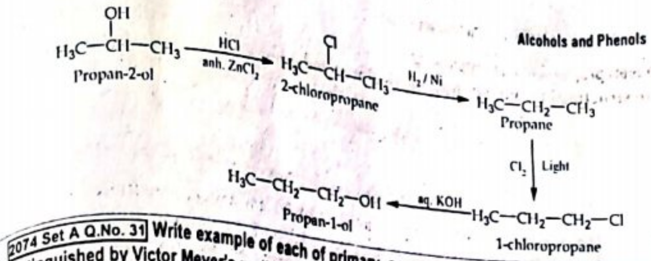
i. Oxo-process:



ii. Baeyer's test:



Conversion: Propan-2-ol into propan-1-ol



54. **2074 Set A Q.No. 31 Write example of each of primary, secondary and tertiary alcohols. How are they distinguished by Victor Meyer's method? Give an example of,**

i. Oxo-process

ii. Dehydration of alcohol

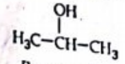
How would you convert popan-1-ol into propan-2-ol? [2+4+2+2]

✎ Example of primary, secondary and tertiary alcohols are given as:

H_3C-CH_2-OH

Ethanol

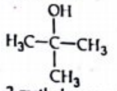
Primary alcohol



$H_3C-CH(OH)-CH_3$

Propan-2-ol

Secondary alcohol



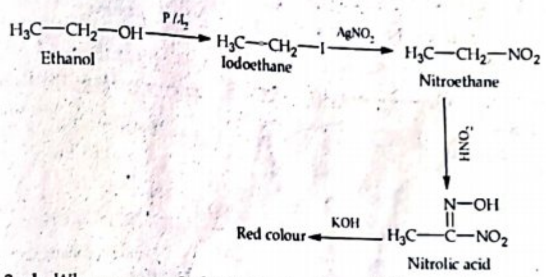
$H_3C-C(OH)(CH_3)-CH_3$

2-methylpropan-2-ol

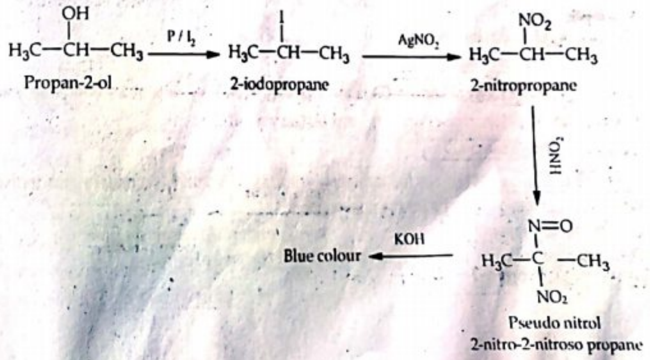
Tertiary alcohol

Victor Meyer's Method for the distinction of primary, secondary and tertiary alcohols:

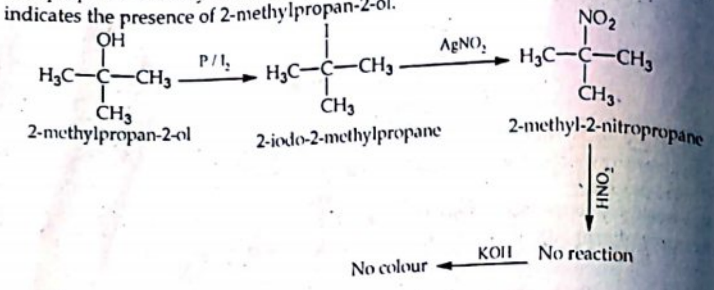
i. **Ethanol:** When ethanol is treated with red P/I_2, Iodoethane is obtained which on treatment with $AgNO_2$ to give Nitroethane. Nitroethane is treated with HNO_2 to give nitrolic acid which on treatment with KOH solution, red colouration is obtained. This indicates the presence of ethanol.



ii. **Propan-2-ol:** When propan-2-ol is treated with red P/I_2, 2-iodopropane is obtained which on treatment with $AgNO_2$ to give 2-nitropropane. 2-nitropropane is treated with HNO_2 to give pseudo nitrol which on treatment with KOH solution, blue colouration is obtained. This indicates the presence of propan-2-ol.

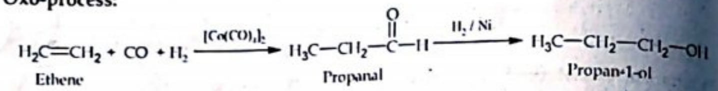


iii. **2-methylpropan-2-ol:** When 2-methylpropan-2-ol is treated with red P/I₂, 2-iodo-2-methylpropane is obtained which on treatment with $AgNO_2$ to give 2-methyl-2-nitropropane. 2-methyl-2-nitropropane does not react with HNO_2 and KOH. This indicates the presence of 2-methylpropan-2-ol.



Example of:

i. **Oxo-process:**

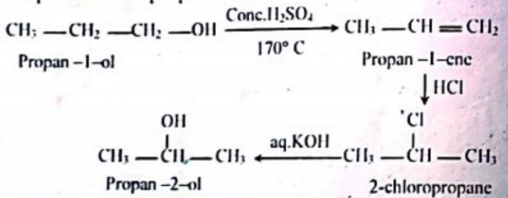


ii. **Dehydration of alcohol:**

$$H_3C{-}CH_2{-}OH + \text{Conc. } H_2SO_4 \xrightarrow[\Delta]{160-170\,^\circ C} H_2C{=}CH_2 + H_2O$$

Ethanol Ethene

Conversion: Propan-1-ol into propan-2-ol:



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55. 2074 Set B Q.No. 31 **Write down the structural formula of tertiary alcohol and its IUPAC name of $C_4H_{10}O$. How would you apply Victor Meyer's method for the distinction of propan-1-ol from propan-2-ol? Write an example of;**
   - i. Oxo-process
   - ii. Baeyer's test

Convert propan -2-ol into propan-1-ol. [2+4+2+2]

Please refer to 2074 Supp. Q.No. 31

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56. 2073 Supp Q.No. 31a **What are the oxidation products of primary, secondary and tertiary alcohols?**

Oxidation of primary, secondary and tertiary alcohols:

Please refer to 2066 Q.No. 21

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57. 2073 Set C Q.No. 31 **What are the oxidation products of primary, secondary and tertiary alcohol? Write down suitable methods for the conversion of** [5+2.5+2.5]

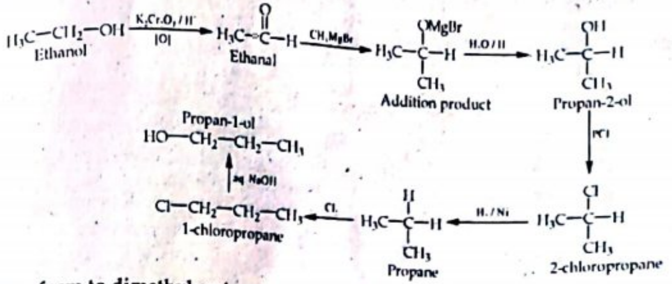
i. **ethanol to propanol** ii. **Chloroform to dimethyl amine.**

Oxidation product of primary, secondary and tertiary alcohol:

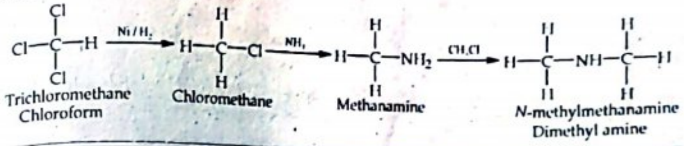
Please refer to 2066 Q. No 21

Converstion:

i. Ethanol to propan-1-ol:



ii. Chloroform to dimethyl amine:



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58. 2073 Set D Q.No. 31 **How would you distinguish propan-2-ol from 2-methylpropan-2-ol by using Victor Meyer's method?Write down suitable method for the conversion of:** [5+2.5+2.5]

i. **Chloroform into dimethylamine** ii. **Ethanamine into methanamine**

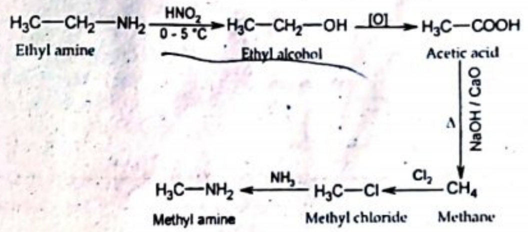
Victror Meyer's method for distinction of propan-2-ol from 2-methylpropan-2-ol:

Please refer to 2075 Set B Q.No. 32

Conversion:

i. Chloroform into dimethyl amine: Please refer to 2073 Set C Q.No. 31

ii. Ethanamine (Ethyl amine) into methanamine (Methyl amine)



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59. 2072 Supp. Q.No. 31b **Write Victor-Meyer's method for the distinction of 1°, 2° and 3° alcohol.** [5]

Please refer to 2069 Set A Q.No. 32

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60. 2072 Set C Q.No. 32 **Describe Victor Meyer's method to distinguish propan –2 – ol and 2-methylpropan –2 –ol. Give a reaction to show the H-atom of the -OH in the alcohol is weakly acidic. Convert the following.** [5+1+2+2]

i. **Propan –1 – ol into Propan –2 – ol** ii. **ethanal into propanone.**

Please refer to 2075 Set B Q.No. 32

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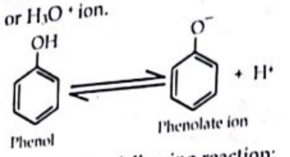
61. 2072 Set D Q.No. 32 **Describe Victor Meyer's method to distinguish propan–2-ol and 2-methylpropan-2-ol. Why is phenol more acidic than alcohol? How would you convert ethanal into propanone and vice-versa?** [5+1+4]

Distinguish propan-2-ol and 2-methyl propan-2-ol:

Please refer to 2075 Set B Q.No. 32

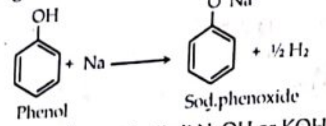
Phenol more acidic than alcohol

Phenol is weakly acidic in nature. Its aqueous solution, phenol slightly ionizes to give phenolate ion and H^+ ion or H_3O^+ ion.

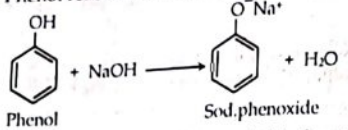


Acidic nature of phenol is supported by following reaction:

Reaction with alkali metals: Like alcohol, active metals Na or K react with phenol to form salt and hydrogen gas.



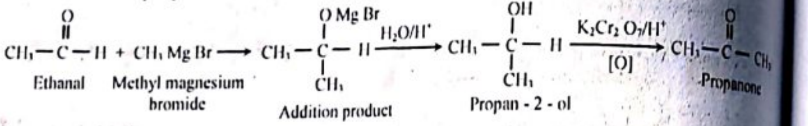
Reaction with alkali: Phenol reacts with alkali NaOH or KOH to give salt and water.



With litmus paper: Phenol turns blue litmus to red. On the other hand alcohols (ROH) are neutral to litmus. So, phenol is stronger acid than alcohol.

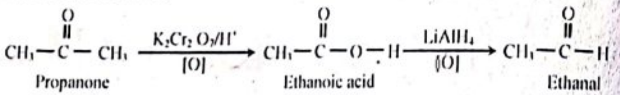
Conversion:

Ethanal into propanone:



$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3MgBr \longrightarrow CH_3-\underset{CH_3}{\overset{OMgBr}{C}}-H \xrightarrow{H_2O/H^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-H \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Propanone into Ethanal:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} CH_3-\overset{\overset{O}{\|}}{C}-O-H \xrightarrow[{[O]}]{LiAlH_4} CH_3-\overset{\overset{O}{\|}}{C}-H$$

62. **2072 Set E Q.No. 31a Distinction of 1°, 2° and 3° alcohol by Victor-Meyer's method.** [5]

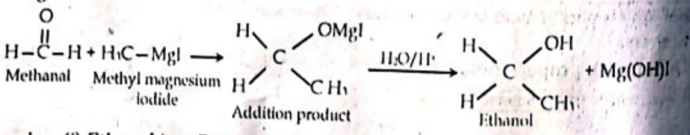
➣ **Distinction of 1°,2°and 3° alcohol by Victor-Meyer's method:** Please refer to 2069 Set A Q.No. 32

63. 2071 Set C Q.No. 31 b (i)

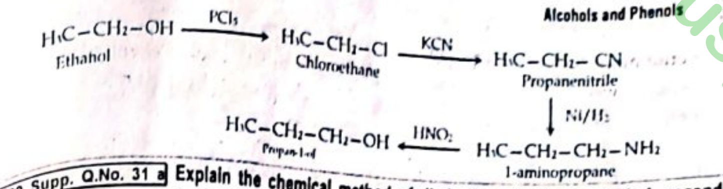
Starting from CH_3MgI, how would you prepare ethanol? Convert [5]

i. ethanol into propan-1-ol

➣ **Preparation of ethanol from CH_3MgI:** When methanal is treated with methyl magnesium iodide, addition product is formed which on hydrolysis in the presence of acid to give ethanol.



Coversion (*i*) Ethanol into Propan-1-ol:



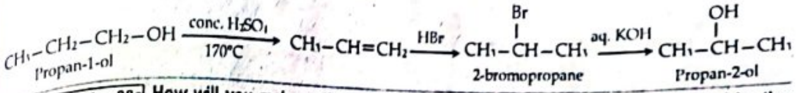
64. **2070 Supp. Q.No. 31 a Explain the chemical method of distinction of primary alcohol, secondary alcohol and tertiary alcohol introduced by Victor Meyer.** [5]

➣ Please refer to 2069 Set A Q.No. 32

65. **2069 (Set B) Q.No. 30 a How would you distinguish between propan-1-ol and propan-2-ol by Victor-Meyer's method? Give a suitable method of conversion of propan-1-ol into propan-2-ol.** [5]

➣ **Distinction between propan-1-ol and propan-2-ol by Victor-Meyer's method:** Please refer to 2070 Set C Q.No. 28

Conversion: propan-1-ol into popan-2-ol.



$$CH_3-CH_2-CH_2-OH \xrightarrow[170^\circ C]{conc.\ H_2SO_4} CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\overset{\overset{Br}{|}}{CH}-CH_3 \xrightarrow{aq.\ KOH} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

66. **2068 Q.No. 28a How will you make a distinction of primary, secondary and tertiary alcohol by the Victor Meyer's Method?** [5]

➣ Please refer to 2069 Set A Q.No. 32

67. **2063 Q.No. 29(a) Describe Victor Meyer's method for the distinction between primary secondary and tertiary alcohols.**

➣ Please refer to 2069 Set A Q.No. 32

68. **2063 Q.31 (iv); 2059 Q.31(a); 2055 Q.31(c); 2054 Q.No. 30(d);**

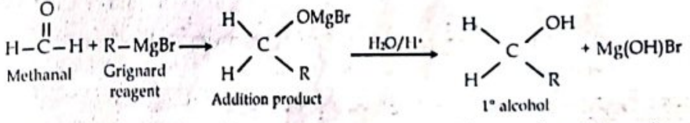
a. **Use of Grignard's regent in the synthesis of 1°, 2°, 3° alcohols.**
b. **Victor Meyer's method for distinction between primary, secondary and tertiary alcohols.**
c. **Distinction between 1°, 2° and 3° alcohols by Victor-Meyer's method.**
d. **Fermentation.**

➣

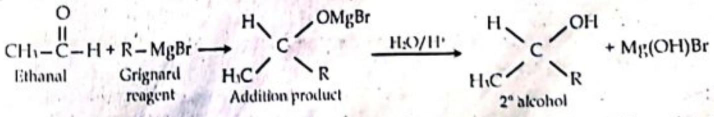
a. Grignard's reagent can be used to prepare 1°, 2° and 3° alcohol. Alkyl magnesium halide is called Grignard's reagent (RMgX)

Preparation of

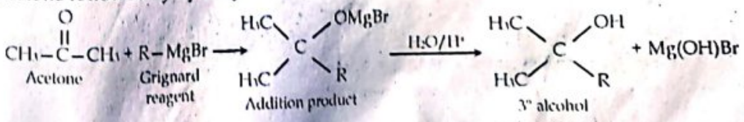
1. **Primary alcohol i.e. 1°alcohol:** 1°alcohol is prepared by treating Grignard's reagent with methanal followed by hydrolysis



2. **Secondary alcohol i.e. 2°alcohol:** 2°alcohol is prepared by treating Grignard's reagent with ethanal followed by hydrolysis



3. **Tertiary alcohol i.e. 3°alcohol:** 3°alcohol is prepared by treating Grignard's reagent with acetone followed by hydrolysis



b. Please refer to 2069 Set A Q.No. 32

c. Please refer to 2069 Set A Q.No. 32

d. Please refer to 2067 Q.No. 31iv

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69. **2062 Q.No. 29a Consider the following reaction** [5]

$$A \xrightarrow{PI_3} B \xrightarrow{KCN} C \xrightarrow{H_2O/H^+} D \xrightarrow{P_2O_5} E$$

The compound, A is a primary alcohol which gives iodoform test. Identify the organic compounds A, B, C, D and E; giving complete reaction.

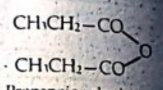
The compound A is a primary alcohol and gives +ve iodoform test. The compound A must be ethanol. Ethanol primary alcohol and gives +ve iodoform test.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod.formate}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + 5NaI + 5H_2O$$

The complete reaction is given as

$$\underset{\substack{\text{Ethanol}\\(A)}}{H_3C-CH_2-OH} \xrightarrow{PI_3} \underset{\substack{\text{Iodoethane}\\(B)}}{H_3C-CH_2-I} \xrightarrow{KCN} \underset{\substack{\text{Ethyl cyanide}\\(C)}}{H_3C-CH_2-CN} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Propanoic acid}\\(D)}}{H_3C-CH_2-COOH}$$

$$\downarrow P_2O_5$$



Propanoic anhydride

(E)

The compounds are

A = Ethanol

B = Iodoethane

C = Ethyl cyanide

D = Propanoic acid

E = Propanoic anhydride

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70. **2058 Q.No. 29a Consider the following reaction** [10]

$$A \xrightarrow[\Delta]{PCl_5} B \xrightarrow[\text{dry ether}]{Mg} C \xrightarrow[\Delta]{CO_2} D \xrightarrow[H_2OH/H^+]{\Delta} E$$

The compound, A is a primary alcohol, which on oxidation gives ethanal. Identify A, B, C, D and E. Convert the above compound A into methanol and ethyne.

The compound (A) is primary alcohol which on oxidation gives ethanal. It means, the primary alcohol should be a two carbon chain alcohol. So (A) should be CH_3CH_2OH.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Ethanal}}{CH_3CHO}$$

Now the given reaction sequence is expressed as,

$$\underset{\substack{\text{Ethanol}\\(A)}}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{\substack{\text{Chloroethane}\\(B)}}{CH_3CH_2Cl} \xrightarrow[\text{Dry ether}]{Mg} \underset{\substack{\text{Ethyl magnesium}\\\text{chloride (C)}}}{CH_3CH_2MgCl} \xrightarrow{CO_2} \underset{\substack{\text{Addition product}\\(D)}}{\begin{matrix} OMgCl \\ | \\ C=O \\ | \\ CH_2CH_3 \end{matrix}}$$

$$\xrightarrow[\Delta]{H_2O/H^+} Mg(OH)Cl + \begin{matrix} OH \\ | \\ C=O \\ | \\ CH_2CH_3 \end{matrix}$$

or CH_3CH_2COOH

Propanoic acid

(E)

Conversion of compound (A) ethanol to methanol:

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Oxd}^n]{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{Decarboxylation}]{NaOH, CaO} \underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2} \underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} \xrightarrow{\text{aq. KOH}} \underset{\text{Methanol}}{CH_3OH}$$

Conversion of compund (A) ethanol to ethyne:

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{SOCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{\substack{\text{alc}\\ \text{~~aq~~ KOH}}} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2} \underset{\text{1,2-dibromoethane}}{H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H}$$

$$\xrightarrow{\text{Alc. KOH}} \underset{\text{Ethyne}}{HC\equiv CH} + 2HBr$$

WRITE SHORT NOTES [5 MARKS]

71. **2072 Set D Q.No. 33d 2070 Set D Q.No. 33 c Distinction between 1°, 2° and 3° alcohol by Victor-Meyer's method.** [5]

Please refer to 2069 Set A Q.No. 32

10.2 Phenols

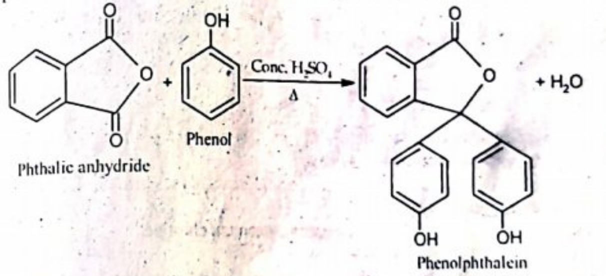
VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 10 Starting from phenol how would you obtain.** [1+1]

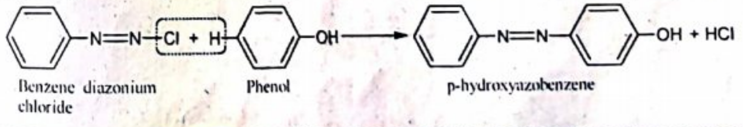
i. **Phenolphthalein**

ii. **p-hydroxyazobenzene**

i. Phenol to phenolphthalein: When phenol is heated with phthalic anhydride in the presence conc. H_2SO_4, phenolphthalein is obtained.



ii. Phenol to p-hydroxyazobenzene: When phenol is treated with benzene diazonium chloride, p-hydroxyazobenzene is obtained. This reaction is known as Coupling reaction.



2. **2076 Set C Q.No. 10 What product would you obtain when phenol is treated with** [1+1]

i. **Benzene diazonium chloride?**

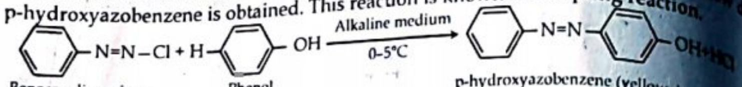
ii. **Phthalic anhydride?**

i. Please refer to 2076 Set B Q.No. 10ii

ii. Please refer to 2076 Set B Q.No. 10i

3. **2074 Set A Q.No. 10** **Starting from phenol, how would you obtain p-hydroxyazobenzene?** [2]

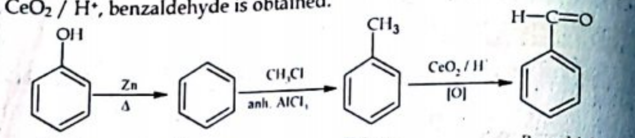
Phenol reacts with benzene diazonium chloride in ice cold alkaline medium, yellow dye p-hydroxyazobenzene is obtained. This reaction is known as **Coupling reaction.**



Benzene diazonium chloride Phenol p-hydroxyazobenzene (yellow dye)

4. **2074 Set B Q.No. 10** **Starting from phenol, how would you obtain benzaldehyde?** [2]

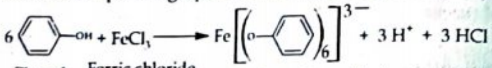
Phenol is heated with zinc metal, benzene is obtained which on treatment with methyl chloride in the presence of anhydrous $AlCl_3$, toluene is obtained. Toluene on oxidation with CeO_2 / H^+, benzaldehyde is obtained.



Phenol Benzene Toluene Benzaldehyde

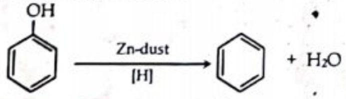
5. **2073 Supp Q.No. 10** **What is the laboratory test of phenol? What happens when phenol is heated with Zn–dust?** [1+1]

Laboratory test of phenol is $FeCl_3$ test: Phenol reacts with ferric chloride solution to form water soluble coloured complexes. In fact, all compounds containing the enol group (=C–OH) give characteristic color with $FeCl_3$. The colour may vary from violet to blue, green or even red depending upon the nature of the phenol.



Phenol Ferric chloride Iron hexaphenoxide ion (Violet Colour)

Phenol is heated with Zn-dust: When phenol is heated with zinc dust, benzene is formed. This reaction is known as reduction.

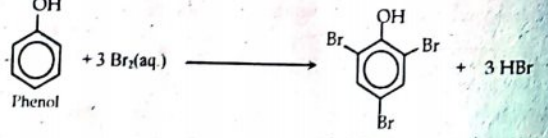


Phenol Benzene

6. **2073 Set C Q.No. 10** **How does phenol react with** [1+1]

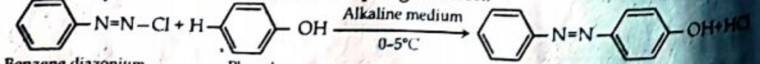
i. aqueous bromine **ii. Benzene diazonium chloride.**

i. **Reaction of phenol with aq. Br_2:** When phenol is treated with aqueous bromine, 2,4,6-tribromophenol is formed.



Phenol 2, 4, 6–tribromophenol

ii. **Reaction of phenol with benzene diazonium chloride:** Phenol reacts with benzene diazonium chloride in ice cold alkaline medium, yellow dye p-hydroxyazobenzene is obtained. This reaction is known as **Coupling reaction.**



Benzene diazonium chloride Phenol p-hydroxyazobenzene (yellow dye)

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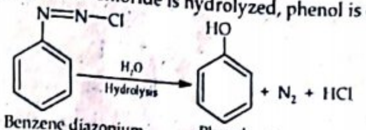
7. **2073 Set D Q.No. 10** **How is phenol obtained from** [1+1]

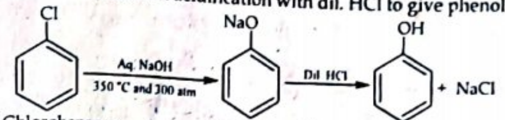
i. benzene diazonium chloride **ii. chlorobenzene**

i. When benzene diazonium chloride is hydrolyzed, phenol is obtained.



Benzene diazonium chloride Phenol

ii. When chlorobenzene is treated with aq. NaOH at 350°C and 300 atm pressure, sodium phenoxide is obtained which on acidification with dil. HCl to give phenol.



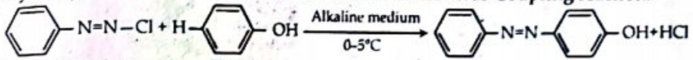
Chlorobenzene Sod. phenoxide Phenol

8. **2071 Set D Q.No. 10** **What happens when phenol is treated with:** [2]

a. **Benzene diazonium chloride**

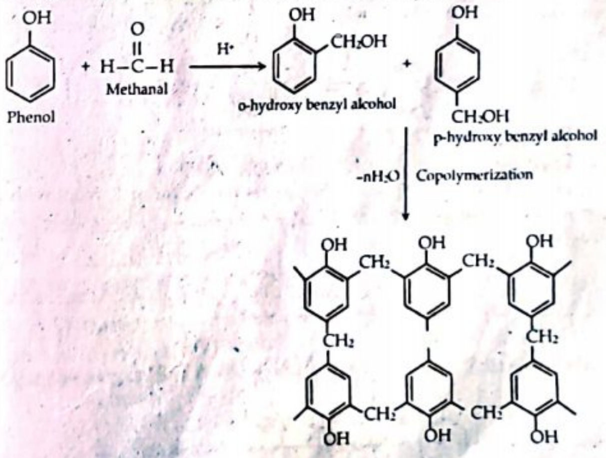
b. **Methanal in acidic medium**

a. Phenol reacts with benzene diazonium chloride in ice cold alkaline medium, yellow dye p-hydroxyazobenzene is obtained. This reaction is known as Coupling reaction.



Benzene diazonium chloride Phenol p-hydroxyazobenzene (yellow dye)

b. Phenol undergoes condensation reaction with methanal in the presence of acidic medium to give synthetic thermosetting plastic called Bakelite.

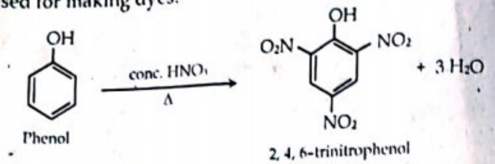


Phenol o-hydroxy benzyl alcohol p-hydroxy benzyl alcohol

Bakelite

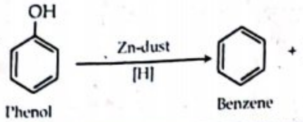
9. **2070 Set C Q.No. 14 How is picric acid prepared? Write its one use.** [2]

When phenol is treated with conc. Nitric acid, 2,4,6-trinitrophenol i.e. picric acid is formed. It is used for making dyes.



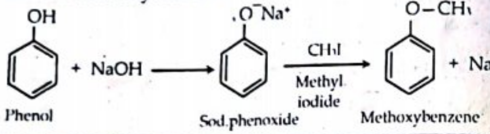
10. **2069 (Set A) Q.No. 8 How would you obtain benzene from phenol?** [2]

When phenol is heated with zinc dust, benzene is formed. This reaction is known as reduction.



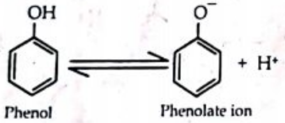
11. **2069 (Set B) Q.No. 10 Starting from phenol, how would you prepare methoxybenzene?** [2]

Phenol reacts with sodium hydroxide, sodium phenoxide is formed which reacts with methyl iodide to form methoxybenzene.



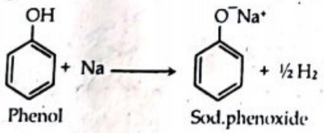
12. **2068 Q.No. 3 Why is phenol more acidic than aliphatic alcohol?** [2]

Phenol is weakly acidic in nature. Its aqueous solution, phenol slightly ionizes to give phenolate ion and H^+ ion or H_3O^+ ion.

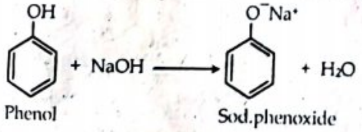


Acidic nature of phenol is supported by following reaction:

Reaction with alkali metals: Like alcohol, active metals Na or K react with phenol to form salt and hydrogen gas.

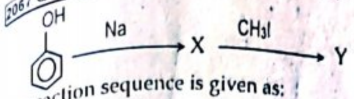


Reaction with alkali: Phenol reacts with alkali NaOH or KOH to give salt and water.

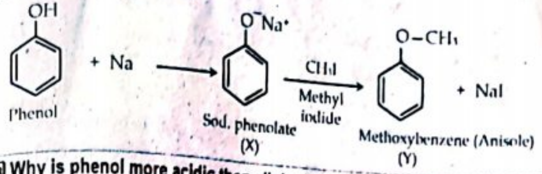


With litmus paper: Phenol turns blue litmus to red. On the other hand alcohols (ROH) are neutral to litmus. So, phenol is stronger acid than alcohol.

13. **2067 Q.No. 7 Name the compound (X) and (Y) in the following reaction.** [2]



The reaction sequence is given as:



14. **2067 Q.No. 8 Why is phenol more acidic than aliphatic alcohol?** [2]

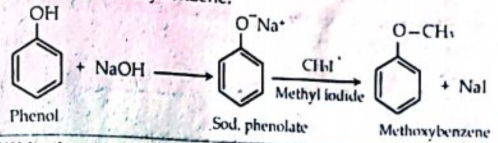
Please refer to 2068 Q.No. 3

15. **2066 Q. No. 8 How would you prepare methoxybenzene from phenol?** [2]

Please refer to 2069 (Set B) Q.No. 10

16. **2064 Q.No. 22(v) What happens when Sodium phenolate reacts with iodomethane?** [1]

Phenol reacts with sodium hydroxide, sodium phenoxide is formed which reacts with methyl iodide to form methoxybenzene.

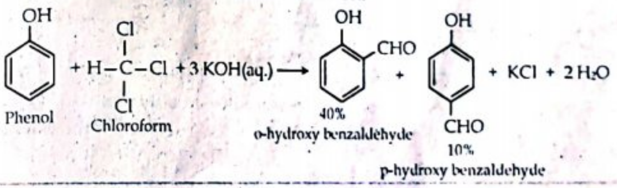


17. **2063 Q.No. 3(ii) Write the action of Monohydroxy benzene with aqueous bromine.** [2]

Please refer to 2073 Set C Q.No. 10

18. **2061 Q.No. 7 Show your acquaintance with Reimer-Tiemann's reaction.**

When phenol is treated with chloroform in the presence of aqueous solution of KOH, a mixture of o-hydroxy benzaldehyde and p-hydroxy benzaldehyde is obtained. This reaction is known as **Reimer-Tiemann's reaction.**



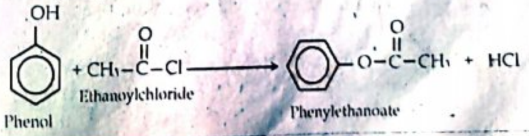
19. **2057 Q.No. 3 Write the reaction between phenol and aq. Br_2.** [2]

Please refer to 2073 Set C Q.No. 10

SHORT ANSWER QUESTIONS [5 MARKS]

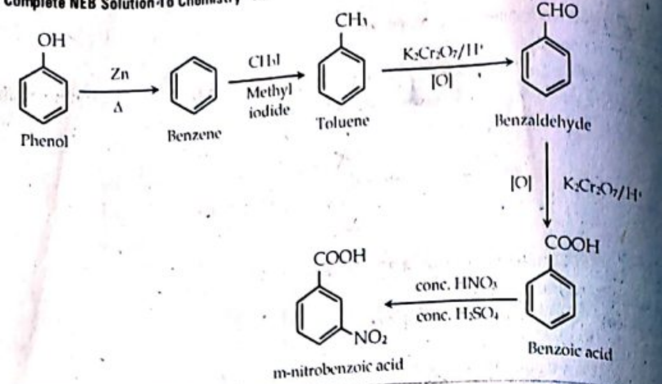
20. **2063 Q.No. 22(iv) What action takes place when Phenol reacts with ethanoylchloride?** [1]

When phenol is treated with ethanoylchloride in the presence of conc. H_2SO_4, phenylethanoate (ester) is formed.



21. **2062 Q.No. 22(i) Convert the following Organic compounds: Phenol to m-nitrobenzoic acid** [1]

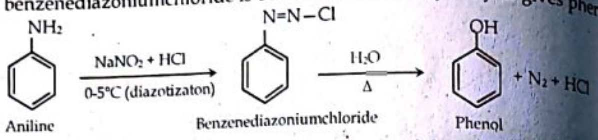
Conversion: Phenol to m-nitrobenzoic acid



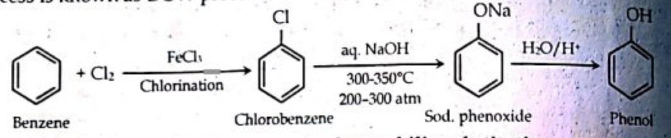
22. **2061 Q.No. 23 How is phenol prepared from (a) aniline and (b) benzene? How do you explain that the –OH group of phenol is ortho / para directing?** **[5]**

Preparation of phenol:

a. **From Aniline:** When aniline is treated with sodium nitrite in the presence of HCl at about 0 - 5°C, benzenediazoniumchloride is obtained which on hydrolysis gives phenol.

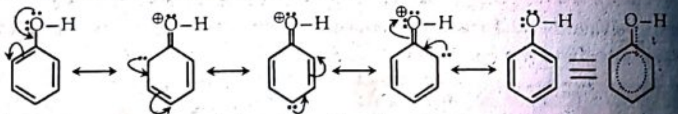


b. **From benzene:** When benzene on chlorination in the presence with $FeCl_3$, chlorobenzene is obtained. The chlorobenzene is heated at high pressure with aq. NaOH then sodium phenoxide is obtained which on hydrolysis in the presence of acid gives phenol. This process is known as DOW process.

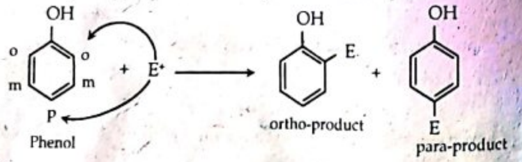


Phenol is ortho / para directing group in electrophilic substitution

Due to the presence of two lone pair of electrons on oxygen atom of the phenol, the lone pair of electrons gets delocalized and forms the resonance structure of phenol.



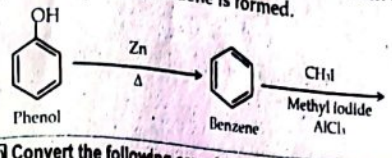
In the resonance structure of phenol, negative charge is developed on the ortho and para position i.e. electron density on ortho and para position is more. Hence, the incoming electrophile is attracted towards the ortho and para position. Thus the OH- group in phenol is ortho and para position in electrophilic substitution.



23. **2059 Q.No. 22(a) How could you synthesise?** **[1]**

Toluene from phenol

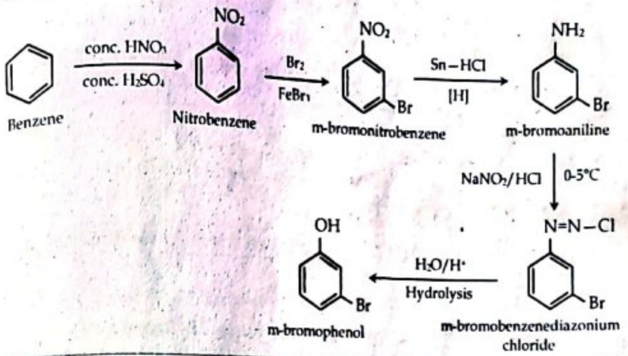
Phenol on reduction with zinc dust, benzene is formed which on treatement with methyl iodide in the presence of $AlCl_3$, toluene is formed.



24. **2058 Q.No. 22(a) Convert the following organic compounds.** **[1]**

a. Benzene to m-bromophenol.

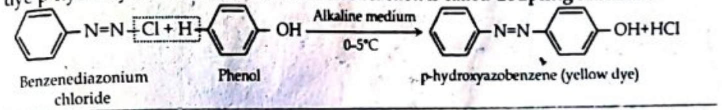
Conversion: Benzene to m-bromophenol:



25. **2057 Q.No. 23(c) Write the chemical equation with conditions for the following reaction.** **[1]**

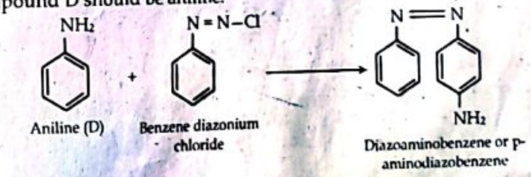
(a) Phenol is coupled with benzene diazonium chloride.

Phenol is coupled with benzenediazoniumchloride in ice cold alkaline medium, yellow dye p-hydroxyazobenzene is obtained. This reaction is called **Coupling reaction.**

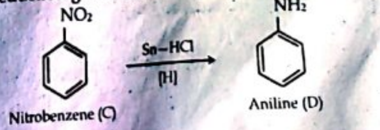


26. **2052 Q.No. 27 An aromatic compound A on reduction yields parent hydrocarbon B.B on nitration gives C.C on reduction in acidic solution gives D. On coupling with diazonium salts, D gives diazoaminobenzene. Give name for A, B, C and D. Write the chemical reaction involved.** **[5]**

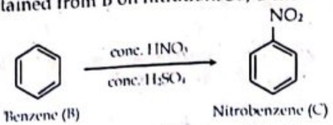
The aromatic compound D on coupling with diazonium salt gives diazoamino benzene. The sompound D should be aniline.



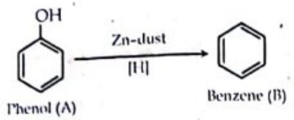
The compound C on reduction gives D, the compound C must be nitrobenzene.



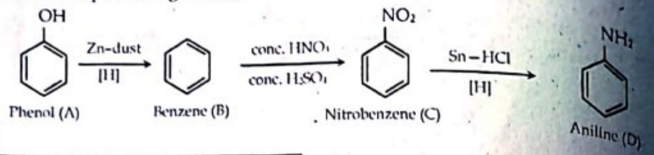
The compound C is obtained from B on nitration. So, B must be benzene.



The compound B is obtained from the reduction of A, the compound A may be either phenol or haloarene.



The reaction sequence is given as:



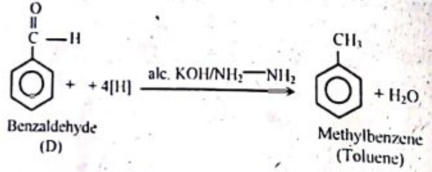
LONG ANSWER QUESTIONS [10 MARKS]

27. **2071 Supp. Q.No. 30b** **Identify the major products A, B, C and D in the following reaction sequences.**

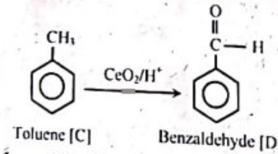
$$A \xrightarrow[\Delta]{Zn} B \xrightarrow[\Delta]{CH_3Cl/\ AlCl_3} C \xrightarrow[\Delta]{CeO_2/H^+} D$$

Compound D gives methylbenzene when heated with alc. KOH and hydrazine.

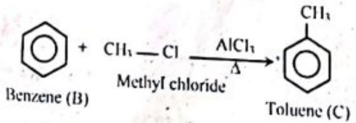
The compound (D) gives methylbenzene when heated with alc. KOH and hydrazine (Wolf-Kishner reduction). The compound 'D' must be aldehyde i.e. **benzaldehyde.**



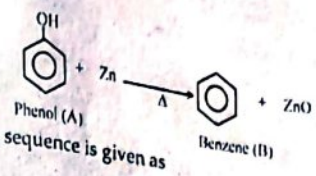
The compound (D) comes from (C). The compound (C) on oxidation with CeO_2/H^+, Benzaldehyde (D) is formed. The compound (C) must be toluene.



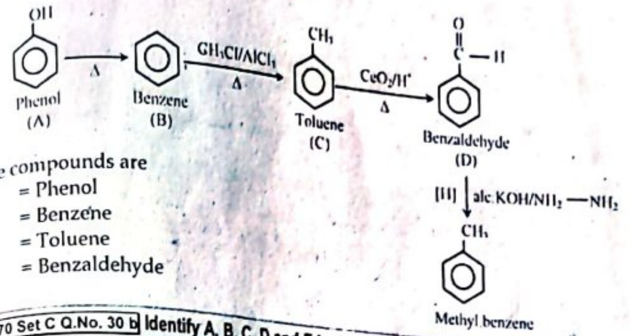
The compound (C) comes from (B) when treated with methyl chloride in the presence of $AlCl_3$. The compound (B) must be Benzene



The compound (B) comes from (A) when heated with Zn. The compound A must be phenol



The complete reaction sequence is given as



The compounds are

A = Phenol
B = Benzene
C = Toluene
D = Benzaldehyde

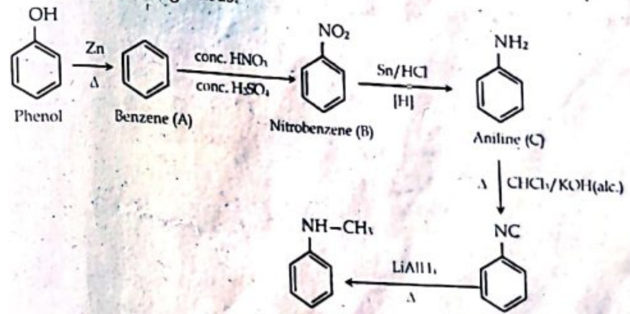
28. **2070 Set C Q.No. 30 b** **Identify A, B, C, D and E in the following reaction sequences.** **[2.5]**

$$(A) \xrightarrow[\Delta]{Con.HNO_3/H_2SO_4} (B) \xrightarrow[\Delta]{Sn/HCl} (C) \xrightarrow[\Delta]{CHCl_3/KOH(alc.)} (D) \xrightarrow[\Delta]{LiAlH_4} (E)$$

Compound A can be obtained by heating phenol in presence of Zn-dust.

The compound A can be obtained by heating phenol in presence of Zn-dust. So, A must be benzene.

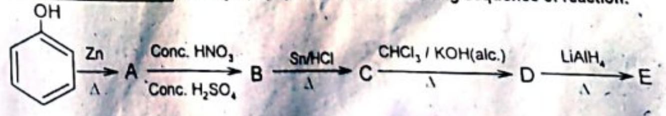
The reaction sequence is given as:



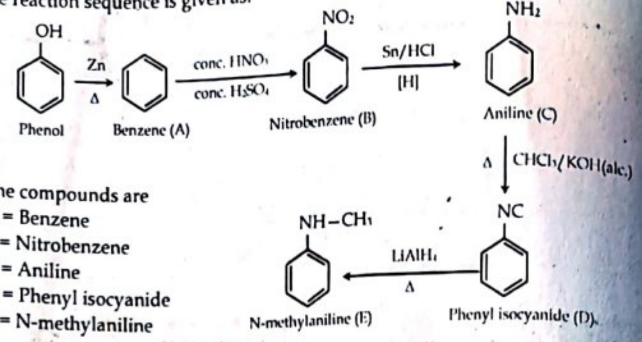
The compounds are

A = Benzene
B = Nitrobenzene
C = Aniline
D = Phenyl isocyanide
E = N-methylaniline

29. **2069 Supp. Set B Q.No. 31 b** **Identify A, B, C, D and E in the following sequence of reaction.** **[10]**



The reaction sequence is given as:



The compounds are
A = Benzene
B = Nitrobenzene
C = Aniline
D = Phenyl isocyanide
E = N-methylaniline

□□□

Unit 11

Ethers

11.1 Aliphatic Ethers

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2076 Set B Q.No. 11 **Identify the major products Ⓐ and Ⓑ giving their IUPAC names in the following reaction sequence:** [1+1]

$$\text{Ethoxyethane} \xrightarrow{\text{Excess HI}} Ⓐ \xrightarrow{\text{Sodium methoxide}} Ⓑ$$

The reaction sequence is given as

$$\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \xrightarrow[\text{Excess}]{HI} \underset{\substack{\text{Iodoethane}\\(A)}}{H_3C-CH_2-I} \xrightarrow[\text{Sod.methoxide}]{H_3C-ONa} \underset{\substack{\text{Methoxyethane}\\(B)}}{H_3C-CH_2-O-CH_3}$$

2. 2075 GIE Q.No. 11 **Prepare methoxyethane by Williamson's synthesis method. What happens when methoxyethane is treated with excess HI?** [1+1]

Preparation of methoxyethane: When sodium ethoxide is treated with iodomethane, methoxyethane is obtained.

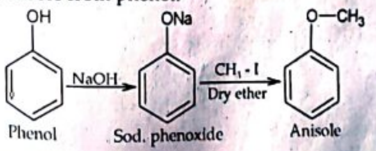
$$\underset{\text{Sodium ethoxide}}{H_3C-CH_2-ONa} + \underset{\text{Iodomethane}}{H_3C-I} \longrightarrow \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3}$$

When methoxyethane is treated with excess of HI, ethanol and iodomethane is obtained.

$$\underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3} \xrightarrow[HI]{\text{Excess}} \underset{\text{Ethanol}}{H_3C-CH_2-OH} + \underset{\text{Iodomethane}}{H_3C-I}$$

3. 2075 Set A Q.No. 11 **How would you obtain** [1+1]
   i. **Anisole from phenol**
   ii. **Methoxyethane from ethoxyethane.**

i. **Anisole from phenol:**



ii. **Methoxyethane from ethoxyethane:**

$$\underset{\text{Methoxyethane}}{H_3C-O-C_2H_5} \xrightarrow[\text{Cold}]{HI} \underset{\text{Ethanol}}{H_5C_2-O-H} \xrightarrow{NaOH} \underset{\text{Sod.ethoxide}}{H_5C_2-ONa} \xrightarrow{C_2H_5-I} \underset{\text{Ethoxyethane}}{H_5C_2-O-C_2H_5}$$

4. **2075 Set B Q.No. 11** **Give an example of unsymmetrical ether and write Williamson's synthesis process for its preparation.** **[1+1]**

Unsymmetrical ether: The ether having different alkyl group around the functional group is called unsymmetrical ether. Example:

$CH_3-O-CH_2-CH_3$ Methoxyethane $\quad$ $CH_3-O-CH_2-CH_2-CH_3$ 1-Methoxypropane

Preparation of Unsymmetrical ether by Williamson's Synthesis

$$\underset{\text{Sod.ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Methyl chloride}}{CH_3-Cl} \longrightarrow CH_3-CH_2-O-CH_3 + NaCl$$

5. **2074 Supp. Q.No. 11** **2074 Set A Q.No. 11** **2074 Set B Q.No. 11** **Write an example of Williamson's etherification reaction. What is its importance?** **[1+1]**

Williamson's etherification reaction: Please refer to 2074 Supp. Q.No. 11

The reaction in which alkyl halide and sod. or pot. alkoxide are reacted to form ether is known as Williamson's etherification reaction.

$$\underset{\text{Sod. alkoxide}}{R-ONa} + \underset{\text{Alkyl halide}}{R'-X} \xrightarrow[\Delta]{} \underset{\text{Ether}}{R-O-R'} + NaX$$

Both symmetrical or unsymmetrical ether can be prepared from this reaction.

$$\underset{\text{Sod. ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Iodoethane}}{I-CH_2-CH_3} \xrightarrow[\Delta]{} \underset{\text{Ethoxyethane}}{CH_3CH_2-O-CH_2CH_3} + NaI$$

Importance of Williamson's etherification reaction:

Following are the importance of Williamson's etherification reaction:

i. It involves the reaction of an alkoxide ion with a primary alkyl halide via an S_N2 reaction.

ii. It helps to prove the structure of ethers.

iii. It is suitable for the preparation of a wide variety of symmetrical or unsymmetrical ether.

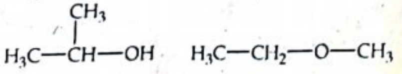
6. **2073 Supp Q.No. 11** **Convert ethoxyethane to methoxyethane.** **[2]**

When ethoxyethane is treated with water in the presence of acid, ethanol is formed. Ethanol is treated with sodium metal, sodium ethoxide is formed which on treatement with iodomethane, methoxyethane is obtained.

$$\begin{tikzcd}
\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \arrow[r, "H_2O/H^+"] & \underset{\text{Ethanol}}{H_3C-CH_2-OH} \arrow[r, "Na"] & \underset{\text{Sod. ethoxide}}{H_3C-CH_2-ONa} \arrow[d, "CH_3I"] \\
 & & \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3}
\end{tikzcd}$$

7. **2073 Set C Q.No. 11** **Write down isomeric ether of isopropyl alcohol and use Williamson's synthesis process for the preparation of such ether.** **[1+1]**

The isomeric ether of isopropyl alcohol is methoxyethane.



$H_3C-CH(CH_3)-OH \quad H_3C-CH_2-O-CH_3$

Isopropyl alcohol $\quad$ Methoxyethane

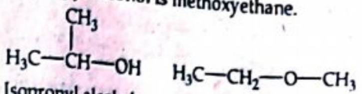
Williamson's synthesis: Methoxyethane is prepared by treating sodium ethoxide with methyl iodide.

CH₂-O CH₂ - C - CH₃ CH₃

$$\underset{\text{Sodium ethoxide}}{H_3C-CH_2-ONa} + \underset{\text{Methyl iodide}}{H_3C-I} \longrightarrow \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3}$$

8. **2073 Set D Q.No. 11** **Write down an isomeric ether of isopropyl alcohol. What happens when the isomeric ether is heated with excess HI?** **[1+1]**

The isomeric ether of isopropyl alcohol is methoxyethane.



$H_3C-CH(CH_3)-OH \quad H_3C-CH_2-O-CH_3$

Isopropyl alcohol $\quad$ Methoxyethane

When methoxyethane is heated with excess of HI, smaller alkyl group forms alkyl iodide and larger alkyl group forms alcohol.

$$\underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3} \xrightarrow[\text{Excess}]{HI} \underset{\text{Ethanol}}{H_3C-CH_2-OH} + \underset{\text{Iodomethane}}{H_3C-I}$$

9. **2072 Supp. Q.No. 11** **Write down the possible unsymmetrical ethers of $C_4H_{10}O$ and their IUPAC names.** **[2]**

Three possible iosomers of $C_4H_{10}O$ are

$\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \quad \underset{\text{1-Methoxypropane}}{H_3C-O-CH_2-CH_2-CH_3} \quad \underset{\text{2-Methoxypropane}}{H_3C-O-CH(CH_3)_2}$

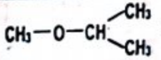
10. **2072 Set C Q.No. 11ii** **How would you obtain methoxyethane from ethanol** **[1]**

Methoxyethane from ethanol:

When ethanol is treated sodium metal, sodium ethoxide is obtained, sod ethoxide is treated with methyl idodide, methoxyethane is obtained.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow{Na} \underset{\text{Sod.ethoxide}}{H_3C-CH_2-ONa} \xrightarrow{CH_3I} \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3} + NaI$$

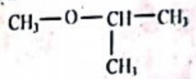
11. **2072 Set D Q.No. 11** **Write IUPAC name of**



$CH_3-O-CH(CH_3)_2$

and use Williamson's synthesis method for its preparation. **[1+1]**

The IUPAC name of structure is



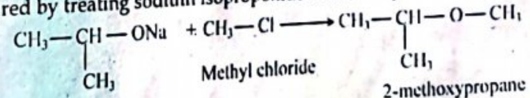
$CH_3-O-CH(CH_3)-CH_3$

2-methoxypropane

CH₃- C - CH₃

Preparation of 2-methoxypropane by Williamson's synthesis:

It is prepared by treating sodium isopropoxide with methyl chloride.



$$\underset{\text{Sod. isopropoxide}}{CH_3-CH(CH_3)-ONa} + \underset{\text{Methyl chloride}}{CH_3-Cl} \longrightarrow \underset{\text{2-methoxypropane}}{CH_3-CH(CH_3)-O-CH_3}$$

12. **2072 Set E Q.No. 11** **How is unsymmetrical ether prepared by Williamson's ether synthesis?** **[2]**

Please refer to 2075 Set B Q.No. 11

13. **2071 Supp. Q.No. 11** **What are unsymmetrical ethers? Give Williamson's synthesis to prepare unsymmetrical ethers.** **[1+1]**

Please refer to 2075 Set B Q.No. 11

14. 2071 Set C Q.No. 11 Write an unsymmetrical ether of C_3H_8O. How would you prepare the ether by using Williamson's synthesis? **[2]**

➢ Unsymmetrical ether of C_3H_8O is

$$CH_3-CH_2-O-CH_3$$

Methoxyethane

Methoxyethane is prepared by heating sodium ethoxide with iodomethane.

$$\underset{\text{Sod. ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Iodomethane}}{CH_3-I} \longrightarrow \underset{\text{Methoxyethane}}{CH_3-CH_2-O-CH_3} + NaI$$

---

15. 2070 Set C Q.No. 11 What is unsymmetrical ether? Write an example and IUPAC name. **[2]**

➢ The ether having two different alkyl groups is called unsymmetrical or mixed ether.

Example:

$$\underset{\text{Methoxyethane}}{H_3C-O-C_2H_5} \qquad \underset{\text{Methoxypropane}}{H_3C-O-C_3H_7}$$

---

16. 2070 Set D Q.No. 11 Prepare $CH_3-O-CH_2CH_3$ by using Williamson's ether synthesis. **[2]**

➢ When sodium ethoxide is heated with iodomethane, methoxyethane is formed. This reaction is called Williamson's ether synthesis.

$$\underset{\text{Sod. ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Iodomethane}}{CH_3-I} \longrightarrow \underset{\text{Methoxyethane}}{CH_3-CH_2-O-CH_3} + NaI$$

---

17. 2069 Supp. Set B Q.No. 11 Name the isomer of C_2H_6O which reacts with excess of HI, gives iodomethane as major product, and write reaction. **[2]**

➢ The functional isomers of C_2H_6O are

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \qquad \underset{\text{Methoxymethane}}{H_3C-O-CH_3}$$

Methoxymethane reacts with excess of HI to form iodomethane.

$$\underset{\text{Methoxymethane}}{H_3C-O-CH_3} + (\text{excess})2HI \longrightarrow \underset{\text{Iodomethane}}{2\,CH_3-I} + H_2O$$

---

18. 2069 Set A Q.No. 10 Give an example of Williamson's etherification. **[2]**

➢ Please refer to 2074 Supp. Q.No. 11

19. 2069 Set B Q.No. 11 Name the isomer of C_2H_6O which reacts with excess HI, gives iodomethane as major product and write reaction for it. **[2]**

➢ Please refer to 2069 Supp. Set B Q.No. 11

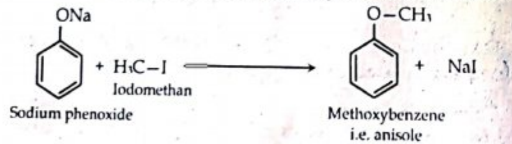
20. 2068 Q.No. 5 Write chemical equation for the reactions taking place when: **[2]**

i. Sodium phenoxide reacts with iodomethane.

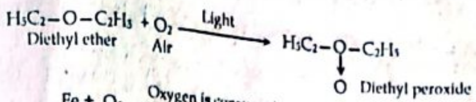
ii. Ethoxyethane is exposed to light and air.

➢

i. Sodium phenoxide reacts with iodomethane, methoxy benzene i.e. anisole is formed.



ii. Ether i.e. diethyl ether is highly reactive towards atmospheric oxygen in the presence of sunlight and forms peroxide which explodes on heating causing serious accident. When ether is kept in bottle containing iron wire the oxygen combines with iron to form iron oxide and it prevents the formation of peroxide. Therefore, ether is stored in a bottle containing iron wire.



$$\underset{\text{Diethyl ether}}{H_5C_2-O-C_2H_5} + \underset{\text{Air}}{O_2} \xrightarrow{\text{Light}} \underset{\substack{\downarrow \\ O}}{H_5C_2-O-C_2H_5} \text{ Diethyl peroxide}$$

$$Fe + O_2 \xrightarrow{\text{Oxygen is consumed}} FeO$$

---

21. **2066 Q. No. 6 What is Williamson's etherification reaction?** **[2]**

➢ The reaction in which alkyl halide and sod. or pot. alkoxide are reacted to form ether is known as **Williamson's etherification reaction.**

$$\underset{\text{Sod. alkoxide}}{R-ONa} + \underset{\text{Alkyl halide}}{R'-X} \xrightarrow[\Delta]{} \underset{\text{Ether}}{R-O-R'} + NaX$$

Both symmetrical or unsymmetrical ether can be prepared from this reaction.

$$\underset{\text{Sod. ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Iodoethane}}{I-CH_2-CH_3} \xrightarrow[\Delta]{} \underset{\text{Ethoxyethane}}{CH_3CH_2-O-CH_2CH_3} + NaI$$

---

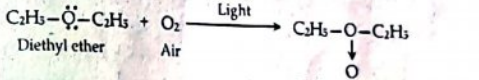
22. **2065 Q.No. 6 Give reason:** **[2]**

i. It is dangerous to boil sample of ether stored for a long time.

ii. Ether is stored in a bottle containing iron wire.

➢

i. Due to the presence of lone pair of electrons on the ethereal oxygen, ether when comes in contact with atmospheric oxygen in the presence of sunlight, ether reacts with oxygen to form ether peroxide or hydroperoxide which are highly unstable and explosive. They explode violently on strong heating causing serious accidents.



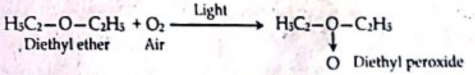
$$\underset{\text{Diethyl ether}}{C_2H_5-\ddot{\underset{\cdot\cdot}{O}}-C_2H_5} + \underset{\text{Air}}{O_2} \xrightarrow{\text{Light}} \underset{\substack{\downarrow \\ O}}{C_2H_5-O-C_2H_5}$$

Ether peroxide (Explosive)

So, the sample of ether stored for a long time may contain some amount of peroxide or hydroperoxide and cause serious accident on heating. Therefore, it is dangerous to boil the sample of ether stored for a long time.

ii. **Ether is stored in a bottle containing iron wire.**

Ether i.e. diethyl ether is highly reactive towards atmospheric oxygen in the presence of sunlight and forms peroxide which explodes on heating causing serious accident. When ether is kept in bottle containing iron wire, the oxygen combines with iron to form iron oxide and it prevents the formation of peroxide. Therefore, ether is stored in a bottle containing iron wire.



$$\underset{\text{Diethyl ether}}{H_5C_2-O-C_2H_5} + \underset{\text{Air}}{O_2} \xrightarrow{\text{Light}} \underset{\substack{\downarrow \\ O}}{H_5C_2-O-C_2H_5} \text{ Diethyl peroxide}$$

$$Fe + O_2 \xrightarrow{\text{Oxygen is consumed}} FeO$$

---

23. 2064 Q.No. 8 There are three possible isomeric ethers of $C_4H_{10}O$. One of them is ethoxyethane. Write other two isomers and give their IUPAC name. **[2]**

➢ Please refer to 2072 Supp. Q.No. 11

24. 2062 Q.No. 4 Write the sequence of chemical reactions for the conversion of ethoxyethane to methoxyethane. **[2]**

➢ Please refer to 2073 Supp Q.No. 11

25. 2061 Q.No. 2 **Write IUPAC names of ethers represented by the molecular formula $C_5H_{12}O$.** [2]

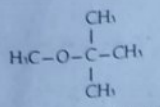
➤ The IUPAC name of ethers having molecular formula $C_5H_{12}O$ are

$H_3C-O-CH_2-CH_2-CH_2-CH_3$

1-Methoxybutane

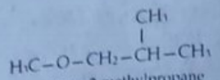
$H_3C-CH_2-O-CH_2-CH_2-CH_3$

1-Ethoxypropane



$H_3C-O-C(CH_3)_2-CH_3$

2-methoxy-2-methylpropane



$H_3C-O-CH_2-CH(CH_3)-CH_3$

1-methoxy-2-methylpropane

---

26. 2060 Q.No. 4 **What is the action of ethoxyethane on:** [2]

i. **PCl_5 and** ii. **aq. HI (cold)?**

➤ **Action of ethoxyethane on:**

i. **PCl_5:** Ethoxyethane reacts with PCl_5, ethyl chloride is obtained.

$$\underset{\text{Ethoxyethane}}{H_5C_2-O-C_2H_5} + PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{2\,H_5C_2-Cl} + POCl_3$$

ii. **Aq.HI (cold):** Ethoxyethane reacts with aq. HI in cold condition, ethyl iodide and ethyl alcohol is formed.

$$\underset{\text{Ethoxyethane}}{H_5C_2-O-C_2H_5} + HI \xrightarrow{\text{Cold}} \underset{\text{Ethyl iodide}}{H_5C_2-I} + \underset{\text{Ethyl alcohol}}{C_2H_5-OH}$$

---

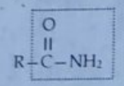
27. 2053 Q.No. 15 **What is the functional group of ether and amide?** [2]

➤ Functional group of (i) ether is

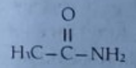
$R-O-R$ Alkoxy group $H_3C-O-CH_3$

Methoxymethane

Functional group of (ii) amide is



$R-\overset{O}{\overset{\|}{C}}-NH_2$



$H_3C-\overset{O}{\overset{\|}{C}}-NH_2$

Ethanamide

SHORT ANSWER QUESTIONS [5 MARKS]

28. 2074 Set A Q.No. 27 **Describe the laboratory method of preparation of ethoxyethane. How is ethoxyethane converted into methoxyethane?** [4+1]

➤ **Laboratory preparation of ethoxyethane:**

Principle: When excess of ethyl alcohol (ethanol) is heated with conc. H_2SO_4 at 140°C diethyl ether or ethoxyethane is obtained.

$$\underset{\substack{\text{Ethyl alcohol}\\ \text{(Ethanol)}}}{H_3C-CH_2-OH} + H_2SO_4 \xrightarrow{100^\circ C} \underset{\text{Ethyl hydrogen sulphate}}{H_3C-CH_2-HSO_4} + H_2O$$

$$\underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{H_3C-CH_2-HSO_4} + \underset{\substack{\text{Ethyl alcohol}\\ \text{(Ethanol)}}}{H_3C-CH_2-OH} \xrightarrow{140^\circ C} \underset{\substack{\text{Diethyl ether}\\ \text{(Ethoxyethane)}}}{H_3C-CH_2-O-CH_2-CH_3} + H_2SO_4$$

Procedure: 50 cc of conc. H_2SO_4 is gradually added with constant shaking to 100 cc of ethanol kept in the distillation flask. The mixture is heated on a water bath at 140°C, when ether begins to distill over. Alcohol is added in the distillation flask from the dropping funnel at nearly the same rate as that of the distillation, the temperature being maintained at 140°C.

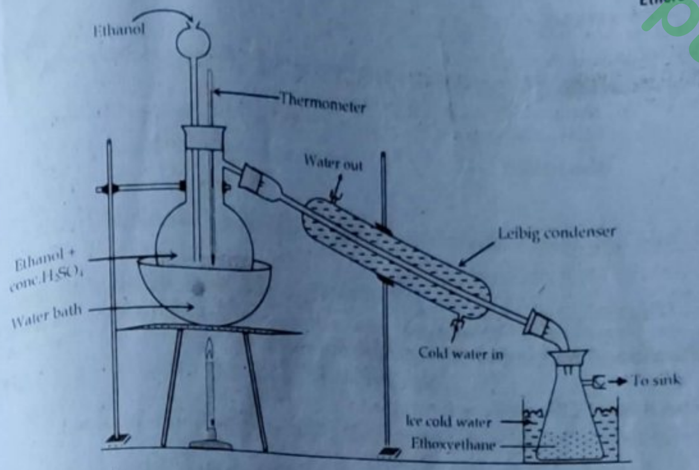


Figure: Laboratory preparation of ethoxyethane

Purification: The distillate contains ether, ethanol, water and sulphur dioxide. It is first washed with dil. NaOH solution and then with water. The upper layer is separated and dried over anhydrous $CaCl_2$. It is then redistilled on a water bath pure ether passes over at 34-35°C.

Conversion: ethoxyethane into methoxyethane:

When ethoxyethane is treated with water in the presence of acid, ethanol is formed. Ethanol is treated with sodium metal, sodium ethoxide is formed which on treatement with iodomethane, methoxyethane is obtained.

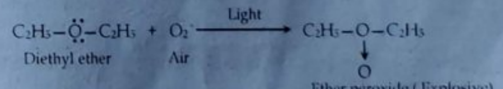
$$\begin{tikzcd}
\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \arrow[r, "H_2O/H^+"] & \underset{\text{Ethanol}}{H_3C-CH_2-OH} \arrow[r, "Na"] & \underset{\text{Sod. ethoxide}}{H_3C-CH_2-ONa} \arrow[d, "CH_3I"] \\
 & & \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3}
\end{tikzcd}$$

---

29. 2074 Set B Q.No. 27 **Describe the laboratory method of preparation of ethoxyethane. Why is it dangerous to boil old sample of ether?** [4+1]

➤ **Laboratory preparation of ethoxyethane:** Please refer to 2074 Set A Q.No. 27

Ether is dangerous to boil old sample: Due to the presence of lone pair of electrons on the ethereal oxygen, ether when comes in contact with atmospheric oxygen in the presence of sunlight, ether reacts with oxygen to form ether peroxide or hydroperoxide which are highly unstable and explosive. They explode violently on strong heating causing serious accidents.



$$\underset{\text{Diethyl ether}}{C_2H_5-\ddot{\underset{..}{O}}-C_2H_5} + \underset{\text{Air}}{O_2} \xrightarrow{\text{Light}} C_2H_5-\underset{\substack{\downarrow\\ O}}{O}-C_2H_5$$

Ether peroxide (Explosive)

So, the sample of ether stored for a long time may contain some amount of peroxide or hydroperoxide and cause serious accident on heating. Therefore, it is dangerous to boil the sample of ether stored for a long time.

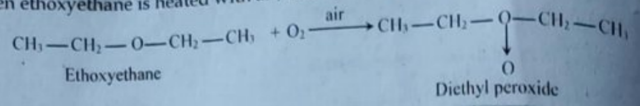
---

30. 2073 Set D Q.No. 27 **Describe the laboratory method of preparation of ethoxyethane. What happens when ethoxyethane is exposed to air?** [4+1]

➤ **Laboratory preparation of ethoxyethane:** Please refer to 2074 Set A Q.No. 27

Ethoxyethane is exposed in air:

When ethoxyethane is heated with air, ether peroxide is obtained.



$$\underset{\text{Ethoxyethane}}{CH_3-CH_2-O-CH_2-CH_3} + O_2 \xrightarrow{\text{air}} \underset{\text{Diethyl peroxide}}{CH_3-CH_2-\underset{\underset{O}{\downarrow}}{O}-CH_2-CH_3}$$

31\. **2072 Supp. Q.No. 28 Write down laboratory method of preparation of ethoxyethane.** [5]

Please refer to 2074 Set A Q.No. 27

32\. **2071 Supp. Q.No. 28 2071 Set C Q.No. 26 2071 Set D Q.No. 28 Write down suitable chemical reaction for the preparation of ethoxyethane from ethanol. How is ethoxyethane converted into methoxyethane? What happens when ethoxyethane is heated with:** [1+2+1+1]

i. air ii. conc. H_2SO_4

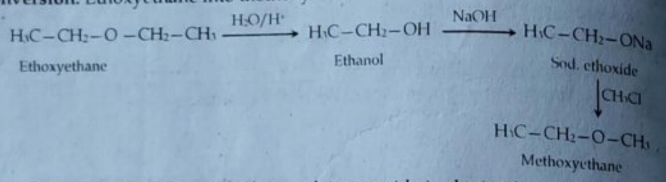
Preparation of Ethoxyethane from ethanol:

When ethanol is heated with conc. H_2SO_4 at 140°C, ethoxyethane is obtained.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + \text{Conc. } H_2SO_4 \xrightarrow[\Delta]{100^\circ C} \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-SO_4H} + H_2O$$

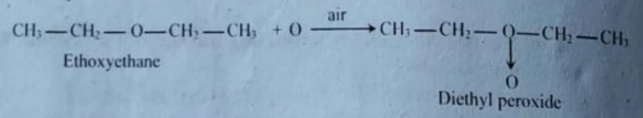
$$\underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-SO_4H} + \underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[\Delta]{140^\circ C} \underset{\text{Ethoxyethane}}{CH_3-CH_2-O-CH_2-CH_3} + H_2SO_4$$

Conversion: Ethoxyethane into methoxyethane



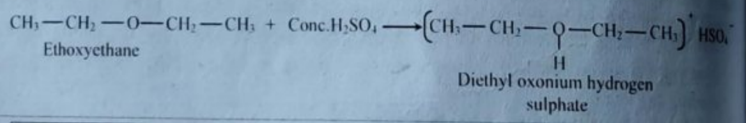
$$\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \xrightarrow{H_2O/H^+} \underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow{NaOH} \underset{\text{Sod. ethoxide}}{H_3C-CH_2-ONa} \xrightarrow{CH_3Cl} \underset{\text{Methoxyethane}}{H_3C-CH_2-O-CH_3}$$

i. When ethoxyethane is heated with air, ether peroxide is obtained.



$$\underset{\text{Ethoxyethane}}{CH_3-CH_2-O-CH_2-CH_3} + O \xrightarrow{\text{air}} \underset{\text{Diethyl peroxide}}{CH_3-CH_2-\underset{\underset{O}{\downarrow}}{O}-CH_2-CH_3}$$

ii. When ethoxyethane is heated with conc. H_2SO_4, diethyl oxonium hydrogen sulphate is obtained.



$$\underset{\text{Ethoxyethane}}{CH_3-CH_2-O-CH_2-CH_3} + \text{Conc.}H_2SO_4 \longrightarrow \underset{\text{Diethyl oxonium hydrogen sulphate}}{\left(CH_3-CH_2-\underset{H}{\underset{|}{O}}-CH_2-CH_3\right)^+ HSO_4^-}$$

33\. **2070 Set D Q.No. 23 How is ethoxyethane prepared in the laboratory in pure and dry state?** [5]

Please refer to 2074 Set A Q.No. 27

34\. **2069 (Set A) Q.No. 28 Describe laboratory preparation of ethoxyethane with a neat and labelled diagram.** [5]

Please refer to 2074 Set A Q.No. 27

35\. **2069 (Set B) Q.No. 24 How is ethoxyethane prepared in the laboratory? Write Williamsons' synthesis for the preparation of an unsymmetrical ether.** [5]

Laboratory preparation: Please refer to 2074 Set A Q.No. 27

Preparation of unsymmerical ether:

$$\underset{\text{Sod.ethoxide}}{CH_3-CH_2-ONa} + \underset{\text{Methyl chloride}}{CH_3-Cl} \longrightarrow CH_3-CH_2-O-CH_3 + NaCl$$

36\. **2065 Q.No. 23 ii Ethoxyethane into methoxyethane** [2.5]

Please refer to 2074 Set A Q.No. 27

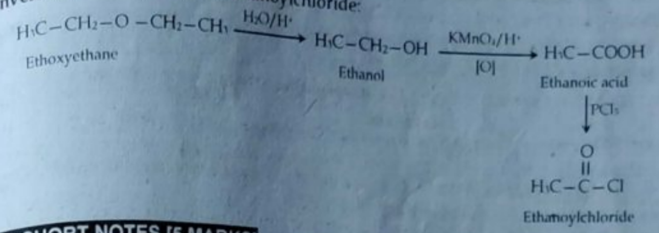
37\. **2063 Q.No. 23 Describe the preparation of ethoxyethane in the laboratory.** [5]

Please refer to 2074 Set A Q.No. 27

38\. **2058 Q.No. 22(b) Convert the following organic compounds.** [2.5]

Ethoxyethane to ethanoylchloride.

Conversion: Ethoxyethane to ethanoylchloride:



$$\underset{\text{Ethoxyethane}}{H_3C-CH_2-O-CH_2-CH_3} \xrightarrow{H_2O/H^+} \underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow[\text{[O]}]{KMnO_4/H^+} \underset{\text{Ethanoic acid}}{H_3C-COOH} \xrightarrow{PCl_5} \underset{\text{Ethanoylchloride}}{H_3C-\overset{\overset{O}{\|}}{C}-Cl}$$

WRITE SHORT NOTES [5 MARKS]

39\. **2076 Set C Q.No. 33iv 2072 Set E Q.No. 33iii 2070 Supp. Q.No. 33b 2070 Set C Q.No. 33d 2066 Q. No. 31i 2068 Q.No. 31iii Laboratory preparation of ethoxyethane** [5]

Please refer to 2074 Set A Q.No. 27

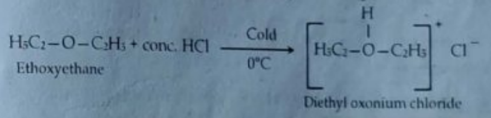
40\. **2060 Q.No. 31(iv) Laboratory preparation of diethyl ether** [5]

Please refer to 2074 Set A Q.No. 27

41\. **2059 Q.No. 29(iv) Predict the major products of the following reactions:** [5]

$$C_2H_5OC_2H_5 \xrightarrow[0^\circ C]{\text{Conc. HCl}} \ldots\ldots\ldots$$

Ethoxyethane reacts with cold and conc. HCl to give diethyl oxonium chloride.



$$\underset{\text{Ethoxyethane}}{H_5C_2-O-C_2H_5} + \text{conc. HCl} \xrightarrow[0^\circ C]{\text{Cold}} \underset{\text{Diethyl oxonium chloride}}{\left[H_5C_2-\overset{\overset{H}{|}}{O}-C_2H_5\right]^+ Cl^-}$$

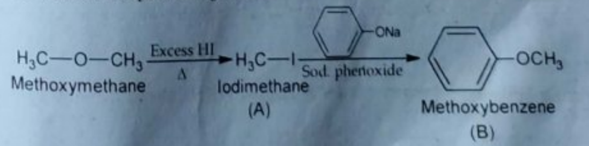
11.2 Aromatic Ether

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1\. **2076 Set C Q.No. 11 Identify the major products Ⓐ and Ⓑ giving their IUPAC names in the given reaction sequence.** [1+1]

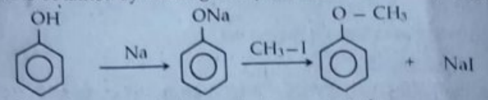
$$\text{Methoxymethane} \xrightarrow[\Delta]{\text{excess HI}} Ⓐ \xrightarrow[\Delta]{\text{Sodium phenoxide}} Ⓑ$$

The reaction sequence is given as



2. **2072 Set C Q.No. 11** **How would you obtain anisole from phenol** [1]

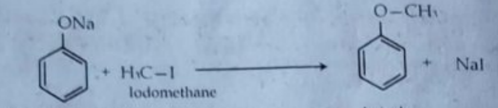
Anisole from phenol: When phenol is treated with sodium metal, sodium phenolate is obtained. Anisole is obtained by treating sod. phenolate with methyl iodide.



Phenol Sod. phenolate Anisole

3. **2071 Set D Q.No. 11 a** **Give correct chemical reaction for the preparation of: anisole** [1]

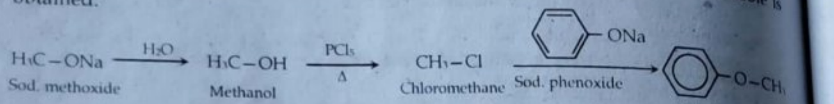
When sodium phenoxide reacts with iodomethane, methoxybenzene i.e. anisole is formed.



Sodium phenoxide Anisole

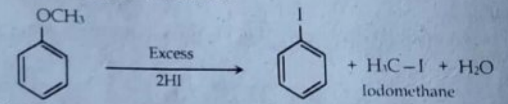
4. **2070 Supp. Q.No. 11** **Starting from CH_3ONa, how would you prepare methoxybenzene? What happens when methoxybenzene is treated with excess HI?**

Preparation of methoxybenzene from CH_3ONa: When sod.methoxide is treated with water, methanol is obtained. Methanol on treatement with PCl_5, chloromethane is obtained. Chloromethane is treated with sod.phenoxide, methoxybenzene i.e. anisole is obtained.



Anisole

When methoxybenzene is treated with excess of HI, only halo compound i.e. iodobenzene and iodomethane is formed.



Methoxybenzene Iodobenzene

5. **2070 Set D Q.No. 11** **Prepare**  **$-OCH_3$ by using Williamson's ether synthesis.**

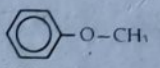
Please refer to 2071 Set D Q.No. 11 a

6. **2063 Q.No. 3(i)** **Write the action of Sodium phenolate with iodomethane.**

Please refer to 2071 Set D Q.No. 11 a

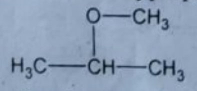
7. **2057 Q.No. 4** **Write the structure of**

i. Anisole and **ii. 2 – methoxypropane.**

i. **Structure of Anisole:** 

हारजित, शत्रु, रातमै
हुदैँ चल्दो, or(आज)

ii. **Structure of 2-methoxypropane**



$$H_3C-\overset{\overset{O-CH_3}{|}}{CH}-CH_3$$

2-methoxypropane

❑❑❑

Unit 12

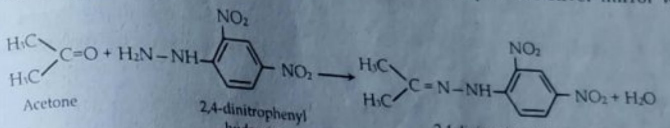
Aldehydes and Ketones

12.1 Aliphatic Aldehydes and Ketones

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 12** **An organic compound C_3H_6O gives orange precipitate with 2,4-dinitrophenyl hydrazine but does not produce silver mirror with Tollen's reagent. Identify the compound and write the reaction involved.** [2]

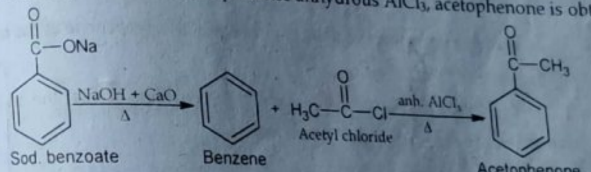
The organic compound having molecular formula C_3H_6O must be acetone which gives orange ppt with 2,4-dinitrophenylhydrazoine but does not produce silver mirror with Tollen's reagent.



Acetone 2,4-dinitrophenyl hydrazine 2,4-dinitrophenylhydrazone (red ppt)

2. **2076 Set C Q.No. 8** **How is sodiumbenzoate converted into acetophenone?** [2]

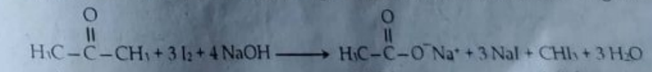
When sod. Benzoate is heated with sodalime, benzene is obtained which on treatment with acetyl chloride in the presence anhydrous $AlCl_3$, acetophenone is obtained.



Sod. benzoate Benzene Acetyl chloride Acetophenone

3. **2076 Set C Q.No. 12** **An organic Compound C_3H_6O does not give silver mirror with Tollen's reagent but gives yellow precipitation with NaOH and I_2. Identify the compound and write the reactions involved.** [2]

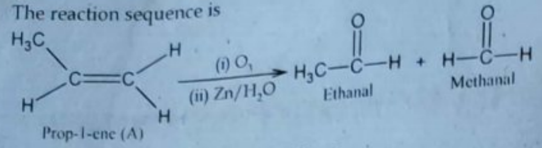
The organic compound having molecular formula C_3H_6O must be acetone which gives yellow ppt with $NaOH/I_2$ but does not give silver mirror with Tollen's reagent.



$$\underset{\text{Acetone}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Sod. Ethanoate}}{H_3C-\overset{\overset{O}{\|}}{C}-O^-Na^+} + 3NaI + \underset{\text{Iodoform}}{CHI_3} + 3H_2O$$

4. **2075 GIE Q.No. 12 An alkene Ⓐ undergoes ozonolysis to give ethanal and methanal as the major products. Identify Ⓐ and give its IUPAC name.** [1+1]

➢ The reaction sequence is

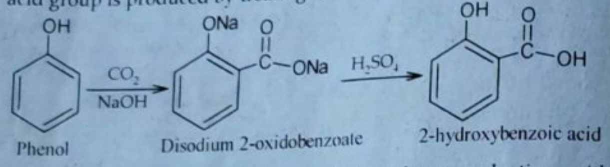


The organic compound A is prop-1-ene.

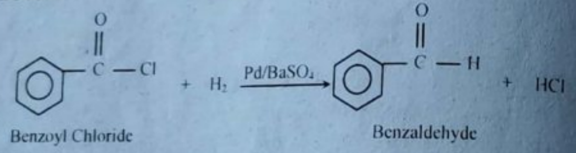
5. **2075 GIE Q.No. 13 Write an example of**
   - **i. Carboxylation reaction**
   - **ii. Rosemunnd's reduction** [1+1]

➢ Example of

i. **Carboxylation reaction**: Carboxylation is a chemical reaction in which a carboxylic acid group is produced by treating a substrate with carbon dioxide.

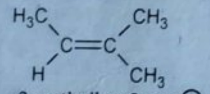


i. **Rosenmund's reduction:** When acid chloride on reduction with hydrogen in the presence of palladium and barium sulphate, aldehyde is obtained. This reaction is called Rosenmund's reduction.



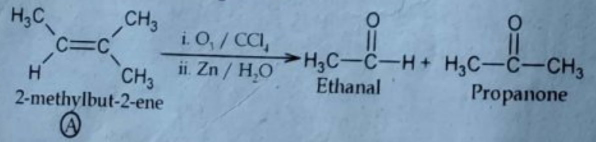
6. **2075 Set A Q.No. 12 An alkene Ⓐ undergoes ozonlysis to give ethanal and propanone as the major products. Identify Ⓐ and write its IUPAC name.** [1+1]

➢ Ethanal contains two carbons and propanone contains three carbons. Thus, the alkene has total five carbons. The structure of alkene Ⓐ must be



2-methylbut-2-ene Ⓐ

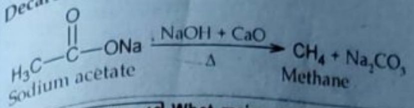
The rection sequence is given as:



7. **2075 Set A Q.No. 13 Write an example of each of the followings.** [1+1]
   - **i. Rosemunnd's reduction**
   - **ii. Decarboxylation reaction**

➢ i. Rosemunnd's reduction: Please refer to 2075 GIE Q.No. 13

ii. Decarboxylation reaction:

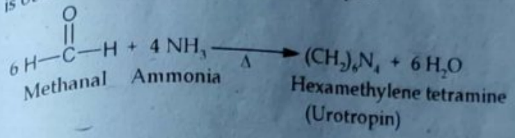


$$H_3C-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow[\Delta]{NaOH + CaO} CH_4 + Na_2CO_3$$

Sodium acetate Methane

8. **2075 Set B Q.No. 12 What major product would you obtain when methanal reacts with ammonia? Write an important use of the product.** [1+1]

➢ When methanal is reacted with ammonia, hexamethylenetetramine $(CH_2)_6N_4$ (Urotropin) is obtained. It is used as urinary antiseptic.



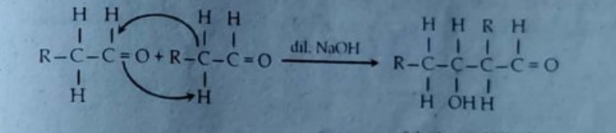
$$6\,H-\overset{O}{\overset{\|}{C}}-H + 4\,NH_3 \xrightarrow{\Delta} (CH_2)_6N_4 + 6\,H_2O$$

Methanal Ammonia Hexamethylene tetramine (Urotropin)

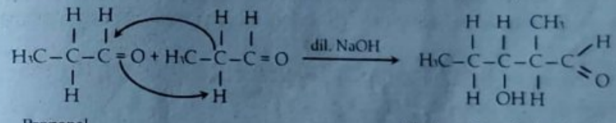
9. **2074 Supp. Q.No. 12 Write an example of each of the following.** [1+1
   - **i. Aldol condensation**
   - **ii. Rosenmund's reduction**

➢

i. **Aldol Condensation:** When two molecules of aldehyde or ketone having at least one α-hydrogen dimerises in the presence of dilute NaOH then β-hydroxy aldehyde or ketone i.e. aldol or ketol is formed. This condensation reaction is known as **Aldol condensation** reaction.



β-hydroxy aldehyde



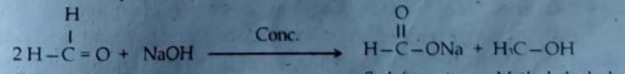
Propanal 3-hydroxy-2-methylpentanal

i. **Rosemunnd's reduction**: Please refer to 2075 GIE Q.No. 13

10. **2074 Set A Q.No. 12 Write an example of each of the following** [1+1]
    - **i. Cannizzaro's reaction**
    - **ii. DNP Test**

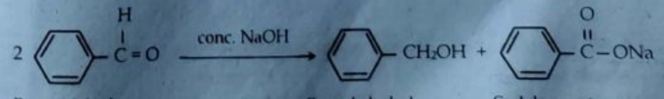
➢

i. **Cannizzaro's reaction:** Aldehyde containing no alpha hydrogen atom, when heated with conc. NaOH undergoes self oxidation-reduction reaction to yield a mixture of an alcohol and a salt of carboxylic acid. This reaction is known as **Cannizzaro's reaction.**



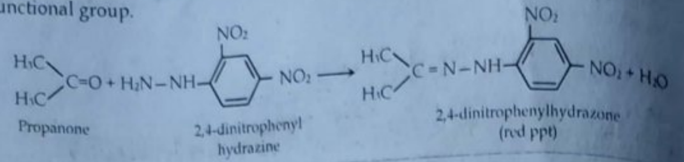
$$2\,H-\overset{H}{\overset{|}{C}}=O + NaOH \xrightarrow{Conc.} H-\overset{O}{\overset{\|}{C}}-ONa + H_3C-OH$$

Formaldehyde Sod. formate Methyl alcohol



Benzaldehyde Benzyl alcohol Sod. benzoate

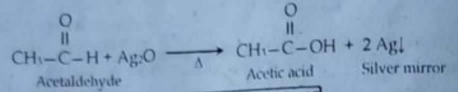
ii. **DNPH test:** Aldehyde or ketone reacts with DNPH i.e. 2,4-dinitrophenyl hydrazine, a red ppt of 2,4-dinitrophenylhydrozone is formed. This test is used to identify carbonyl functional group.



11. 2074 Set B Q.No. 12 **Write an example of each of the following** [1+1]
    i. Tollen's test
    ii. Aldol condensation

i. **Tollen's test:**

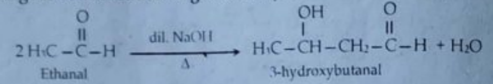
$$2AgNO_3 + 2NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2NH_4NO_3 + H_2O$$


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

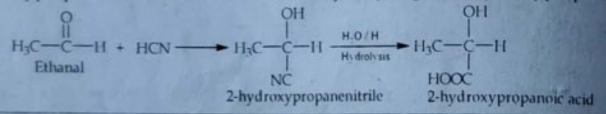
ii. **Aldol condensation:** Please refer to 2074 Supp. Q.No. 12

12. 2073 Supp Q.No. 12 **Starting from ethanal, how would you obtain**
    i. 3 - hydroxybutanal
    ii. 2-hydroxypropanoic acid [1+1]

i. **3-hydroxybutanal from ethanal:** Ethanal is heated with dil.NaOH, two molecules of ethanal undergoes condensation to give aldol product i.e. 3-hydroxybutanal.


$$\underset{\text{Ethanal}}{2H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} \xrightarrow[\Delta]{\text{dil. NaOH}} \underset{\text{3-hydroxybutanal}}{H_3C-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

ii. **2-hydroxypropanoic acid from ethanal:** When ethanal is treated with HCN, 2-hydroxypropanenitrile is obtained which on hydrolysis gives 2-hydroxypropanoic acid.

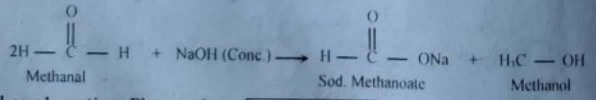

$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCN \longrightarrow \underset{\text{2-hydroxypropanenitrile}}{H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle NC}{|}}{C}}-H} \xrightarrow[\text{Hydrolysis}]{H_2O/H^+} \underset{\text{2-hydroxypropanoic acid}}{H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle HOOC}{|}}{C}}-H}$$

13. 2073 Set C Q.No. 12 **How would you obtain** [1+1]
    i. 3-hydroxybutanal and
    ii. 2-hydroxypropanoic acid from ethanal?

Please refer to 2073 Supp Q.No. 12

14. 2073 Set D Q.No. 12 **Write an example of**
    i. Cannizzaro's reaction
    ii. Aldol Condensation

i. **Cannizzaro's Reaction:** Aldehyde containing no α-hydrogen when treated with aqueous or ethanolic alkali, undergo disproportion to produce corresponding acid and alcohol. This simultaneous oxidation and reduction of aldehyde is known as Cannizzaro's reaction.


$$\underset{\text{Methanal}}{2H-\overset{\overset{\displaystyle O}{\|}}{C}-H} + NaOH\,(\text{Conc.}) \longrightarrow \underset{\text{Sod. Methanoate}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa} + \underset{\text{Methanol}}{H_3C-OH}$$

ii. **Aldol condensation:** Please refer to 2074 Supp. Q.No. 12

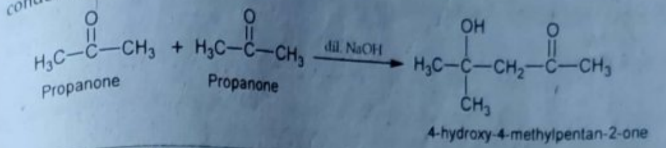
15. 2072 Set C Q.No. 12 **Write an example of:** [1+1]
    i. Rosenmund's reduction
    ii. Cannizzaro's reaction

i. **Rosemunnd's reduction:** Please refer to 2075 GIE Q.No. 13

ii. **Cannizzaro's reaction:** Please refer to 2073 Set D Q.No. 12

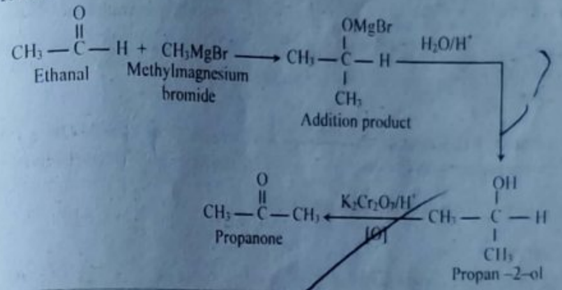
16. 2072 Set E Q.No. 12 **What happens when Propanone is treated with dilute NaOH solution.** [1]

When two molecules of propanone is condensed with dilute NaOH solution at room temperature, 4-hydroxy-4-methylpentan-2-one is obtained. This reaction is called aldol condensation.


$$\underset{\text{Propanone}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + \underset{\text{Propanone}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{\text{dil. NaOH}} \underset{\text{4-hydroxy-4-methylpentan-2-one}}{H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

17. 2071 Supp. Q.No. 12 **How is ethanal converted into propanone?** [2]

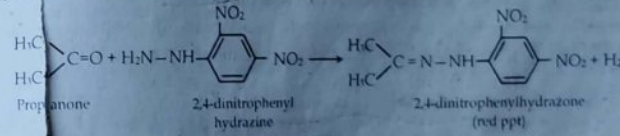
Conversion:


$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \underset{\text{Methylmagnesium bromide}}{CH_3MgBr} \longrightarrow \underset{\text{Addition product}}{CH_3-\overset{\overset{\displaystyle OMgBr}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H} \xrightarrow{H_2O/H^+} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{Propanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

18. 2071 Set C Q.No. 12 **Give an application of each:** [2]
    i. DNP test
    ii. Tollen's test

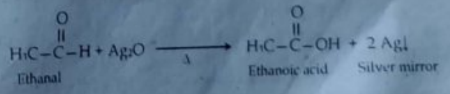
Application of

i. **DNP test:** This test identifies the organic compound having carbonyl group. Aldehyde or ketone both have carbonyl group and shows the DNP test.



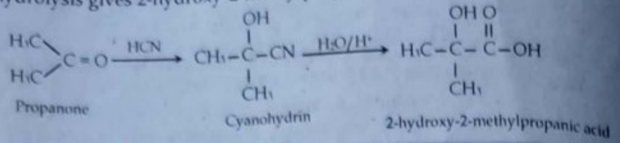
ii. **Tollen's test:** This test identifies the organic compound having aldehydic functional group. Ketone does not give this test.

$$2AgNO_3 + 2NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2NH_4NO_3 + H_2O$$


$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

19. **2071 Set D Q.No. 12 Starting from propanone, how would you prepare 2-hydroxy-2methylprop acid?**

Propanone is treated with hydrogen cyanide (HCN), cyanohydrin is formed which acid hydrolysis gives 2-hydroxy-2-methylpropanoic acid.



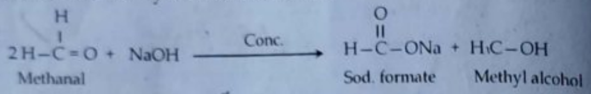
$$\underset{\text{Propanone}}{(H_3C)_2C=O} \xrightarrow{HCN} \underset{\text{Cyanohydrin}}{CH_3-\overset{OH}{\overset{|}{C}}(CH_3)-CN} \xrightarrow{H_2O/H^+} \underset{\text{2-hydroxy-2-methylpropanic acid}}{H_3C-\overset{OH}{\overset{|}{C}}(CH_3)-\overset{O}{\overset{\|}{C}}-OH}$$

20. **2070 Supp. Q.No. 12 How does methanal reacts with**
    - i. **ammonia**
    - ii. **conc. NaOH**

i. **Methanal with NH$_3$:** Formaldehyde i.e. methanal reacts with ammonia giv hexamethylene tetramine which is used as urinary antiseptic.

$$\underset{\text{Methanal}}{6\,H-\overset{O}{\overset{\|}{C}}-H} + 4\,NH_3 \longrightarrow \underset{\text{Hexamethylenetetramine}}{(CH_2)_6N_4} + 6\,H_2O$$

ii. **Methanal with conc. NaOH:** Methanal or formaldehyde reacts with conc. NaOH sodium formate and methyl alcohol is obtained.



$$\underset{\text{Methanal}}{2\,H-\overset{H}{\overset{|}{C}}=O} + NaOH \xrightarrow{Conc.} \underset{\text{Sod. formate}}{H-\overset{O}{\overset{\|}{C}}-ONa} + \underset{\text{Methyl alcohol}}{H_3C-OH}$$

21. **2070 Set D Q.No. 12 How does methanal react with**
    - **i. NH$_3$**
    - **ii. Conc. NaOH**

Please refer to 2070 Supp. Q.No. 12

22. **2069 Supp. Set B Q.No. 12 Starting from propanone, how would you obtain 2-hydroxy-2-methylpropanoic acid?**

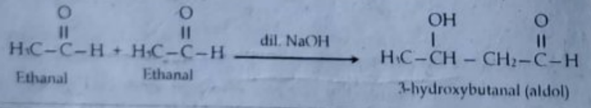
Please refer to 2071 Set D Q.No. 12

23. **2069 Set A Q.No. 11 How would you obtain 2-hydroxy-2-methylpropanoic acid from propanone?**

Please refer to 2071 Set D Q.No. 12

24. **2069 Set A Q.No. 32a Give the example of Aldol condensation**

Two molecules of ethanal are condensed in the presence of dil. NaOH to give an aldol product i.e. 3-hydroxybutanal is called aldol condensation.



$$\underset{\text{Ethanal}}{H_3C-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{Ethanal}}{H_3C-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{\text{dil. NaOH}} \underset{\text{3-hydroxybutanal (aldol)}}{H_3C-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-H}$$

25. **2069 (Set A) Q.No. 32c Give the example of DNPH test**

Please refer to 2074 Set A Q.No. 12

26. **2069 (Set B) Q.No. 12 Give a reaction for each:**
    - i. **DNP test**
    - ii. **Cannizzaro's reaction**

i. **DNP test:** Please refer to 2074 Set A Q.No. 12

ii. **Cannizzaro's reaction:** Please refer to 2074 Set A Q No. 12

27. **2068 Q.No. 4 How is 3-hydroxybutanal obtained from ethanal?** [2]

Please refer to 2073 Supp Q.No. 12

28. **2068 Q.No. 7a Write an examples of each of the followings:** [2]
Cannizzaro's reaction.

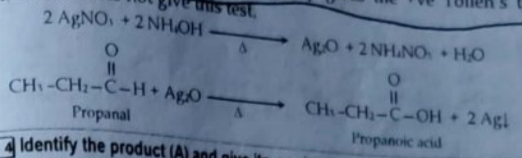
Please refer to 2074 Set A Q.No. 12

29. **2068 Q.No. 9 Write the functional isomer of CH$_3$COCH$_3$ and give a chemical test to distinguish them.**

The functional isomers are

CH_3COCH_3	CH_3CH_2CHO
Acetone (Propan-2-one)	Propanal

Tollen's Test: Only aldehydic functional group gives the +ve Tollen's test i.e. silver mirror test. Ketone does not give this test.



$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$

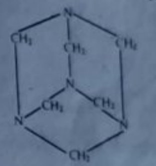
$$\underset{\text{Propanal}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Propanoic acid}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH} + 2\,Ag\downarrow$$

30. **2067 Q.No. 4 Identify the product (A) and give its one important use in the following:** [2]

$HCHO + NH_3 \longrightarrow A + H_2O$

In the above reaction $HCHO + NH_3 \longrightarrow A + H_2O$, A is the product hexamethylenetetramine (Urotropin).

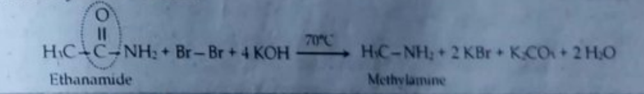
$$6H-\overset{O}{\overset{\|}{C}}-H + 4\,NH_3 \xrightarrow[\Delta]{} \underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4} + 6\,H_2O$$



Use: It is used as urinary antiseptic.

31. **2067 Q.No. 5 What is decarbonylation reaction? Write an example of it.** [2]

Decarbonylation reaction: The reaction of removal of carbonyl group (-CO-) is known as decarbonylation reaction. Hoffmann-Bromamide reaction is an example of decarbonylation reaction.



$$\underset{\text{Ethanamide}}{H_3C-\overset{O}{\overset{\|}{C}}-NH_2} + Br-Br + 4\,KOH \xrightarrow{70^\circ C} \underset{\text{Methylamine}}{H_3C-NH_2} + 2\,KBr + K_2CO_3 + 2\,H_2O$$

32. **2066 Q. No. 4 ii Write an example of each of the followings: Carbonylation reaction** [1]

Carbonylation reaction: The reaction of addition of carbonyl group is known as carbonylation reaction. Oxo-process is an example of carbonylation reaction.

$$\underset{\text{Ethene}}{CH_2=CH_2} + CO + H_2 \xrightarrow{[Co(CO)_4]_2} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

33. **2066 Q. No. 5 Give balanced chemical equations for the followings:** [2]
    - i. **Ethanal is heated with iodine and aqueous NaOH.**
    - ii. **Propanone is heated with hydrazine in presence of glycerol.**

i. **Ethanal is heated with iodine and aq. NaOH:**
When ethanal is heated with I$_2$ and aq.NaOH, iodoform is obtained.

$$\underset{\text{Ethanal}}{CH_3CHO} + 3I_2 \longrightarrow \underset{\text{Tri-iodoacetaldehyde}}{I_3C-CHO} + 3HI$$

$$\underset{\text{Tri-iodoacetaldehyde}}{I_3C-CHO} + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod.formate}}{HCOONa}$$

ii. **Propanone is heated with hydrazine in presence of glycerol:**

When propanone is heated with hydrazine in the presence of glycerol, propane is obtained.

$$\underset{\text{Propanone}}{CH_3-CO-CH_3} + \underset{\text{Hydrazine}}{H_2N-NH_2} \xrightarrow{\text{glycerol}} \underset{\text{Propane}}{CH_3-CH_2-CH_3} + N_2 + H_2O$$

34. **2065 Q.No. 4 Write a reaction of each of the following:**

i. **Tollen's test** ii. **Cannizzaro's reaction** [2]

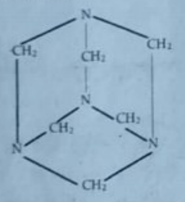
i. **Tollen's test:** Please refer to 2074 Set B Q.No. 12

ii. **Cannizzaro's reaction:** Please refer to 2074 Set A Q.No. 12

35. **2064 Q.No. 5(i) Write the action of Methanal with Ammonia.** [1]

Formaldehyde i.e. methanal reacts with ammonia to give hexamethylene tetramine (Urotropin) which is used as urinary antiseptic.

$$\underset{\text{Methanal}}{6H-\overset{\overset{\large O}{\|}}{C}-H} + \underset{\text{Ammonia}}{4NH_3} \xrightarrow[\Delta]{} \underset{\text{Hexamethylene tetramine Urotropin}}{(CH_2)_6N_4} + 6H_2O$$

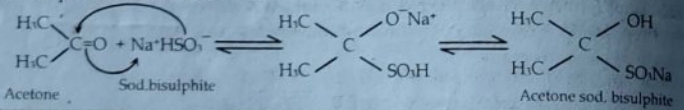


Structure of hexamethylenetetramine

36. **2064 Q.No. 5(ii) Write the action of Propanone with sodium bisulphite.** [1]

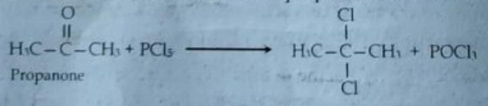
Propanone with sodium bisulphite:

Acetone i.e. propanone on addition with sodium bisulphite, a crystalline bisulphite addition product is formed.



37. **2064 Q.No. 22(ii) What happens when Propanone reacts with PCl₅?**

When propanone reacts with PCl_5, 2,2- dichloropropane is obtained.

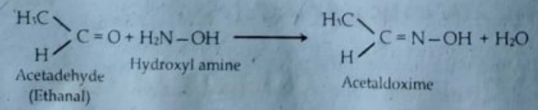


$$\underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{\|}}{C}-CH_3} + PCl_5 \longrightarrow H_3C-\underset{\underset{\large Cl}{|}}{\overset{\overset{\large Cl}{|}}{C}}-CH_3 + POCl_3$$

2,2-dichloropropane

38. **2064 Q.No. 22(iii) What happens when Ethanal if allowed to react with hydroxyl amine?** [2]

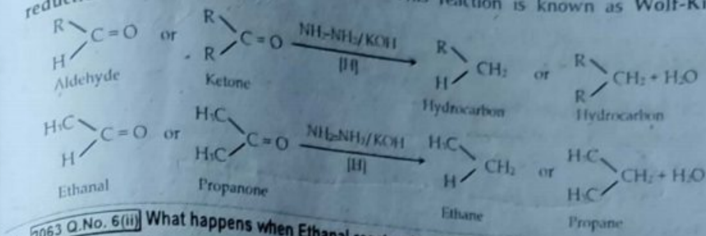
When ethanal or acetaldehyde is allowed to react with hydroxyl amine, acetaldehyde oxime is obtained.



39. **2063 Q.No. 5(b) Give an example of each of the following reactions: Wolf-Kishner reduction** [1]

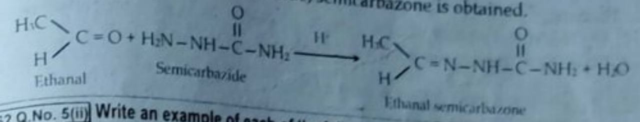
Wolf-Kishner reduction

Aldehyde or ketone can be changed into hydrocarbon on reduction with hydrazine and KOH in the presence of ethylene glycol. This reaction is known as Wolf-Kishner reduction.



40. **2063 Q.No. 6(ii) What happens when Ethanal reacts with semicarbazide?** [1]

When ethanal reacts with semicarbazide, semicarbazone is obtained.



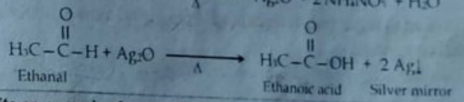
41. **2062 Q.No. 5(ii) Write an example of each of the following reactions giving appropriate conditions: Cannizzaro's reaction** [1]

Please refer to 2074 Set A Q.No. 12

42. **2062 Q.No. 6 Suggest a suitable chemical test to distinguish ethanal from propanone. Give chemical reaction too.** [2]

Tollen's reagent test distinguishes ethanal from propanone. Few mL of Tollen's reagent is added to the test tube containing ethanal and test tube is kept in warm water for 5 minutes. A white silver mirror is seen on the inner wall of test tube, this indicate the presence of ethanal. Propanone does not give this test.

$$2AgNO_3 + 2NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2NH_4NO_3 + H_2O$$



$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{\large O}{\|}}{C}-H} + Ag_2O \xrightarrow[\Delta]{} \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\large O}{\|}}{C}-OH} + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

43. **2061 Q.No. 4 Write an example of each of the following reaction:** [2]

a. **Aldol condensation** b. **Cannizzaro Reaction**

a. **Aldol condensation:** Please refer to 2074 Supp. Q.No. 12

b. **Cannizzaro's reaction:** Please refer to 2074 Set A Q.No. 12

44. **2060 Q.No. 7 Write the action of**

i. **Ammonia with methanal** ii. **Acetone with hydrazine.** [2]

i. **Methanal with ammonia:** Please refer to 2064 Q.No. 5(i)

ii. **Acetone is heated with hydrazine in presence of glycerol:**

When acetone is heated with hydrazine in the presence of glycerol, propane is obtained. This reaction is known as Wolf-Kishner reduction.

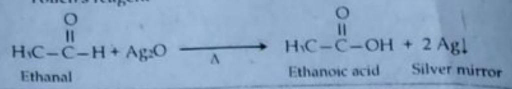
$$\underset{\text{Acetone}}{CH_3-CO-CH_3} + \underset{\text{Hydrazine}}{H_2N-NH_2} \xrightarrow{\text{glycerol}} \underset{\text{Propane}}{CH_3-CH_2-CH_3} + N_2 + H_2O$$

45. **2059 Q.No. 6 What happens when ethanal is warmed with Tollen's reagent?** [2]

When ethanal is warmed with Tollen's reagent, a silver mirror is deposited on the inner wall of test tube.

$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$

Tollen's reagent



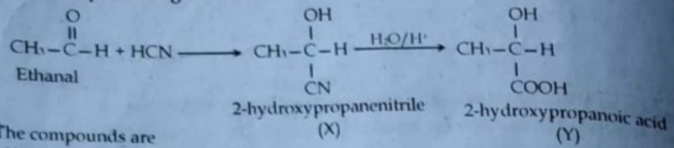
$$H_3C-\overset{\overset{O}{\|}}{C}-H + Ag_2O \xrightarrow[\Delta]{} H_3C-\overset{\overset{O}{\|}}{C}-OH + 2\,Ag\downarrow$$

Ethanal Ethanoic acid Silver mirror

46. 2058 Q.No. 6 **Identify the products (X) and (Y) in the following reaction.** [2]

$$CH_3\,CHO \xrightarrow{HCN} (X) \xrightarrow{H_2O/H^+} (Y)$$

The reaction sequence is given as:



$$CH_3-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H \xrightarrow{H_2O/H^+} CH_3-\underset{\underset{COOH}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

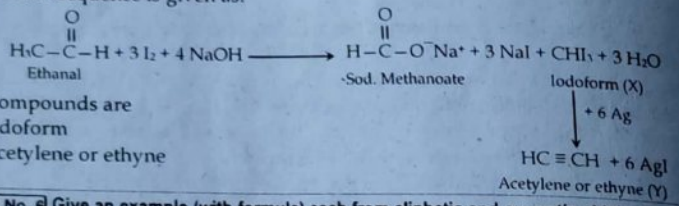
Ethanal 2-hydroxypropanenitrile (X) 2-hydroxypropanoic acid (Y)

The compounds are
X = 2 - hydroxypropanenitrile
Y = 2 = hydroxypropanoic acid

47. 2057 Q.No. 2 **Identify X and Y in the following reaction** [2]

$$CH_3CHO \xrightarrow[\Delta]{I_2/NaOH} X \xrightarrow[\Delta]{Ag} Y$$

The reaction sequence is given as:



$$H_3C-\overset{\overset{O}{\|}}{C}-H + 3\,I_2 + 4\,NaOH \longrightarrow H-\overset{\overset{O}{\|}}{C}-O^-Na^+ + 3\,NaI + CHI_3 + 3\,H_2O$$

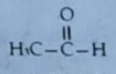
$$CHI_3 \xrightarrow{+6\,Ag} HC\equiv CH + 6\,AgI$$

Ethanal ·Sod. Methanoate Iodoform (X) Acetylene or ethyne (Y)

The Compounds are
X = Iodoform
Y = Acetylene or ethyne

48. 2057 Q.No. 6 **Give an example (with formula) each from aliphatic and aromatic aldehydes, which give aldol condensation reaction.** [2]

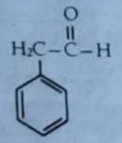
Aliphatic aldehyde wich gives aldol condensation is



$$H_3C-\overset{\overset{O}{\|}}{C}-H$$

Acetaldehyde

Aromatic aldehyde which gives aldol condensation is



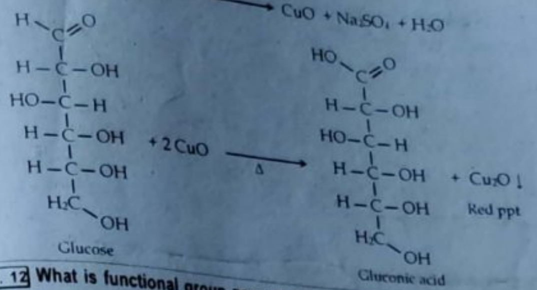
2-phenylacetaldehyde

Both aliphatic and aromatic aldehyde contains alpha (α) hydrogen and gives aldol condensation reaction. Aldehyde having alpha hydrogen only gives aldol condensation reaction.

49. 2056 Q.No. 17 **What reagent is used to diagonise diabetes in human urine?** [2]

Fehling solution or Benedict's solution is used to diagnose diabetes in human urine. The urine of diabetes patient contains glucose and glucose contains aldehydic functional group. Fehling solution reduces reddish brown ppt of cuprous oxide i.e. Cu_2O.

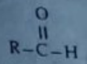
$$CuSO_4 + 2\,NaOH \xrightarrow{Na-K\ tartarate} CuO + Na_2SO_4 + H_2O$$



Glucose + 2 CuO →(Δ) Gluconic acid + $Cu_2O\downarrow$ Red ppt

50. 2055 Q.No. 12 **What is functional group present in a compound that gives a positive Tollen's test? Write an equation showing the reaction involved in a positive Tollen's test.** [2]

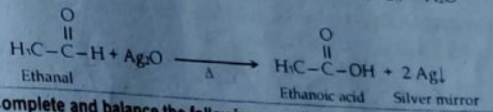
The organic compound having functional group 'aldehydic group' gives positive Tollen's reagent test.



$$R-\overset{\overset{O}{\|}}{C}-H$$

Aldehydic group

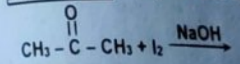
$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$



$$H_3C-\overset{\overset{O}{\|}}{C}-H + Ag_2O \xrightarrow[\Delta]{} H_3C-\overset{\overset{O}{\|}}{C}-OH + 2\,Ag\downarrow$$

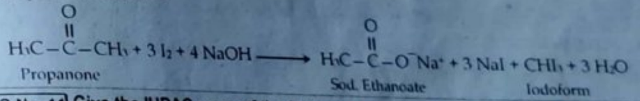
Ethanal Ethanoic acid Silver mirror

51. 2055 Q.No. 13 **Complete and balance the following equation:** [2]



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + I_2 \xrightarrow{NaOH}$$

The complete reaction is

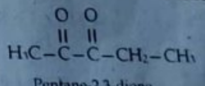


$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}-O^-Na^+ + 3\,NaI + CHI_3 + 3\,H_2O$$

Propanone Sod. Ethanoate Iodoform

52. 2054 Q.No. 11 **Give the IUPAC name of the following compounds: $CH_3\,CO\,CO\,CH_2\,CH_3$** [1]

IUPAC name of



$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

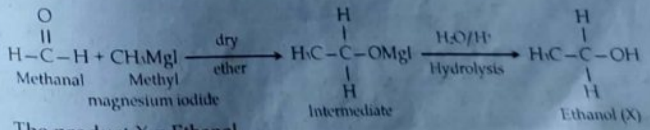
Pentane-2,3-dione

Word root = Pent
P.Suffix = -ane
S.Suffix = 2,3-dione

53. 2054 Q.No. 14 **Identify the product X in the reaction.** [2]

$$HCHO + CH_3MgI \xrightarrow{dry\ ether} intermediate \xrightarrow{H^+/H_2O} X$$

The reaction sequence is given as:



$$H-\overset{\overset{O}{\|}}{C}-H + CH_3MgI \xrightarrow[ether]{dry} H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OMgI \xrightarrow[Hydrolysis]{H_2O/H^+} H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH$$

Methanal Methyl magnesium iodide Intermediate Ethanol (X)

The product X = Ethanol

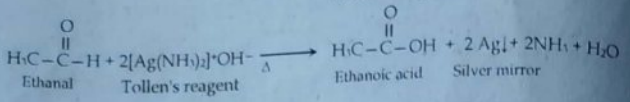
54. 2053 Q.No. 6 **What is Tollen's reagent? What happens when acetaldehyde is heated with Tollen's reagent?** [2]

Tollen's reagent: Ammoniacal solution of silver nitrtate is called Tollen's reagent. When acetaldehyde i.e. ethanal is heated with Tollen's reagent, silver mirror is seen on the inner wall of test tube. This reagent is used to identify organic compound having aldehydic functional group.

$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$

$$Ag_2O + 4\,NH_4OH \longrightarrow 2[Ag(NH_3)_2]^+OH^- + 3\,H_2O$$

Tollen's reagent



$$H_3C-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^+OH^- \xrightarrow[\Delta]{} H_3C-\overset{O}{\overset{\|}{C}}-OH + 2\,Ag\downarrow + 2NH_3 + H_2O$$

Ethanal Tollen's reagent Ethanoic acid Silver mirror

SHORT ANSWER QUESTIONS [5 MARKS]

55. 2075 GIE Q.No. 27 **Give any three methods of preparation of ethanal. How would you convert ethanal into propanone?** [3+2]

Three methods of preparation of ethanal:

a. **From alcohol:** Ethanol on oxidation with acidified solution of $K_2Cr_2O_7$, ethanal is formed.

$$CH_3-CH_2-OH + [O] \xrightarrow{K_2Cr_2O_7/H^+} CH_3-CHO + H_2O$$

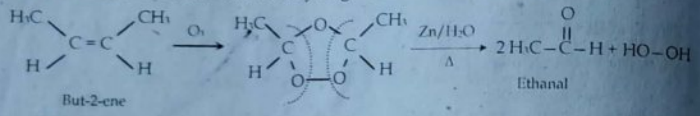
Ethanol Ethanal

b. **From Ethanoylchloride:** When ethanoylchloride is reduced with $Pd/BaSO_4$ as reducing agent, ethanal is obtained.

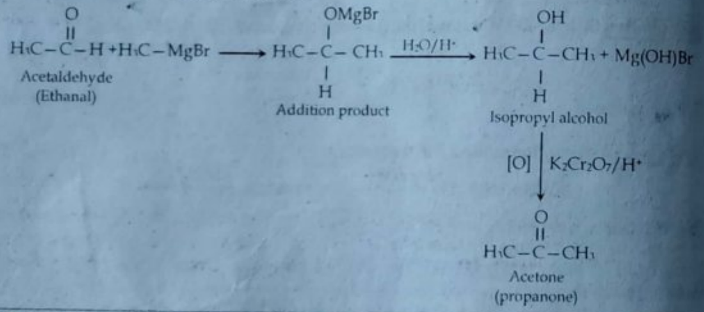
$$CH_3-CO-Cl + [H] \xrightarrow{Pd/BaSO_4} CH_3-CHO + HCl$$

Ethanoyl chloride Ethanal

c. **From but-2-ene:** But-2-ene on ozonolysis gives two molecules of ethanal.



Conversion: Ethanal into propanone:

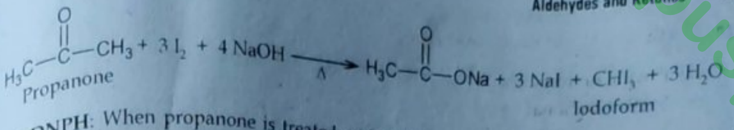


56. 2075 Set A Q.No. 27 **Write down any three methods of preparation of propanone. What products would you expect when propanone is treated with (i) I_2 and NaOH (ii) 2, 4-DNPH.** [3+2]

Three methods of preparation of propanone: Please refer to 2075 GIE Q.N. 27

Reaction of propanone with:

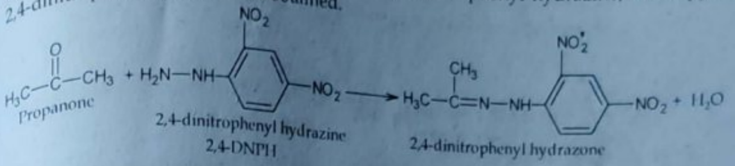
i. **I_2 and NaOH:** When propanone is warmed with I_2 and NaOH solution, yellow ppt of iodoform is obtained.



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 3\,I_2 + 4\,NaOH \xrightarrow[\Delta]{} H_3C-\overset{O}{\overset{\|}{C}}-ONa + 3\,NaI + CHI_3 + 3\,H_2O$$

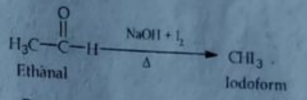
Propanone Iodoform

ii. **2,4-DNPH:** When propanone is treated with 2,4-dinitrophenyl hydrazine, a red ppt of 2,4-dinitrophenyl hydrazone is obtained.



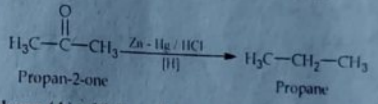
57. 2074 Supp. Q.No. 29 2074 Set A Q.No. 29 **An alkene (A) undergoes ozonolysis to give an aldehyde and a ketone as the major products. The aldehyde gives positive iodoform reaction and the ketone undergoes Clemmensen's reduction to yield propane. Identify (A) abd gives its IUPAC name. Also write reactions involved.** [5]

The aldehyde gives +ve iodoform test. So, the aldehyde may be ethanal. The ketone undergoes Clemenson's reduction to yield propane. So, the ketone may be propan-2-one.



$$H_3C-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{NaOH + I_2} CHI_3$$

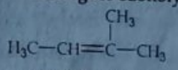
Ethanal Iodoform



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[{[H]}]{Zn-Hg/HCl} H_3C-CH_2-CH_3$$

Propan-2-one Propane

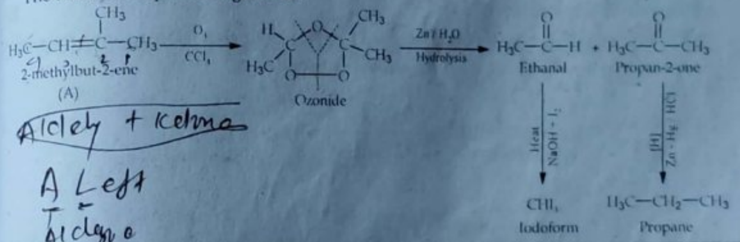
The structure of alkene (A) which undergoes ozonolysis give aldehyde and ketone is



$$H_3C-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$$

2-methylbut-2-ene

The reaction sequence is given as:



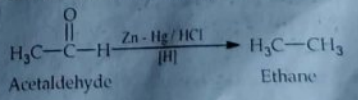
Aldehy + Ketone

A Left

Aldehyde

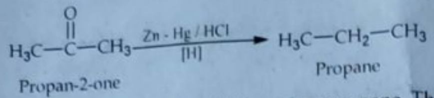
58. 2074 Set B Q.No. 29 **An alkene (A) undergoes ozonolysis to give an aldehyde and ketone as the major products. The aldehyde and the ketone further undergo Clemensen's reduction to yield ethane and propane respectively. Identify (A) and give its IUPAC name. What product your expect when (A) is treated with HBr?** [4+1]

The aldehyde and ketone on Clemensen's reduction to yield ethane and propane. The aldehyde having two carbons and ketone having three carbons.

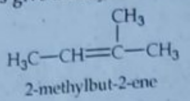


$$H_3C-\overset{O}{\overset{\|}{C}}-H \xrightarrow[{[H]}]{Zn-Hg/HCl} H_3C-CH_3$$

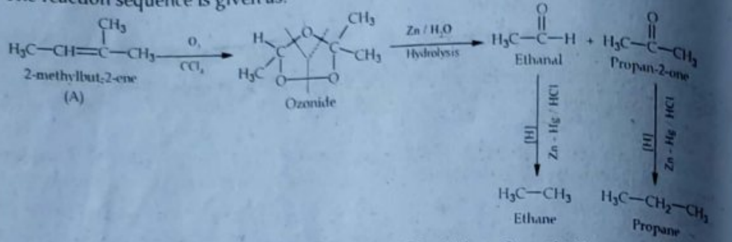
Acetaldehyde Ethane



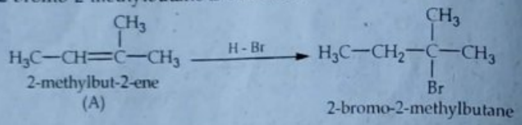
The aldehyde is acetaldehyde (ethanal) and ketone is propanone. The structure of alkene (A) which undergoes ozonolysis give aldehyde and ketone is



The reaction sequence is given as:

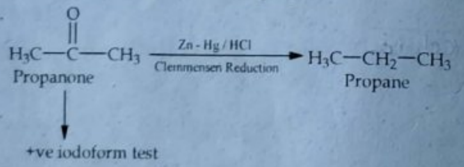


The reaction of 2-methylbut-2-ene (A) with HBr: When 2-methylbut-2-ene is treated with HBr, 2-bromo-2-methylbutane is obtained.

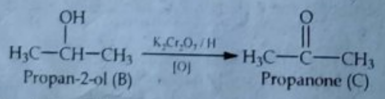


59. **2073 Supp Q.No. 29 An aliphatic compound Ⓐ react with aq. NaOH to give Ⓑ. Ⓑ on oxidation with $K_2Cr_2O_7/H^+$ produce Ⓒ. The compound Ⓒ undergoes Clemmensen's reduction to give propane. If compound Ⓒ responses positive iodoform test, identify Ⓐ, Ⓑ and Ⓒ. What product would you expect when Ⓐ is heated with H_2/Ni ?** [5]

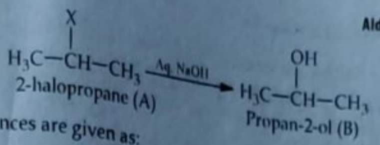
The compound (C) undergoes Clemmensen's reduction to give propane and responses +ve iodoform test. The compound (C) must be propanone.



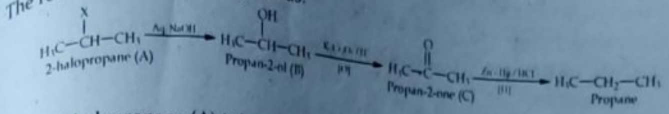
The compound (C) is obtained by oxidation of (B). The compound (B) must be propan-2-ol.



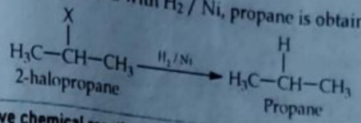
The compound (B) is obtained by treating (A) with aq. NaOH. The compound (A) must be 2-halopropane.



The reaction sequences are given as:



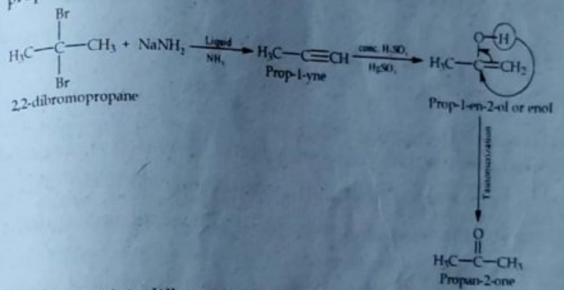
When 2-halopropane (A) is heated with H_2 / Ni, propane is obtained.



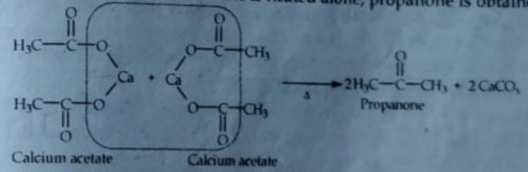
60. **2073 Set C Q.No. 28 Give chemical reactions for the preparation of propanone from**
i. 2,2-dibromopropane ii. calcium acetate
iii. propan-2-ol
How is propanone converted into 2-methylpropan-2 ol? [1+1+1+2]

Preparation of propanone from

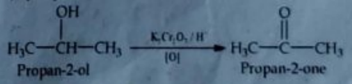
i. 2,2-dibromopropane: When 2,2-dibromopropane is heated with sodamide in the presence of liquid ammonia, propyne is obtained. Propyne is treated with water in the presence of $HgSO_4$ and conc. H_2SO_4, enol is formed which on tautomerization gives propanone.



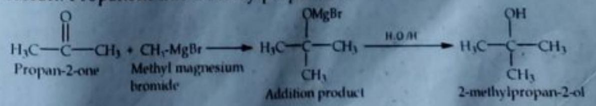
ii. **Calcium acetate:** When calcium acetate is heated alone, propanone is obtained.



iii. **Propan-2-ol:** When propan-2-ol is oxidized with acidified solution of potassium dichromate ($K_2Cr_2O_7$), propanone is obtained.



Conversion: Propanone into 2-methylpropan-2-ol



61. 2073 Set C Q.No. 29 An aliphatic compound Ⓐ reacts with aq. NaOH to give Ⓑ. Ⓑ on oxidation $K_2Cr_2O_7/H^+$ produce Ⓒ. The compound Ⓒ undergoes Clemmensen's reduction to give propa compound Ⓒ responses positive Iodoform test, identify Ⓐ, Ⓑ and Ⓒ. What product would expect when Ⓐ is heated with H_2/Ni?

Please refer to 2073 Supp Q No. 29

62. 2073 Set D Q.No. 28 Give chemical reactions for the preparation of ethanal from

i. 1, 1-dibromoethane

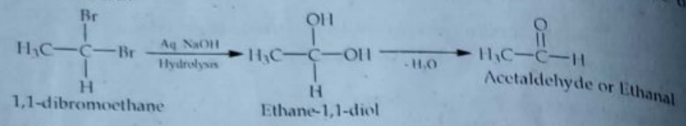
ii. ethyne

iii. ethanoyl chloride.

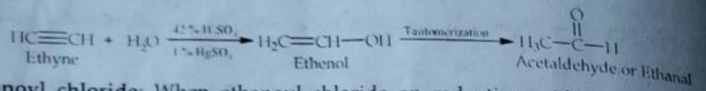
How is ethanal converted into propan-2-ol?

Preparation of ethanal from

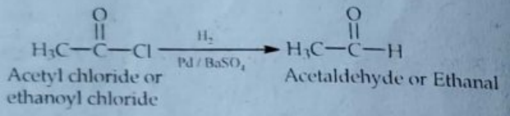
i. **1,1-dibromoethane**: When 1,1-dibromoethane is hydrolyzed in the presence of alkal ethanal is obtained.



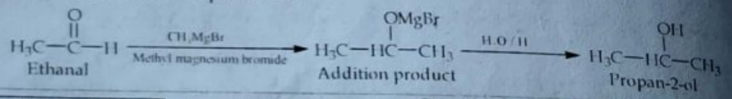
ii. **Ethyne**: When ethyne is passed through 42 % H_2SO_4 and 1 % $HgSO_4$ at 60°C, ethanal is obtained.



iii. **Ethanoyl chloride**: When ethanoyl chloride on reduction with $Pd/BaSO_4$, ethanal is obtained.

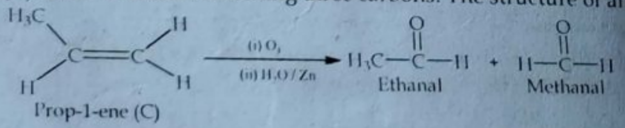


Conversion: Ethanal into proan-2-ol

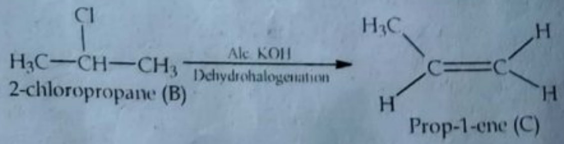


63. 2073 Set D Q.No. 29 An aliphatic compound Ⓐ reacts with $SOCl_2$ to give Ⓑ. Ⓑ on dehydrohalogenation yields Ⓒ. The compound Ⓒ on ozonolysis gives a mixture of ethanal and methanal. If Ⓐ is an alcohol which responses iodoform test. Identify Ⓐ, Ⓑ and Ⓒ. What product would you expect when compound Ⓑ is heated with H_2/Ni? [5]

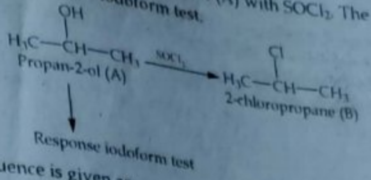
The compound (C) on ozonolysis gives a mixture of ethanal and methanal. The compound (C) must be alkene containing three carbons. The structure of alkene must be



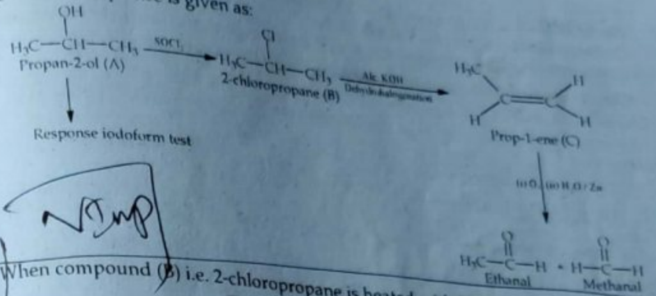
The compound (C) is obtained by the dehydrohalogenation of the compound (B). So, the compound (B) must be chloroalkane containing three carbon atoms. The structure of chloropropane must be



The compound (B) is obtained by treatment of (A) with $SOCl_2$. The compound (A) must be propan-2-ol which response iodoform test.

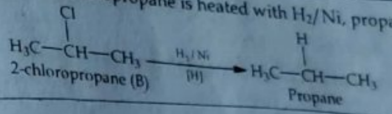


The reaction sequence is given as:



V.Imp

When compound (B) i.e. 2-chloropropane is heated with H_2/Ni, propane is obtained.



64. 2070 Supp. Q.No. 28 Write any three methods of preparation of ethanal. How would you convert ethanal into [5]

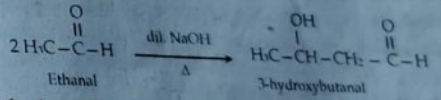
i. 3-hydroxybutanal

ii. 2-hydroxy2-methylpropanoic acid

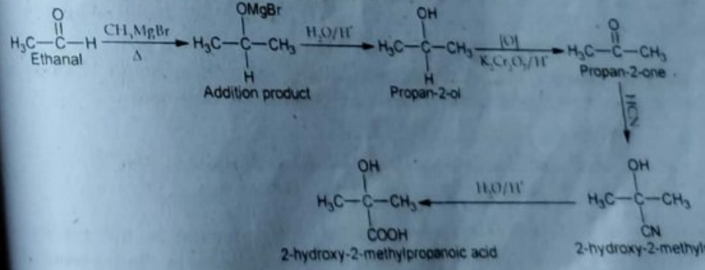
Three methods of preparation of ethanal: Please refer to 2075 GIE Q No. 27

Conversion:

i. **Ethanal into 3-hydroxybutanal:**



ii. **Ethanal into 2-hydroxy-2-methylpropanoic acid:**



65. **2068 Q.No. 21** **An organic compound A reacts with sodium metal to give hydrogen gas. The compound A on treatment with alkaline iodine forms a yellow crystalline substance and on oxidation with acidified dicromate forms an aldehyde with molecular formula C_2H_4O. Identify the compound and write equation for these reactions.** [5]

The compound 'A' reacts with sodium metal to give hydrogen gas. The compound 'A' may be alcohol or acid.

$$\underset{\text{Alcohol}}{2\,R-OH} + 2\,Na \longrightarrow \underset{\text{Sod.alkoxide}}{2\,R-ONa} + H_2$$

$$\underset{\text{Carboxylic acid}}{2\,R-COOH} + 2Na \longrightarrow \underset{\text{Sod.carboxylate}}{2\,R-COONa} + H_2$$

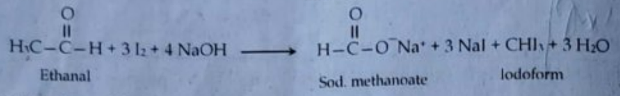
Compound 'A' gives iodoform test and on oxidation gives aldehyde having molecular formula C_2H_4O. So, 'A' must be alcohol and having two carbons.

$$\underset{\text{Ethanol}}{2\,CH_3-CH_2-OH} + 2\,Na \longrightarrow \underset{\text{Sod.ethoxide}}{2\,CH_3-CH_2-ONa} + H_2$$

Iodoform test:

$$2\,NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + NaOI \longrightarrow \underset{\text{Ethanal}}{CH_3-CHO} + NaI + H_2O$$



$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{\large O}{||}}{C}-H} + 3\,I_2 + 4\,NaOH \longrightarrow \underset{\text{Sod. methanoate}}{H-\overset{\overset{\large O}{||}}{C}-O^-Na^+} + 3\,NaI + \underset{\text{Iodoform}}{CHI_3} + 3\,H_2O$$

Oxidation with acidified $K_2Cr_2O_7$:

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + [O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Ethanal}}{CH_3-CHO} + H_2O$$

66. **2067 Q.No. 22** **How is propanone prepared from:** [5]

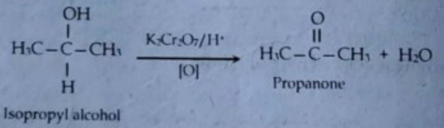
i. **Isopropyl alcohol**
ii. **Ethanoic acid**
iii. **2,2-dichloropropane.**

Give the action of propanone on

a. **Grignard's reagent**
b. **Chloroform**

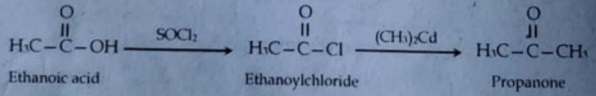
Preparation of propanone from:

i. **Isopropyl alcohol:** Isopropyl alcohol on oxidation with acidified solution of $K_2Cr_2O_7$, propanone is obtained.



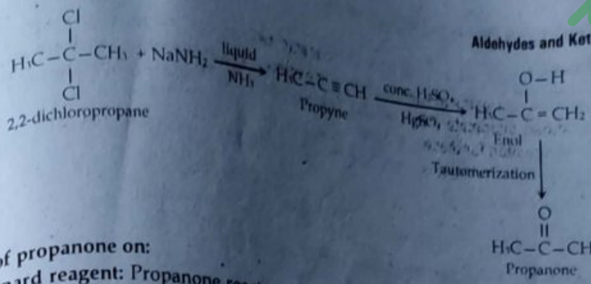
$$\underset{\text{Isopropyl alcohol}}{H_3C-\overset{\overset{\large OH}{|}}{\underset{\underset{\large H}{|}}{C}}-CH_3} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_3} + H_2O$$

ii. **Ethanoic acid:** Ethanoic acid is treated with thionyl chloride, ethanoyl chloride is obtained which is treated with dimethyl cadmium, propanone is obtained.



$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\large O}{||}}{C}-OH} \xrightarrow{SOCl_2} \underset{\text{Ethanoylchloride}}{H_3C-\overset{\overset{\large O}{||}}{C}-Cl} \xrightarrow{(CH_3)_2Cd} \underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_3}$$

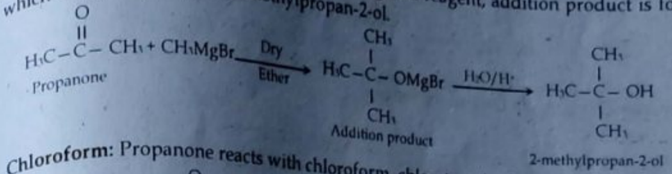
iii. **2,2-dichloropropane:** 2,2-dichloropropane is heated with sodamide in the presence liquid ammonia, propyne is obtained. Propyne is treated with water in the presence of $HgSO_4$ and conc.H_2SO_4, enol is formed which on tautomerization gives propanone.



$$\underset{\text{2,2-dichloropropane}}{H_3C-\overset{\overset{\large Cl}{|}}{\underset{\underset{\large Cl}{|}}{C}}-CH_3} + NaNH_2 \xrightarrow[NH_3]{\text{liquid}} \underset{\text{Propyne}}{H_3C-C\equiv CH} \xrightarrow[HgSO_4]{\text{conc. }H_2SO_4} \underset{\text{Enol}}{H_3C-\overset{\overset{\large O-H}{|}}{C}=CH_2} \xrightarrow{\text{Tautomerization}} \underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_3}$$

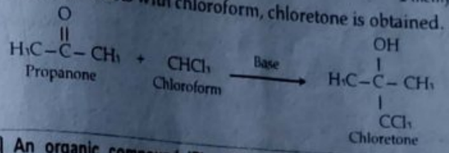
Action of propanone on:

a. **Grignard reagent:** Propanone reacts with Grignard reagent, addition product is formed which on hydrolysis gives 2-methylpropan-2-ol.



$$\underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_3} + CH_3MgBr \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Addition product}}{H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OMgBr} \xrightarrow{H_2O/H^+} \underset{\text{2-methylpropan-2-ol}}{H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-OH}$$

b. **Chloroform:** Propanone reacts with chloroform, chloretone is obtained.



$$\underset{\text{Propanone}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_3} + \underset{\text{Chloroform}}{CHCl_3} \xrightarrow{\text{Base}} \underset{\text{Chloretone}}{H_3C-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CCl_3}{|}}{C}}-CH_3}$$

67. **2066 Q. No. 23** **An organic compound 'P' which reduces Tollen's reagent. On oxidation with potassium permanganate, formed a compound 'Q' having same number of carbon atoms as 'P'. Q reacts with Na_2CO_3 (aq.) to give carbon dioxide. 'Q' on reaction with ethanol in the presence of Sulphuric acid formed an ester having molecular formula $C_4H_8O_2$ 'R'. Identify P, Q, R and write their IUPAC names.** [5]

Organic compound 'P' reduces Tollen's reagent.

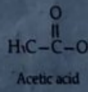
$$P \xrightarrow{\text{Oxidation}} Q \quad \text{(having the same number of carbon atom)}$$

Again, $Q + Na_2CO_3 \longrightarrow CO_2$

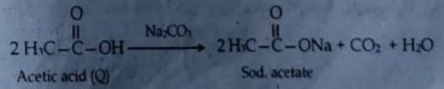
$$Q + C_2H_5-OH \xrightarrow{\text{conc. }H_2SO_4} C_4H_8O_2 \text{ (Ester)}$$

The compound Q and alcohol reacts to form ester. That means alkoxy group of ester must come from alcohol having the carbon atom two. The Q must be acid having two carbon atoms because acid and alcohol reacts to give ester. This can be also proved by acid and Na_2CO_3 which gives carbon dioxide.

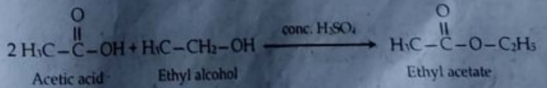
The structure of Q is



$$\underset{\text{Acetic acid}}{H_3C-\overset{\overset{\large O}{||}}{C}-OH}$$



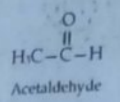
$$\underset{\text{Acetic acid (Q)}}{2\,H_3C-\overset{\overset{\large O}{||}}{C}-OH} \xrightarrow{Na_2CO_3} \underset{\text{Sod. acetate}}{2\,H_3C-\overset{\overset{\large O}{||}}{C}-ONa} + CO_2 + H_2O$$



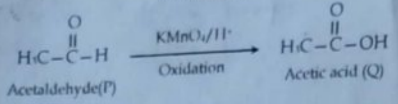
$$\underset{\text{Acetic acid}}{2\,H_3C-\overset{\overset{\large O}{||}}{C}-OH} + \underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH} \xrightarrow{\text{conc. }H_2SO_4} \underset{\text{Ethyl acetate}}{H_3C-\overset{\overset{\large O}{||}}{C}-O-C_2H_5}$$

The compound 'Q' comes from the oxidation of 'P' and both having the same number of carbon atom. This shows that 'P' must be aldehyde which reduce Tollen's reagent.

The structure of 'P' is



$H_3C-\overset{O}{\overset{\|}{C}}-H$



$$H_3C-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{Oxidation}]{KMnO_4/H^+} H_3C-\overset{O}{\overset{\|}{C}}-OH$$

Therefore, the IUPAC name of the compounds are

P = Acetaldehyde or Ethanal

Q = Acetic acid or Ethanoic acid

R = Ethyl acetate or Ethylethanoate

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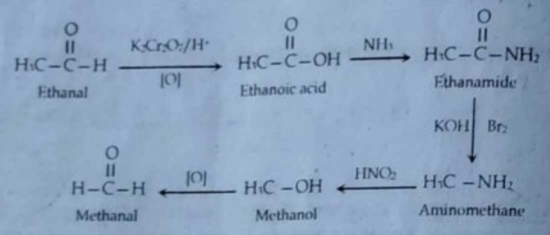
68. **2065 Q.No. 23** **Convert Ethanal into Methanal**



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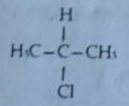
69. **2064 Q.No. 23** **An alcohol (A) reacts with thionyl chloride to produce (B), which on dehydrohalogenation yielded a compound (C). The compound (C) on ozonolysis gave the mixture of ethanal and methanol. If the alcohol (A) responses positive iodoform test. Identify A, B and C. How could you convert the above compound (B) into propanone?** [5]

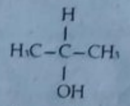
The compound (C) on ozonolysis gave the mixture of ethanal and methanol. So, the structure of (C) must be

The compound (C) obtained by the dehydrohlogenation of (B). The structure of B must be

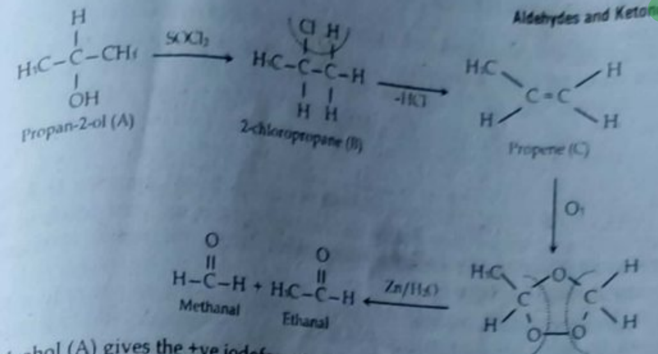


The compound (B) is obtained by the reaction of thionyl chloride with (A).

The compound (A) is alcohol and gives the +ve iodoform test. So, the structure of (A) must be



The conversion can be confirmed by the following reactions.



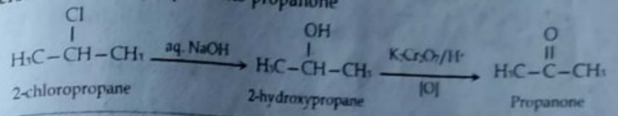
The alcohol (A) gives the +ve iodoform test

$$\underset{\text{Propan-2-ol}}{CH_3-CH(OH)-CH_3} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 5NaI + H_2O$$

Therefore, the compounds are

A = Propan-2-ol B = 2-chloropropane C = Propene

Conversion: 2-chloropropane into propanone

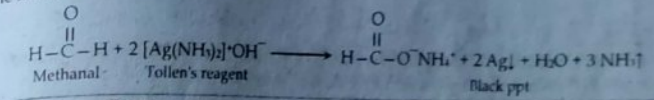


$$\underset{\text{2-chloropropane}}{H_3C-\overset{Cl}{\overset{|}{CH}}-CH_3} \xrightarrow{aq.\ NaOH} \underset{\text{2-hydroxypropane}}{H_3C-\overset{OH}{\overset{|}{CH}}-CH_3} \xrightarrow[{[O]}]{K_2Cr_2O_7/H^+} \underset{\text{Propanone}}{H_3C-\overset{O}{\overset{\|}{C}}-CH_3}$$

---

70. **2063 Q.No. 22a** **What action takes place when: Methanal is warmed with Tollen's reagent?** [2.5]

When methanal is warmed with Tollen's reagent, a black ppt. of silver is deposited on the inner wall of test tube.

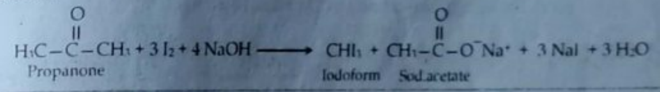


$$\underset{\text{Methanal}}{H-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow H-\overset{O}{\overset{\|}{C}}-O^-NH_4^+ + \underset{\text{Black ppt}}{2Ag\downarrow} + H_2O + 3NH_3\uparrow$$

---

71. **2063 Q.No. 22(iii)** **What action takes place when: propanone is warmed with iodine and aqueous sodium hydroxide?** [1]

When propanone is warmed with iodine and aq. sodium hydroxide, iodoform is obtained.

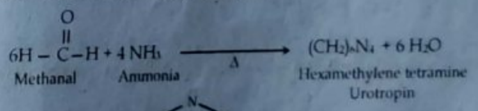


$$\underset{\text{Propanone}}{H_3C-\overset{O}{\overset{\|}{C}}-CH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod.acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+} + 3NaI + 3H_2O$$

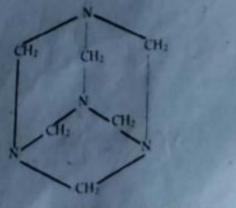
---

72. **2062 Q.No. 23 b** **What happens when Methanal reacts with ammonia:** [1]

Formaldehyde i.e. methanal reacts with ammonia to give hexamethylene tetramine (Urotropin) which is used as urinary antiseptic.



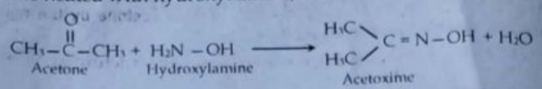
$$\underset{\text{Methanal}}{6H-\overset{O}{\overset{\|}{C}}-H} + \underset{\text{Ammonia}}{4NH_3} \xrightarrow{\Delta} \underset{\substack{\text{Hexamethylene tetramine}\\ \text{Urotropin}}}{(CH_2)_6N_4 + 6H_2O}$$



Structure of hexamethylenetetramine

73. **2062 Q.No. 23(d) What happens when: Acetone reacts with hydroxyl amine:** [1]

When acetone is heated with hydroxyl amine, acetoxime is obtained.

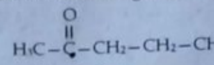


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2N-OH \longrightarrow (H_3C)_2C=N-OH + H_2O$$

---

74. **2058 Q.No. 21 An organic compound ($C_5H_{10}O$) reacts with phenyl hydrazine to form phenyl hydrazone. The compound does not reduce Fehling's solution but gives iodoform test. The compound on Clemmensen's reduction gives pentane. Identify the organic compound giving necessary chemical equations.** [5]

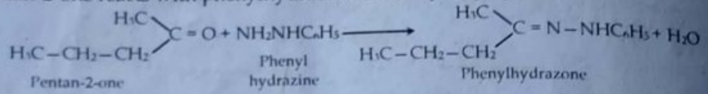
The organic compound having molecular formula $C_5H_{10}O$ does not reduce Fehling's solution but give iodoform test and reduction gives n-pentane. The compound must have five carbons having ketonic functional group and the structure must be



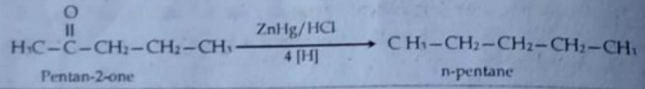
$$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$$

Pentan-2-one

Pentan-2-one reacts with phenylhydrazine to form phenylhydrazone.



Pentan-2-one on Clemmensen's reduction gives n-pentane.



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3 \xrightarrow[4\,[H]]{ZnHg/HCl} CH_3-CH_2-CH_2-CH_2-CH_3$$

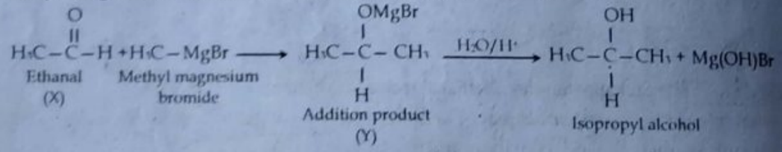
---

75. **2057 Q.No. 21**

a. **A carbonyl compound (X) gives addition product (Y) with methyl magnesium bromide. The compound (Y) on hydrolysis gives isopropyl alcohol. Identify X and Y.**

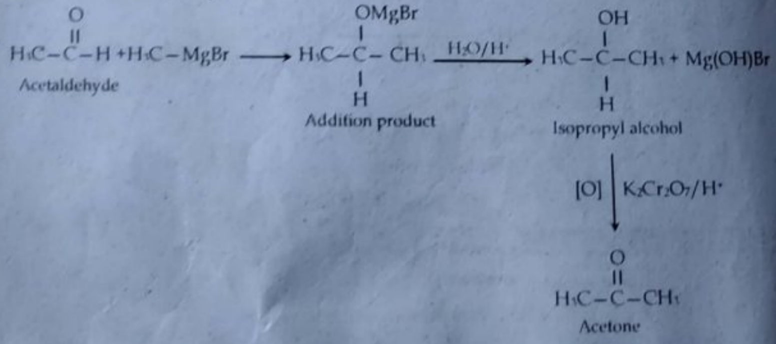
b. **Convert acetaldehyde to acetone.** [5]

a. The compound (Y) on hydrolysis gives isopropyl alcohol. The compound (Y) must be addition product of ethanal. The addition product is formed by the addition of (X) with methyl magnesium bromide. The compound (X) must be ethanal.



$$H_3C-\overset{O}{\overset{\|}{C}}-H + H_3C-MgBr \longrightarrow H_3C-\underset{H}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_2O/H^+} H_3C-\underset{H}{\overset{OH}{C}}-CH_3 + Mg(OH)Br$$

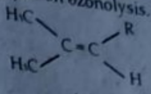
b. **Conversion:** Acetaldehyde into acetone:



$$H_3C-\overset{O}{\overset{\|}{C}}-H + H_3C-MgBr \longrightarrow H_3C-\underset{H}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_2O/H^+} H_3C-\underset{H}{\overset{OH}{C}}-CH_3 + Mg(OH)Br \xrightarrow{[O]\ K_2Cr_2O_7/H^+} H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

2054 Q.No. 21 An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid B. When B is treated with Br_2 / P it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with HCN followed by hydrolysis. Identify the compounds A, B, C and D. [5]

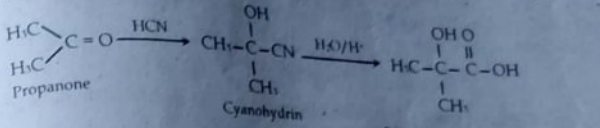
Alkene 'A' gives acetone and aldehyde on ozonolysis. The structure of 'A' may be



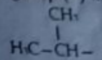
(A)

Again, from questions

The hydroxy acid 'D' can also be obtained from acetone or propanone by the reaction of HCN followed by hydrolysis.

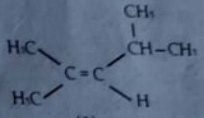


In the structure of alkene 'A' the alkyl group (R) must have group



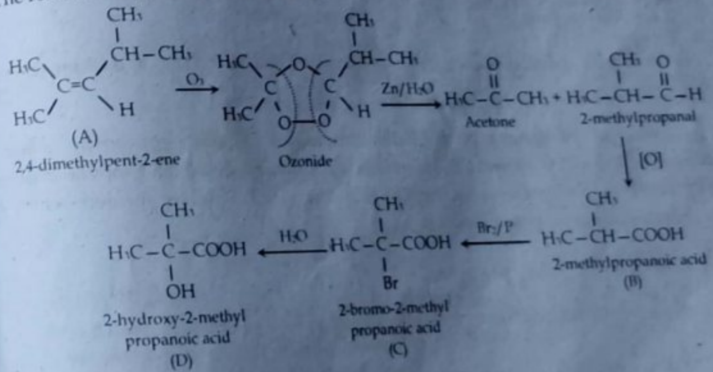
$$H_3C-\overset{CH_3}{CH}-$$

The structure of A must be



(A)

The reaction sequence can be shown as:



Therefore, the compounds (A) = 2,4-dimethylpent-2-ene

(B) = 2-methylpropanoic acid

(C) = 2-bromo-2-methylpropanoic acid

(D) = 2-hydroxy-2-methylpropanoic acid

LONG ANSWER QUESTIONS [10 MARKS]

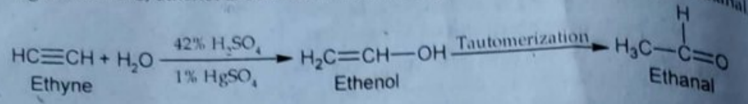
77. **2076 Set B Q.No. 31a How is ethanal prepared from**

(i) Ethyne (ii) But-2-ene (iii) 1,1 - dichloroethane?

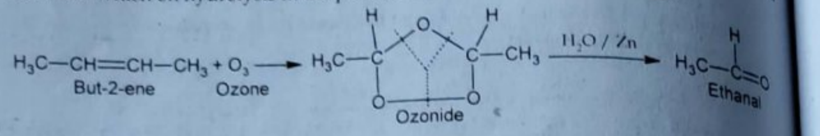
Write down suitable method for the conversion of ethanal into 2-hydroxypropanoic acid. [1.5×4]

»

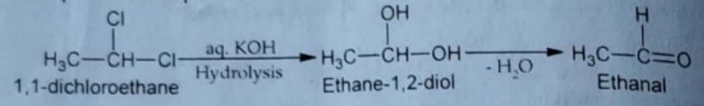
i. **Preparation of ethanal from ethyne:** When ethyne is passed through 42% H_2SO_4 and 1% $HgSO_4$ at 60°C, ethenol is obtained which undergoes tautomerization to give ethanal.



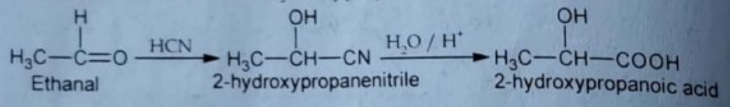
ii. **Preparation of ethanal from but-2-ene:** When but-2-ene is treated with ozone, ozonide is obtained which on hydrolysis in the presence zinc dust, ethanal is obtained.



iii. **Preparation of ethanal from 1,1-dichloroethane:** When 1,1-dichloroethane is hydrolyzed in the presence of aq. Alkali, ethanal is obtained.



Conversion of ethanal into 2-hydroxypropanoic acid:



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78. 2076 Set C Q.No. 31a **How is propanone one prepared from**

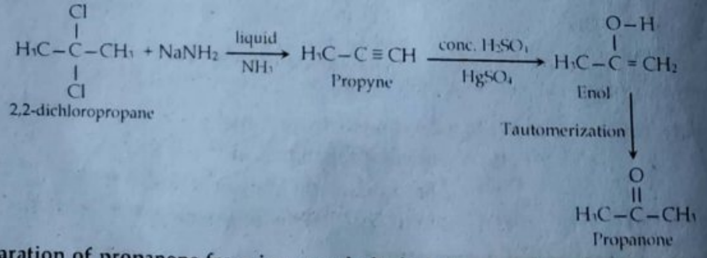
i. 2,2-dichloropropane **ii. Isopropyl alcohol**

iii. Propyne

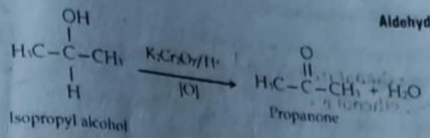
Give the suitable chemical reaction for the conversion of ethanoicacid into (i) methane (ii) methyl ethanoate. [3+2]

»

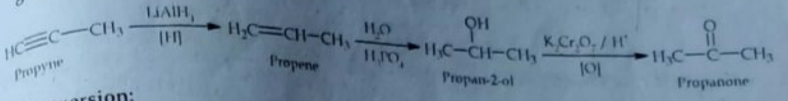
i. **Preparation of propanone from 2,2-dichloropropane:** 2,2-dichloropropane is heated with sodamide in the presence liquid ammonia, propyne is obtained. Propyne is treated with water in the presence of $HgSO_4$ and conc.H_2SO_4, enol is formed which on tautomerization gives propanone.



ii. **Preparation of propanone from isopropyl alcohol:** Isopropyl alcohol on oxidation with acidified solution of $K_2Cr_2O_7$, propanone is obtained.

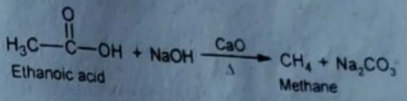


iii. **Preparation of propanone from propyne:** When propyne is reduced with $LiAlH_4$, propene is obtained. Propene is treated with water in the presence of phosphoric acid, propan-2-ol is obtained. Propan-2-ol on oxidation with $K_2Cr_2O_7$ in the presence of acid to give propanone.

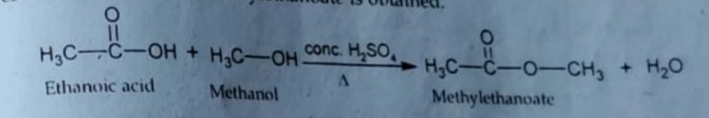


Conversion:

i. **Ethanoic acid into methane:** Ethanoic acid is heated with sodalime i.e. NaOH + CaO, methane is fomed.



ii. **Ethanoic acid into methylethanoate:** Ethanoic acid is treated with methanol in the presence of conc.H_2SO_4, methylethanoate is obtained.



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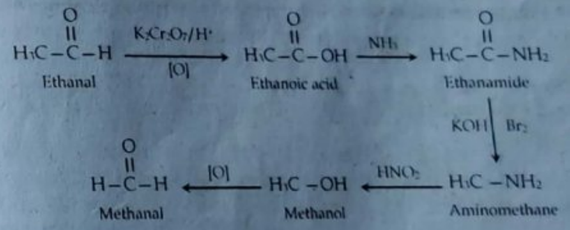
79. 2073 Supp Q.No. 31b **How is ethanal converted into methanal? Write the action of methanal on** [2+1.5+1.5]

i. **ammonia**

ii. **conc. NaOH**

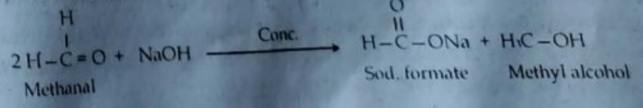
» **Conversion of ethanal into methanal:**



Action of methanal on:

i. **Ammonia:** Formaldehyde i.e. methanal reacts with ammonia gives hexamethylene tetramine which is used as urinary antiseptic.

ii. **Conc. NaOH:** Methanal or formaldehyde reacts with conc. NaOH, sodium formate and methyl alcohol is obtained.



80. 2072 Supp. Q.No. 31a **How is propanone prepared from:** [3+2]

i. 2, 2-dichloropropane ii. Iso-propyl alcohol

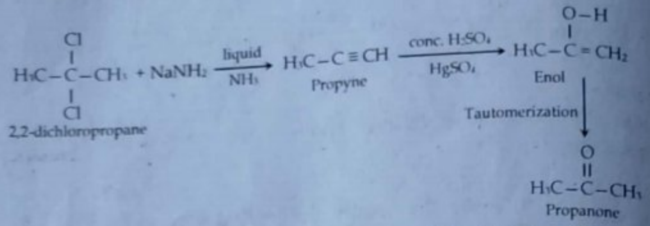
iii. Propyne

Give suitable chemical reaction for the conversion of ethanoic acid into

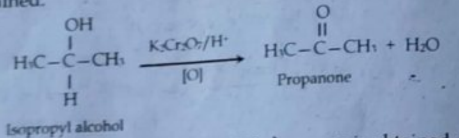
i. Methane ii. Methylethanoate

Preparation of propanone from:

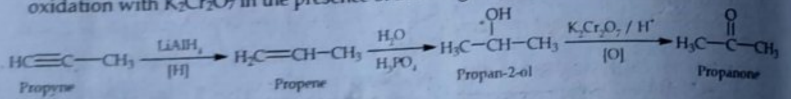
i. **2,2-dichloropropane:** 2,2-dichloropropane is heated with sodamide in the presence liquid ammonia, propyne is obtained. Propyne is treated with water in the presence of $HgSO_4$ and conc.H_2SO_4, enol is formed which on tautomerization gives propanone.



ii. **Isopropyl alcohol:** Isopropyl alcohol on oxidation with acidified solution of $K_2Cr_2O_7$, propanone is obtained.

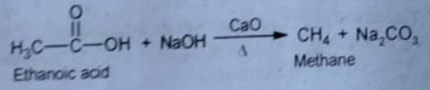


iii. **Propyne:** When propyne is reduced with $LiAlH_4$, propene is obtained. Propene is treated with water in the presence of phosphoric acid, propan-2-ol is obtained. Propan-2-ol on oxidation with $K_2Cr_2O_7$ in the presence of acid to give propanone.



Conversion:

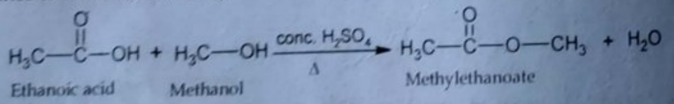
i. **Ethanoic acid into methane:** Ethanoic acid is heated with sodalime i.e. NaOH + CaO, methane is fomed.



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Ethanoic acid Methane

ii. **Ethanoic acid into methylethanoate:** Ethanoic acid is treated with methanol in the presence of conc.H_2SO_4, methylethanoate is obtained.

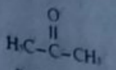


$$H_3C-\overset{O}{\overset{\|}{C}}-OH + H_3C-OH \xrightarrow[\Delta]{conc.\ H_2SO_4} H_3C-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_2O$$

Ethanoic acid Methanol Methylethanoate

81. 2071 Supp. Q.No. 31b **An alkene Ⓐ undergoes ozonolysis to give two carbonyl compounds Ⓑ and Ⓒ. The compound Ⓑ on reduction with Zn-Hg/H⁺ gives propane. The compound Ⓒ reacts with HCN and followed by hydrolysis to produce 2-hydroxypropanic acid as the major product. Write chemical reactions involved and give the IUPAC name of Ⓐ, Ⓑ and Ⓒ.**

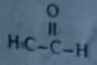
The carbonyl compound 'B' on reduction with Zn-Hg/H⁺ gives propane. The compound 'B' must be propanone.



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

Propanone (B)

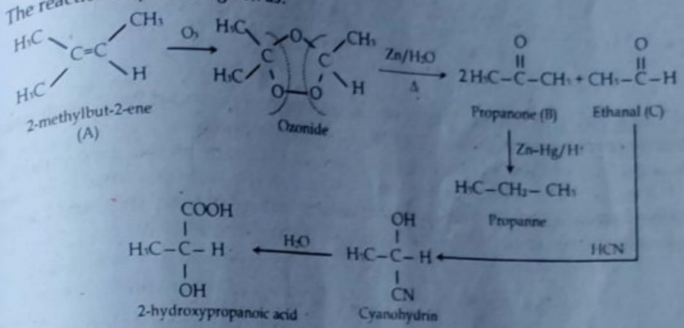
The carbonyl compound 'C' reacts with HCN and followed by hydrolysis gives 2-hydroxypropanoic acid. The compound 'C' must be ethanal.



$$H_3C-\overset{O}{\overset{\|}{C}}-H$$

Ethanal (C)

The reaction sequence is given as:



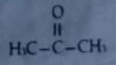
The compounds A = 2-methylbut-2-ene
B = Propanone
C = Ethanal

82. 2071 Set D Q.No. 31 b **An alkene Ⓐ undergoes ozonolysis to give two carbony compounds Ⓑ and Ⓒ. The compound Ⓑ on reduction with Zn–Hg / H⁺ gives propane. The compound Ⓒ reacts with HCN and followed by hydrolysis to produce 2-hydroxypropanic acid as the major product. Write chemical reactions involved and give the IUPAC name of A, B and C.** [5]

Please refer to 2071 Supp. Q.No. 31b

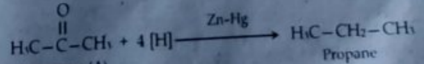
83. 2070 Set- C Q.No. 29 **An organic compound (A) reacts with HCN to give (B). On hydrolysis of (B) in acidic medium gives (C). Compound (A) also produces propane when treated with zinc amalgam and HCl. Identify A,B,C with reactions and give their IUPAC names. What product would you expect when (A) is treated with trichloromethane in alkaline medium?** [10]

The compound (A) produces propane when treated with Zn-Hg/HCl. So, (A) should be ketone having three carbons. The structure of (A) is



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

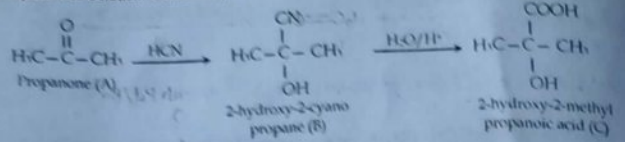
Propanone (A)



$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + 4[H] \xrightarrow{Zn-Hg} H_3C-CH_2-CH_3$$

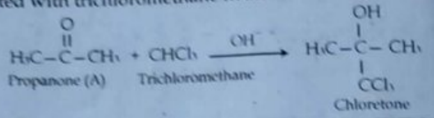
Propanone (A) Propane

The reaction sequence is gives as:



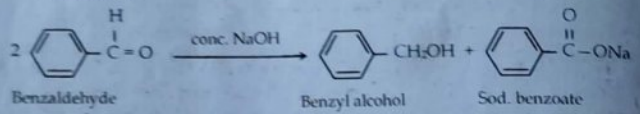
The compounds A = Propanone
B = 2-hydroxy-2-cyanopropane
C = 2-hydroxy-2-methylpropanoic acid

Propanone is treated with trichloromethane in alkaline medium, chloretone is formed.

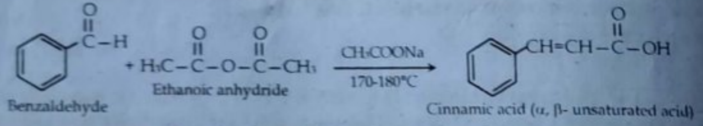


84. **2070 Set D Q.No. 31 a** **Show your acquaintance with Cannizzaro reaction and Perkin Condensation. What happens when propanone is treated with 2, 4 - dinitrophenylhydrazine.** [5]

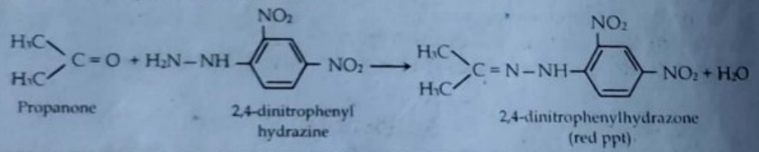
Acquaintance of Cannizzaro's reaction: Aldehyde containing no α-hydrogen (such as C_6H_5CHO,HCHO) when treated with aqueous or ethanolic alkali, undergo disproportionation to produce corresponding acid and alcohol. This simultaneous oxidation and reduction of aldehyde is khown as Cannizzaro's reaction.



Perkin Condensation: The condensation of an aromatic aldehyde with an acid anhydride in the presence of sodium or potassium salt of the same acid to produce α, β-unsaturated acid is known as the Perkin condensation.



When propanone is treated with 2,4-dinitrophenylhydrazine, red ppt of 2,4-dinitrophenylhydrazone is formed.

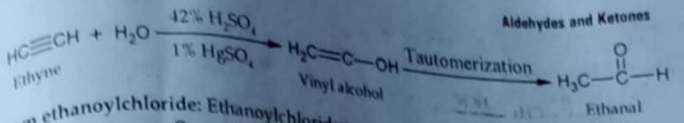


85. **2070 Set C Q.No. 31 a** **Write any three methods of preparation of ethanal. How is ethanal converted into**

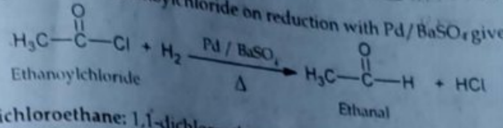
i. 3 - hydroxylbutanal **ii. Ethanoic acid** [5]

Preparation of ethanal:

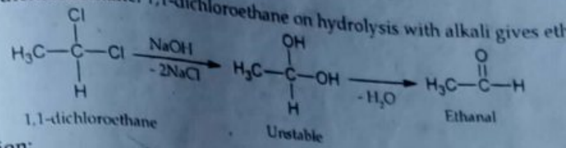
i. **From ethyne:** When ethyne is passed through 42% H_2SO_4 in presence of 1% $HgSO_4$ at 60°C, ethanal is obtained.



ii. **From ethanoylchloride:** Ethanoylchloride on reduction with Pd/$BaSO_4$ gives ethanal.

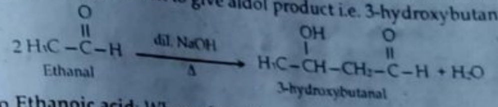


iii. **From 1,1-dichloroethane:** 1,1-dichloroethane on hydrolysis with alkali gives ethanal.

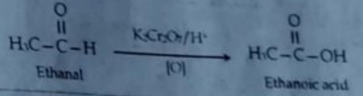


Conversion:

i. **Ethanal into 3-hydroxy butanal:** Ethanal is heated with dil.NaOH, two molecules of ethanal undergoes condensation to give aldol product i.e. 3-hydroxybutanal.

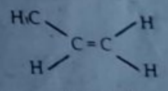


ii. **Ethanal into Ethanoic acid:** When ethanal is oxidized with acidified solution of $K_2Cr_2O_7$, ethanoic acid is obtained.



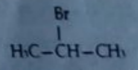
86. **2069 Set-B Q.No. 25** **An organic compound (A) reacts with PBr_3 to give (B). Compound (B) produces (C) when heated with alc. KOH. The compound (C) undergoes ozonolysis to yield ethanal and methanal as major products. The compound (A) responces iodoform test. Identify A,B,C and write reactions involved. How is (A) obtained from CH_3MgBr.** [5]

The compound 'C' on ozonolysis gives ethanal and methanal and the structure of 'C' must be



Propene (C)

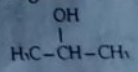
The compound 'B' produces 'C' when heated with alc. KOH. The structure of 'B' must be



$$H_3C-\overset{\overset{\large Br}{|}}{C}H-CH_3$$

2-bromopropane (B)

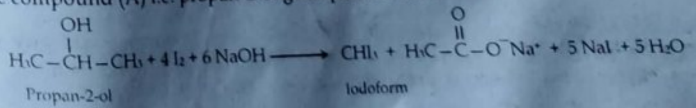
The compound 'A' reacts with PBr_3 to give 'B'. The structure of 'A' must be



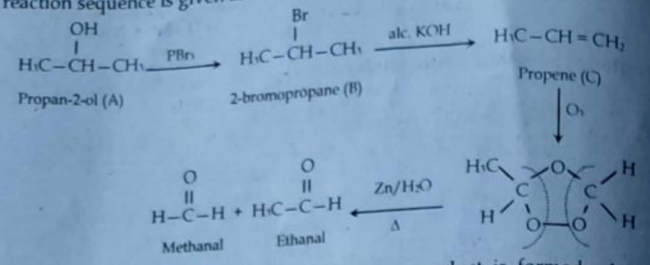
$$H_3C-\overset{\overset{\large OH}{|}}{C}H-CH_3$$

Propan-2-ol (A)

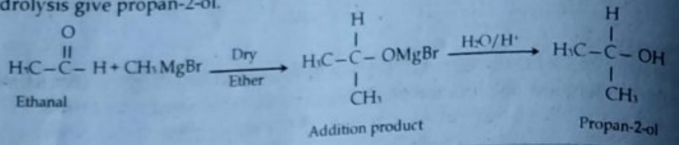
The compound (A) i.e. propan-2-ol gives positive iodoform test.



The reaction sequence is given as:



When CH_3MgBr is treated with ethanal, addition product is formed which on acid hydrolysis give propan-2-ol.

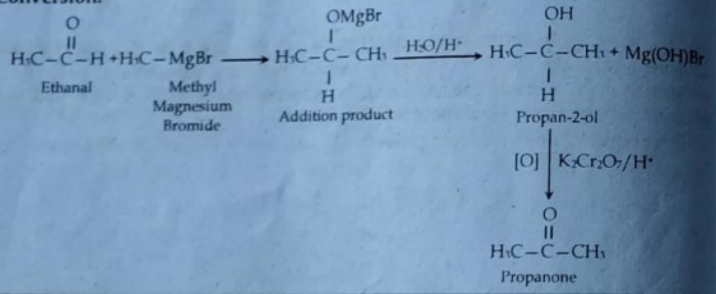


87. **2069 Supp. Set B Q.No. 32 b Give suitable chemical reaction for the preparation of ethanal from.**
   - **i. Ethyne**
   - **ii. Ethanoylchloride**
   - **iii. 1, 1-dichloroethane**

   How would you convert ethanal to propanone [5]

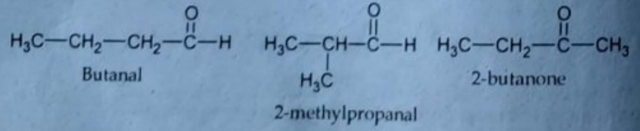
Preparation of ethanal: Please refer to 2070 Set C Q.No. 31 a

Conversion:

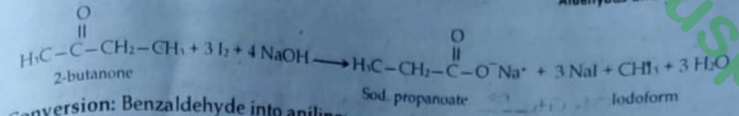


88. **2060 Q.No. 29**
   - **i. Write the possible isomeric aldehydes and ketones that can be formed from C_4H_8O. Give their IUPAC names. Which one of these isomers give iodoform test and why?**
   - **ii. Convert benzaldehyde into aniline and vice versa.** [10]

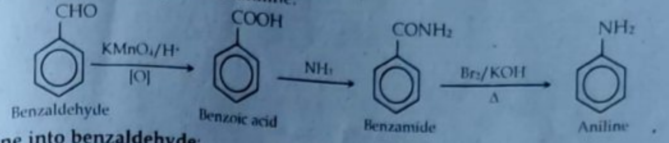
i. The possible isomers of C_4H_8O are



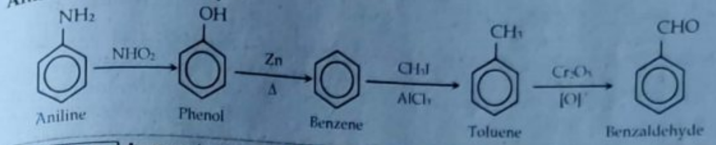
Out of these three isomeric aldehyde and ketone, only 2-butanone will give positive iodoform test. Because methyl group is directly linked with carbonyl carbon.



ii. Conversion: Benzaldehyde into aniline:

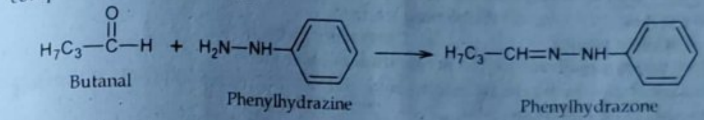


Aniline into benzaldehyde:

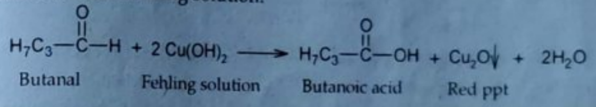


89. **2059 Q.No. 29a An organic compound A (C_4H_8O) forms phenyl hydrazone with phenyl hydrazine and reduces Fehling's solution. It has negative Iodoform test. Identify the organic compound A.** [5]

The organic compound having formula C_4H_8O forms phenyl hydrazone with phenyl hydrazine and reduces Fehling's solution and gives negative iodoform test. So, the compound must be butanal.



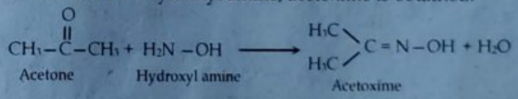
Butanal also reduces Fehling solution.



90. **2059 Q.No. 29b-(iii) Predict the major products of the following reactions:** [1]

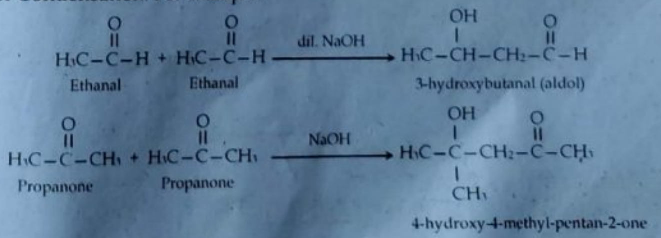
$$CH_3COCH_3 \xrightarrow{NH_2OH} \text{......}$$

When acetone is heated with hydroxyl amine, acetoxime is obtained.



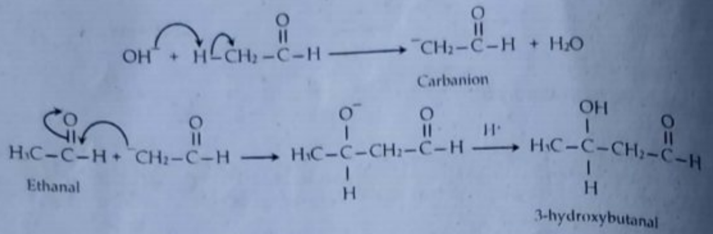
91. **2056 Q.No. 30 b-(iii) Show your acquaintance with the following: Aldol condensation** [5]

Two molecules of an aldehyde or ketone, under the influence of a dilute alkali combine to form a β-hydroxy aldehyde or β-hydroxy ketone. This condensation reaction is called **Aldol Condensation**. For example:



This reaction is called aldol condensation as the product contains both a hydroxyl group and a aldehyde group. (ald = aldehyde and ol = alcohol). Similar condensation of two molecules of ketones is also designed as aldol condensation but the product is known as ketol (ket = ketone; ol = alcohol). The mechanism of aldol condensation is given as below:

$$NaOH \rightleftharpoons Na^+ + OH^-$$



The aldol condensation can occur: (a) between two aldehydes (identical or different), (b) between two ketones (identical or different) and (c) between an aldehyde and a ketone. Whatever the nature of carbonyl compound, it is only the α-hydrogen atoms which are involved in the aldol condensation.

92. **2055 Q.No. 30** **Give three general methods of preparation of aldehydes. Show your acquaintance with the following reactions** **[10]**

i. Aldol condensation **ii. Cannizzaro's reaction**

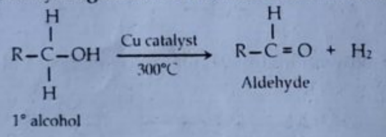
Three general methods for the preparation of aldehyde:

1. **From alcohol:** When primary alcohol is heated with $K_2Cr_2O_7$ and H_2SO_4, it is oxidized to corresponding aldehyde.

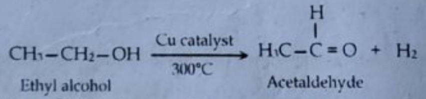
$$\underset{\text{Alcohol}}{RCH_2OH} + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Aldehyde}}{RCHO} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

2. **By the catalytic dehydrogenation of alcohols:** When vapour of an alcohol is passed over copper gauze catalyst, dehydrogenation of alcohol occurs and an aldehyde is formed.

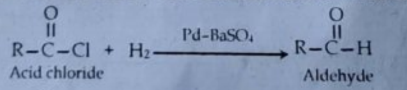


$$\underset{1^\circ\text{ alcohol}}{R-\overset{H}{\underset{H}{C}}-OH} \xrightarrow[300^\circ C]{\text{Cu catalyst}} \underset{\text{Aldehyde}}{R-\overset{H}{C}=O} + H_2$$

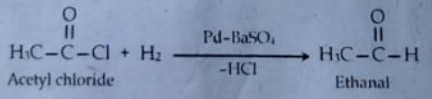


$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow[300^\circ C]{\text{Cu catalyst}} \underset{\text{Acetaldehyde}}{H_3C-\overset{H}{C}=O} + H_2$$

3. **From acid Chloride:** Aldehyde can be prepared by reducing acid chloride with hydrogen in the presence of Pd-BaSO₄. This reaction is known as Rosenmund's reaction.



$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow{Pd-BaSO_4} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H}$$

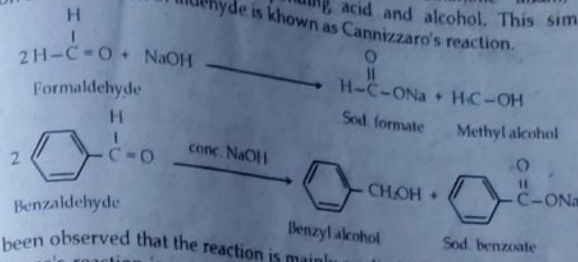


$$\underset{\text{Acetyl chloride}}{H_3C-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[-HCl]{Pd-BaSO_4} \underset{\text{Ethanal}}{H_3C-\overset{O}{\overset{\|}{C}}-H}$$

Acquaintance of the reaction:

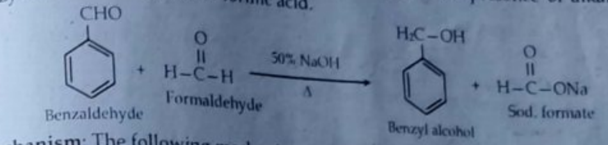
i. **Aldol Condensation:** Please refer to **2056 Q.No. 30 b-(iii)**

ii. **Acquaintance of Cannizzaro's reaction:** Aldehyde containing no α-hydrogen (such as $C_6H_5CHO, HCHO$) when treated with aqueous or ethanolic alkali, undergo disproportionation to produce corresponding acid and alcohol. This simultaneous oxidation and reduction of aldehyde is known as Cannizzaro's reaction.



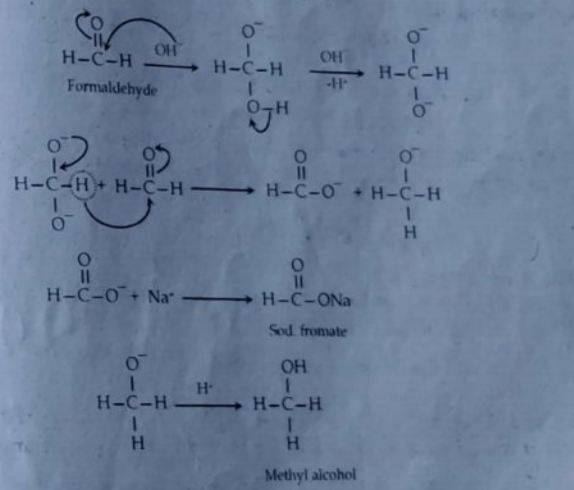
$$2H-\overset{H}{C}=O + NaOH \longrightarrow \underset{\text{Sod. formate}}{H-\overset{O}{\overset{\|}{C}}-ONa} + \underset{\text{Methyl alcohol}}{H_3C-OH}$$

It has been observed that the reaction is mainly applicable to aromatic aldehyde. Cannizzaro's reaction is not confined to the interaction of similar aldehydes. It can take place even between two different aldehyde and this type of Cannizzaro's reaction is known as"Crossed Cannizzaro's reaction".
For example, formaldehyde and benzaldehyde react in the presence of alkali to form benzyl alcohol and the salt of formic acid.



Mechanism: The following mechanism is proposed for Cannizzaro's reaction.

$$NaOH \rightleftharpoons Na^+ + OH^-$$



WRITE SHORT NOTES ON [5 MARKS]

93. **2052 Q.No. 28a** **2053 Q.No. 28b** **Cannizzaro's reaction**

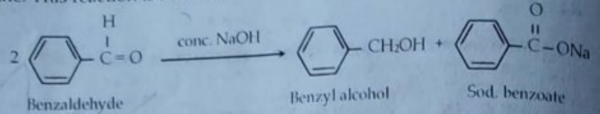
Please refer to **2055 Q.No. 30ii**

12.2 Aromatic Aldehydes and Ketones

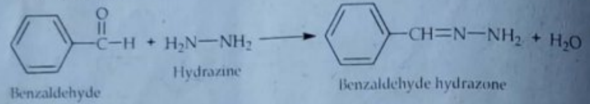
VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2072 Supp. Q.No. 12 **What happens when benzaldehyde is treated with:**
   i. **conc. NaOH solution** ii. **hydrazine.** [1+1]

i. **With conc. NaOH solution:** When benzaldehyde is warmed with aq. NaOH solution, it undergoes self oxidation and reduction gives a mixture of benzyl alcohol and sodium benzoate. This reaction is known as Cannizzaro's reaction.



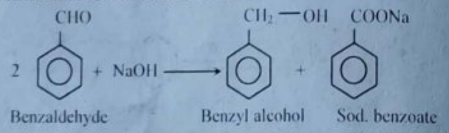
ii. **With hydrazine:** When benzaldehyde is treated with hydrazine, benzaldehyde hydrazone is obtained.



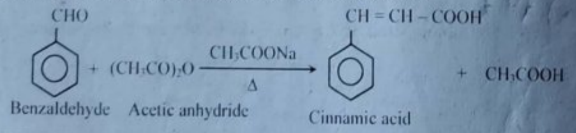
2. 2072 Set D Q.No. 12 **How does benzaldehyde reacts with:** [1+1]
   i. **Conc. NaOH**
   ii. **Acetic anhydride**

Reaction of benzaldehyde with

i. **Conc. NaOH:**
Benzaldehyde reacts with conc. NaOH, benzyl alcohol and sod. benzoate is obtained. This reaction is known as Cannizzaro's reaction.



ii. **With Acetic anhydride:**
Benzaldehyde reacts with acetic anhydride in the presence of sodium acetate, cinnamic acid is obtained. This reaction is known as Perkin's reaction.

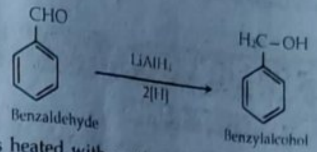


3. 2072 Set E Q.No. 12ii **What happens when Benzaldehyde is heated with conc. NaOH solution.** [1]

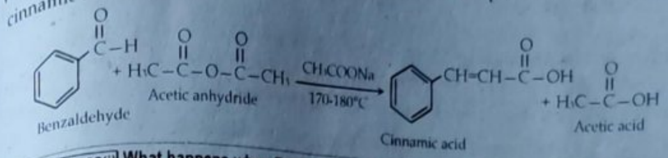
Please refer to 2072 Supp. Q.No. 12

4. 2070 Set C Q.No. 12 **What happens when benzaldehyde is heated with**
   i. LiAlH₄ ii. Acetic anhydride in presence of sodium acetate.

i. When benzaldehyde is reduced with LiAlH₄, benzylalcohol is formed.



ii. When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, cinnamic acid is formed.

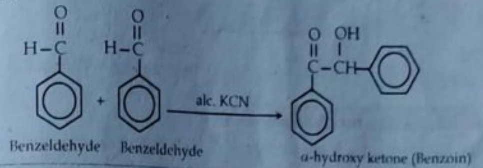


5. 2064 Q.No. 22(i) **What happens when Benzaldehyde is warmed with aqueous NaOH?**

Please refer to 2072 Supp. Q.No. 12

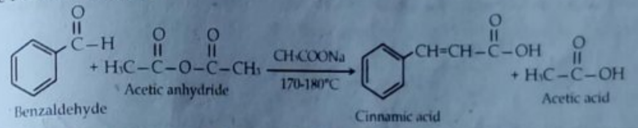
6. 2063 Q.No. 5(a) **Give an example of each of the following reactions: Benzoin condensation**

Benzoin condensation: When benzaldehyde is heated with alcoholic solution of KCN, two molecules of benzaldehyde join to form α-hydroxy ketone known as Benzoin condensation.



7. 2060 Q.No. 5(i) **Write an example of each of the following reaction: Perkin's condensation**

The condensation of an aromatic aldehyde with an acid anhydride in the presence of sodium or potassium salt of the same acid to produce α, β -unsaturated acid is known as the Perkin's reaction.

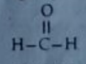


8. 2059 Q.No. 5 **Write an example of Perkin's condensation.**

Please refer to 2060 Q.No. 5(i)

9. 2058 Q.No. 5 **Give an example (with formula) each from aliphatic and aromatic aldehydes which give Cannizzaro's reaction.**

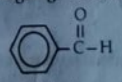
Aliphatic aldehyde having no α- hydrogen gives Cannizzaro's reaction is



$$H-\overset{\overset{O}{\|}}{C}-H$$

Methanal

Aromatic aldehye having no α- hydrogen gives Cannizzaro's reaction

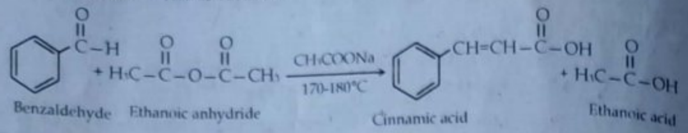


Benzaldehyde

SHORT ANSWER QUESTIONS [5 MARKS]

10. **2063 Q.No. 22 ii What action takes place when: Benzaldehyde is heated with ethanoic anhydride in presence of sodium ethanoate**

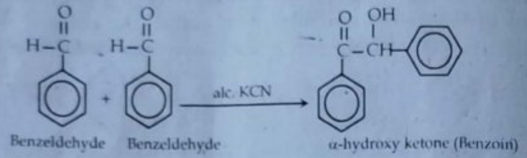
When benzaldehyde is heated with ethanoic anhydride in the presence of sodium ethanaote, cinnamic acid is formed.



11. **2062 Q.No. 23 a What happens when Benzaldehyde is refluxed with alcoholic KCN.**

Benzaldehyde is refluxed with alcoholic KCN:

Benzaldehyde on heating in the presence of alcoholic solution of KCN, a bimolecular condensation gives benzoin. This reaction is called **Benzoin condensation.**



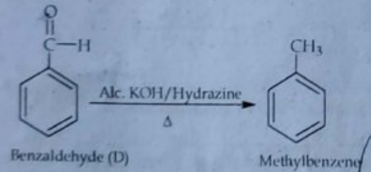
LONG ANSWER QUESTIONS [10 MARKS]

12. **2072 Supp. Q.No. 30b Identify the major products A, B, C, D in the following reaction sequence:**

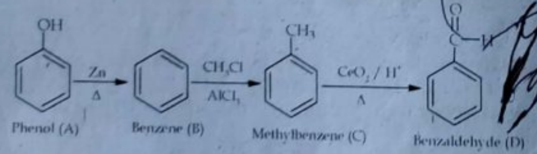
$$A \xrightarrow[\Delta]{Zn} B \xrightarrow[\Delta]{CH_3Cl/AlCl_3} C \xrightarrow[\Delta]{CeO_2/H^+} D$$

Compound Ⓓ gives methylbenzene when heated with alc. KOH and hydrazine.[4+1]

The compound D reacts with alc. KOH and hydrazine to give methylbenzene i.e. toluene. The compound D must be benzaldehyde

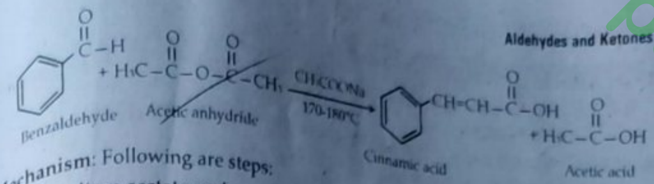


The reaction sequence is given as:



13. **2055 Q.No. 30 iii Show your acquaintance in the following reactions Perkin reaction.**

Perkin reaction: The condensation of an aromatic aldehyde with an acid anhydride in the presence of sodium or potassium salt of the same acid to produce α, β -unsaturated acid is known as the Perkin's reaction.



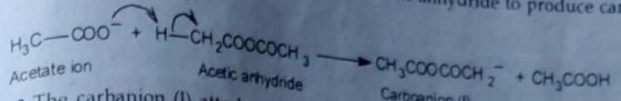
Mechanism: Following are steps:

Step: 1 Sodium acetate undergoes ionization to give acetate ion and sodium ion.

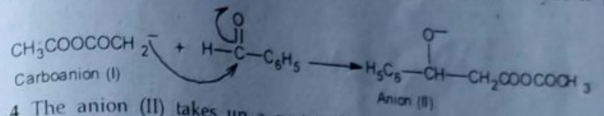
$$H_3C-COONa \rightleftharpoons H_3C-COO + Na$$

Sod. acetate — Acetate ion

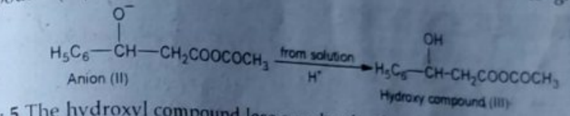
Step: 2 Acetate ions abstracts a proton (H^+) from acetic anhydride to produce carbanion (I)



Step: 3 The carbanion (I) attacks on the carbonyl carbon of benzaldehyde to produce carbanion (II).



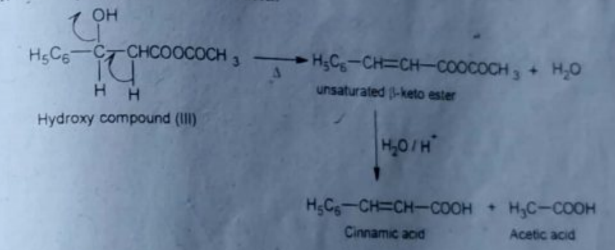
Step: 4 The anion (II) takes up a proton from aqueous solution to give hydroxyl compound (III).



$$H_5C_6-\overset{O^-}{\overset{|}{C}H}-CH_2COOCOCH_3 \xrightarrow[H^+]{\text{from solution}} H_5C_6-\overset{OH}{\overset{|}{C}H}-CH_2COOCOCH_3$$

Anion (II) — Hydroxy compound (III)

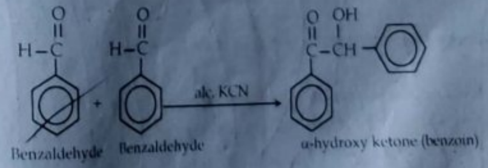
Step: 5 The hydroxyl compound lose a molecule of water to produce β-keto ester which upon hydrolysis gives cinnamic acid.



WRITE SHORT NOTES ON [5 MARKS]

14. **2052 Q.No. 28(a) 2053 Q.28(b) Benzoin condensation**

Benzoin condensation: When benzaldehyde is heated with alcoholic solution of KCN, two molecules of benzaldehyde join to form α-hydroxy ketone known as Benzoin condensation.

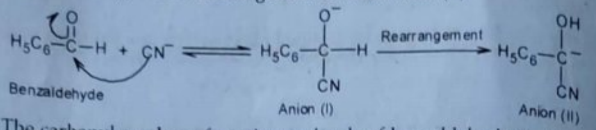


Mechanism: Following are the steps:

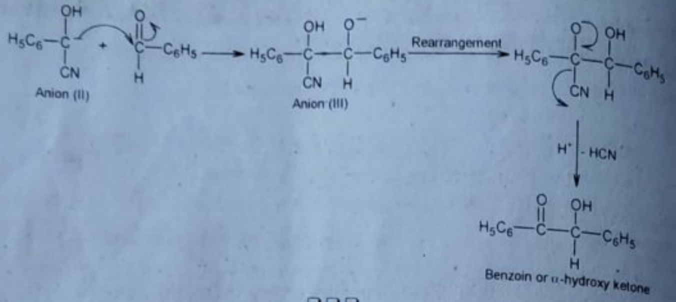
Step: 1 Alcoholic solution of KCN ionizes as

$$KCN \rightleftharpoons K^+ + \underset{\text{Nucleophile}}{CN^-}$$

Step: 2 The nucleophile (CN^-) attacks on carbonyl carbon of benzaldehyde to form cyanohydrins anion (I) which rearrangement to form anion (II).



Step: 3 The carbonyl carobon of another molecule of benzaldehyde is attacked by anion (II) to give anion (III) and loose a molecule of HCN to form benzoin i.e. α-hydroxy ketone.



❑❑❑

Unit 13

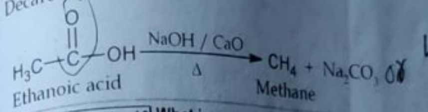
Carboxylic Acids

13.1 Aliphatic Carboxylic Acids

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2075 Set B Q.No. 15i** **Write an example of Decarbonxylation reaction** [1]

Decarboxylation reaction:

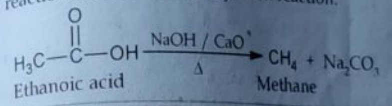


$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\Delta]{NaOH / CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

or heating di carboxylic acid at 160°C

2. **2074 Supp. Q.No. 13** **What is meant by decarboxylation reaction? Give an example of it.** [1+1]

The reaction in which carbondioxide molecule is removed, is called decarboxylation. When sodium salt of carboxylic acid is heated with sodalime, alkane is obtained. This reaction is called decarboxylation reaction.

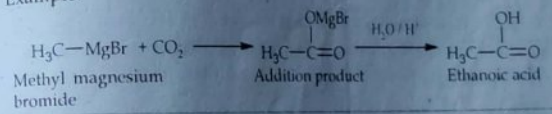


$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\Delta]{NaOH / CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

3. **2074 Set A Q.No. 13** **2074 Set B Q.No. 13** **What is meant by carboxylation reaction? Write an example of it.** [1+1]

Carboxylation is a chemical reaction where a carboxylic acid functional group is introduced into a substrate.

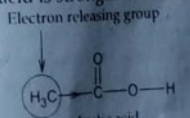
Example:



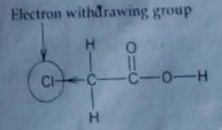
$$\underset{\text{Methyl magnesium bromide}}{H_3C-MgBr} + CO_2 \longrightarrow \underset{\text{Addition product}}{H_3C-\overset{\overset{OMgBr}{|}}{C}=O} \xrightarrow{H_2O/H^+} \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{OH}{|}}{C}=O}$$

4. **2073 Supp Q.No. 13** **Why is chloroacetic aicd stronger acid than acetic acid?** [2]

The greater the tendency of acid to release proton i.e. H^+ ion, stronger the acidic character. In acetic acid, methyl group is electron releasing group, due to this proton of acid does not loose easily but in chloroacetic acid, chlorine is electron withdrawing group and withdraw the electron, due to this proton of acid loose easily. Therefore, chloroacetic acid is stronger acid than acetic acid.



Acetic acid



Chloroacetic acid

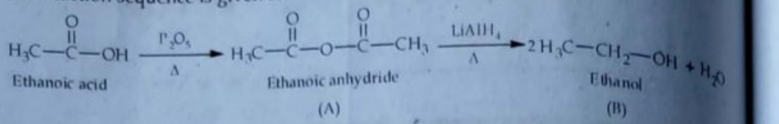
5. **2073 Set D Q.No. 13 Why is chloroacetic acid stronger acid than acetic acid?** [2]

Please refer to 2073 Supp Q No. 13

6. **2072 Supp. Q.No. 13 Identify the product Ⓐ and Ⓑ and give their IUPAC name.** [1+1]

$$CH_3COOH \xrightarrow[\Delta]{P_2O_5} A \xrightarrow[\Delta]{LiAlH_4} B$$

The reaction sequence is given as

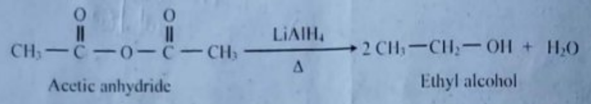


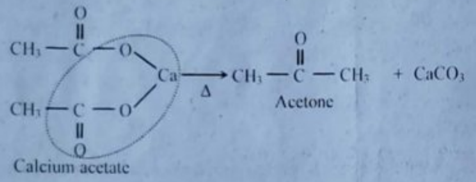
7. **2072 Set D Q.No. 13 Predict the major products of the following reaction:** [1+1]

i. $(CH_3\,CO)_2\,O \xrightarrow[\Delta]{LiAlH_4}$

i. $(CH_3\,COO)_2\,Ca \xrightarrow{\Delta}$

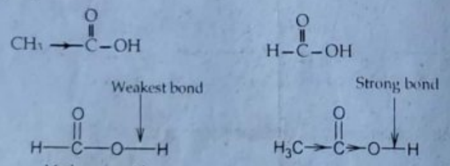
The major products of

i. 

ii. 

8. **2072 Set E Q.No. 13 Why methanoic acid is more acidic than ethanoic acid?** [2]

This is because of increasing positive inductive effect of alkyl groups attached to the -COOH group in acids as shown below.



Methanoic acid has no alkyl group no inductive effect

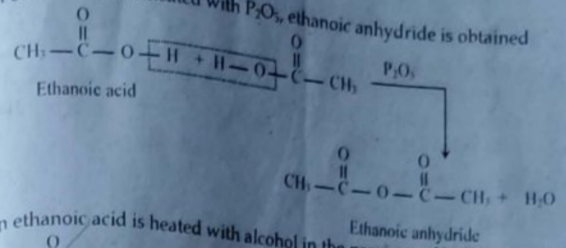
Ethanoic acid the direction of inductive effect is towards the direction of the arrow.

The methanoic acid will ionizes more in aqueous solution than ethanoic acid. Electron releasing group i.e -CH_3 group contains ethanoic acid and increase the electron density on the carboxylic group -COOH. Due to this hydrogen ion is not easily lost. Methanoic acid does not contain electron releasing group and hydrogen ion is lost easily. Larger the value of acidity constant (Ka), stronger will be the acid. The Ka value of methanoic acid is 17.7×10^{-5} and value of Ka in ethanoic acid is 1.76×10^{-5}. Therefore, methanoic acid is stronger than ethanoic acid.

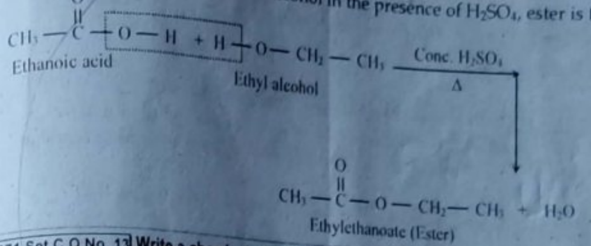
9. **2071 Supp. Q.No. 13 What happens when ethanoic acid is heated?** [1+1]

i. **With P_2O_5**
ii. **With alcohol in presence of H_2SO_4**

i. When ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained



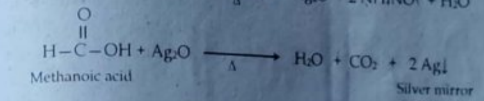
ii. When ethanoic acid is heated with alcohol in the presence of H_2SO_4, ester is formed.



10. **2071 Set C Q.No. 13 Write a chemical test to distinguish ethanoic acid from methanoic acid.** [2]

Tollen's reagent test is suitable test to identify whether the given acid is methanoic i.e. formic acid or ethanoic acid i.e. acetic acid. The two acids is taken in two separate test tubes, added Tollen's reagent and boiled for a few minutes. A silver mirror is deposited on the inner wall of test tube which shows the presence of methanoic acid. Methanoic acid only gives the silver mirror test but ethanoic acid does not give. In this way ethanoic and methanoic acid is identified.

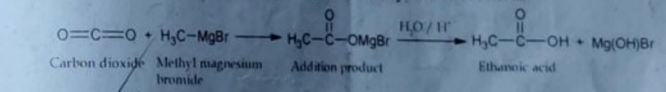
$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2\,NH_4NO_3 + H_2O$$



$$\underset{\text{Methanoic acid}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + Ag_2O \xrightarrow[\Delta]{} H_2O + CO_2 + \underset{\text{Silver mirror}}{2\,Ag\downarrow}$$

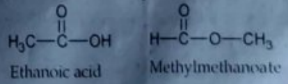
11. **2071 Set D Q.No. 13 a Write an example of each of: Carboxylation reaction** [1]

Carboxylation reaction: The chemical reaction in which carboxylic acid functional group is introduced in to the substance is called **Carboxylation reaction.**



12. **2070 Supp. Q.No. 13 2070 Set D Q.No. 13 What is the functional isomer of ethanoic acid? Give its IUPAC name.** [2]

Functional isomer of ethanoic acid is methylmethanoate.



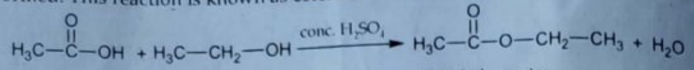
13. **2070 Set C Q.No. 13 Why is ethanoic acid weaker acid than methanoic acid?** [2]

Please refer to 2072 Set E Q.No. 13

14. **2069 Supp. Set B Q.No. 13** **How does enthanoic acid reacts with** **[2]**
   i. **ethanol**
   ii. **PCl_5**

Ethanoic acid reacts with:

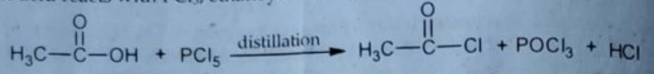
i. **Ethanol:** Ethanoic acid reacts with ethanol in the presence of conc.H_2SO_4, ethylethanoate is formed. This reaction is known as **esterification reaction**.



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + H_3C-CH_2-OH \xrightarrow{\text{conc. } H_2SO_4} H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$$

Ethanoic acid Ethanol Ethylethanoate

ii. Ethanoic acid reacts with PCl_5, ethanoylchloride is formed.

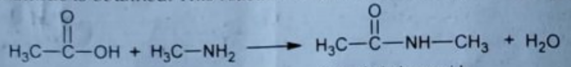


$$H_3C-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \xrightarrow{\text{distillation}} H_3C-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

Ethanoic acid Ethanoylchloride

15. **2069 (Set A) Q.No. 13 i** **Write an example of each of carboxylamine reaction** **[2]**

Carboxylamine reaction: When carboxylic acid is treated with aliphatic amine, N-substituted amide is obtained. This reaction is known as **Carboxylamine reaction.**

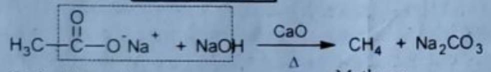


$$H_3C-\overset{O}{\overset{\|}{C}}-OH + H_3C-NH_2 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-NH-CH_3 + H_2O$$

Ethanoic acid Methanamine N-methylethanamide

16. **2069 (Set A) Q.No. 13 ii** **Write an example of each of decarboxylation reaction.** **[2]**

Please refer to 2074 Supp. Q.No. 13

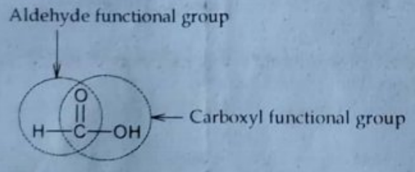


$$H_3C-\boxed{\overset{O}{\overset{\|}{C}}-O^-Na^+ + NaOH} \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sod. ethanoate Methane

17. **2069 (Set B) Q.No. 13** **'Methanoic acid gives Tollen's test but ehnanoic acid does not' give reason.** **[2]**

Methanoic acid contains aldehydic functional group but ethanoic acid does not contain aldehydic group. Due to this methanoic acid gives Tollen's test, ethanoic acid does not.



$$2AgNO_3 + 2NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2NH_4NO_3 + H_2O$$

$$H-\overset{O}{\overset{\|}{C}}-OH + Ag_2O \xrightarrow[\Delta]{} H_2O + CO_2 + 2Ag\downarrow$$

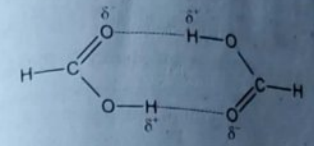
Methanoic acid Silver mirror

18. **2065 Q.No. 8** **Write a chemical test to distinguish methanoic acid from ethanoic acid.** **[2]**

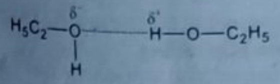
Please refer to 2071 Set C Q.No. 13

19. **2064 Q.No. 7** **The boiling point of methanoic acid is higher than ethanol though they have same molecular mass. Explain.** **[2]**

Methanoic acid have higher boiling point than ethanol though they have the same molecular mass. In the case of methanoic acid the carbonyl group is electron withdrawing group and due to this group hydrogen and oxygen bond is more polarized than the hydrogen oxygen bond in ethanol. Methanoic acid forms more hydrogen bond and exists in cyclic dimer than the ethanol. Therefore, methanoic acid have higher b.p. than ethanol.



H-bonding in methanoic acid
(b.p. = 100°C)



H-bonding in ethanol
(b.p. = 78°C)

20. **2063 Q.No. 7** **You are given two test tubes, one containing methanoic acid and other ethanoic acid. Suggest a suitable chemical test to identify them. Give chemical reaction too.** **[2]**

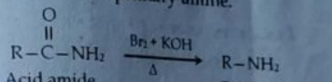
Please refer to 2071 Set C Q.No. 13

21. **2060 Q.No. 6** **Suggest a suitable chemical test to identify methanoic acid from ethanoic acid.** **[2]**

Please refer to 2071 Set C Q.No. 13

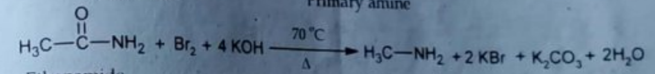
22. **2060 Q.No. 8** **What is decarbonylation? Give one example.** **[2]**

The reaction in which carbonyl group (-CO-) is remeoved, is called decarbonylation. Hoffmann Hypobromite reaction is the decarbonylation reaction in which carbonyl group is removed. Whe acid amide is heated with Br_2 in the presence of KOH, decarbonylation to form primary amine.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{Br_2 + KOH} R-NH_2$$

Acid amide Primary amine



$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4KOH \xrightarrow[\Delta]{70\,^\circ C} H_3C-NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Ethanamide Aminomethane

23. **2059 Q.No. 7** **Why is chloroacetic acid stronger than acetic acid?** **[2]**

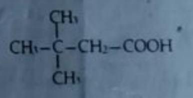
Please refer to 2073 Supp Q.No. 13

24. **2058 Q.No. 7** **Why is methanoic acid stronger than ethanoic acid?** **[2]**

Please refer to 2072 Set E Q.No. 13

25. **2056 Q.No. 18(b)** **Write the name of the following components according to the IUPAC rule.** **[2]**
$CH_3-C(CH_3)_2-CH_2-COOH$

IUPAC name

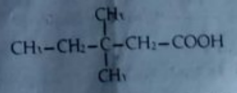


$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-COOH$$

3,3-dimethylbutanoic acid

26. **2052 Q.No. 10(b)** **Name: $CH_3-CH_2-C(CH_3)_2-CH_2-COOH$ according to IUPAC rule** **[2]**

The IUPAC name of



$$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-COOH$$

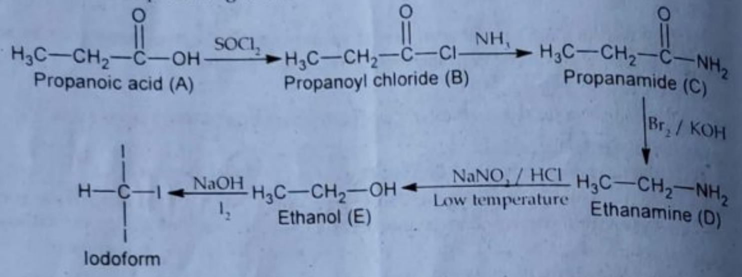
3,3-dimethylpentanoic acid

SHORT ANSWER QUESTIONS [5 MARKS]

27. **2076 Set B Q.No. 29 2076 Set C Q.No. 29 An aliphatic compound Ⓐ reacts with $SOCl_2$ to give Ⓑ. The compound Ⓑ is heated with ammonia to produce Ⓒ. The compound Ⓒ is further heated with Br_2/KOH to yield Ⓓ. The compound Ⓓ gives Ⓔ when treated with $NaNO_2$/HCl at low temperature. The compound Ⓔ is primary alcohol which gives positive idoform test. Identify ⒶⒷⒸⒹ and Ⓔ. Write reactions involved.** [5]

The compound E is primary alcohol having two carbon atom and gives +ve iodoform test. The compound E must be ethanol.

The reaction sequence is given as



The compounds are

Ⓐ = Propanoic acid | Ⓑ = Propanoyl chloride

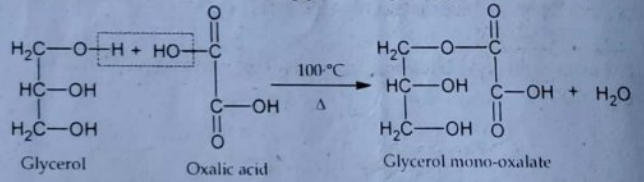
Ⓒ = Propanamide | Ⓓ = Ethanamine

and Ⓔ = Ethanol

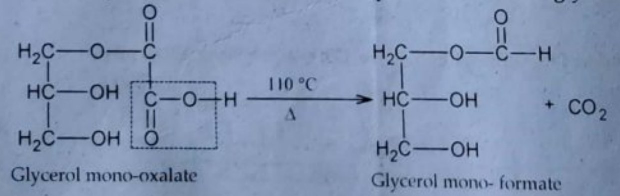
28. **2075 GIE Q.No. 28 Describe the laboratory preparation of anhydrous formic acid.** [5]

Theory: Formic acid is prepared in the laboratory by the decarboxylation of oxalic acid with glycerol at 110°C. Following reactions occur and formic acid is obtained.

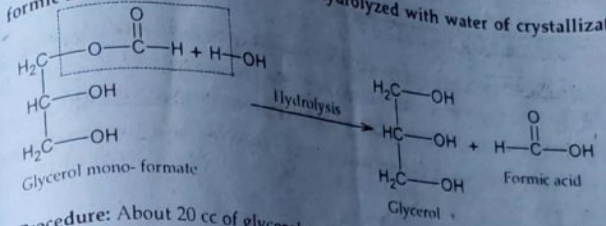
Step:- I Oxalic acid reacts with glycerol to give glycerol mono-oxalate



Step:- II Glycerol mono-oxalate is decomposed at 110°C into glycerol mono-formate



Step:- III Glycerol mono-formate is hydrolyzed with water of crystallization to give formic acid



Procedure: About 20 cc of glycerol and 30 gram of powdered oxalic acid are taken in the flask fitted with a thermometer and a condenser, the mixture is heated on water bath at 110°C when formic acid distills out. It is cooled in the condenser and aqueous formic acid collects in the conical flask.

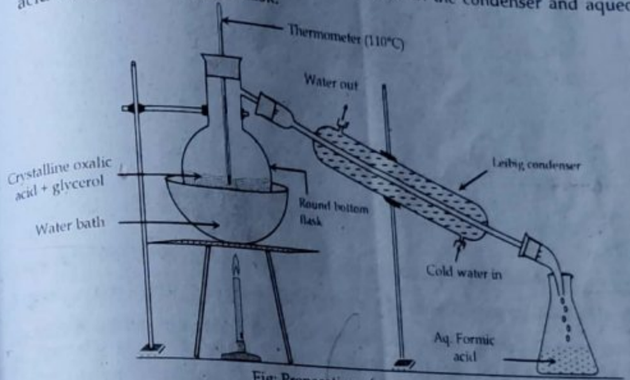


Fig: Preparation of aqueous formic acid

Preparation of Anhydrous formic acid: The aquous formic acid is neutralized with lead carbonate when lead formate is crystallized and the crystals of lead formate are filtered by means of a Buchner funnel, washed thoroughly with water and finally dried. The dry lead formate is packed in the inner tube of a Leibig's condenser and treated with dry H_2S gas. As a result of this, anhydrous formic acid is liberated which collects in the receiver.

$$\underset{\text{Lead carbonate}}{PbCO_3} + \underset{\text{Formic acid}}{2HCOOH} \longrightarrow \underset{\text{Lead formate}}{Pb(HCOO)_2} + CO_2 + H_2O$$

$$\underset{\text{Lead formate}}{Pb(HCOO)_2} + H_2S \longrightarrow \underset{\text{Black ppt}}{PbS\downarrow} + \underset{\text{Anhydrous formic acid}}{2HCOOH}$$

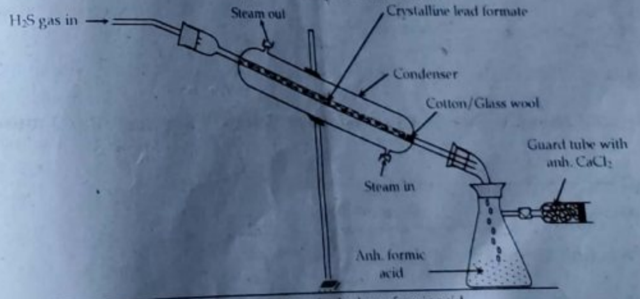


Fig: Preparation of anhydrous formic acid

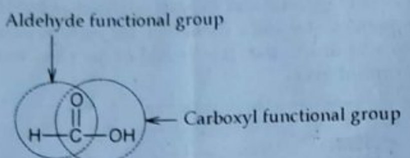
29. **2075 Set A Q.No. 28** **Describe the laboratory preparation of anhydrous formic acid.** [5]

➣ Please refer to 2075 GIE Q.No. 28

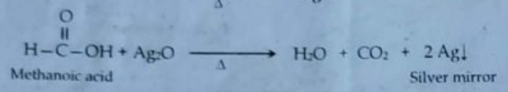
30. **2075 Set B Q.No. 28** **How is anhydrous formic acid prepared in the laboratory? Why does methanoic acid give Tollen's test?** [3+2]

➣ **Laboratory preparation of anhydrous formic acid:** Please refer to 2075 GIE Q.No. 28

Tollen's test of methanoic acid: Methanoic acid i.e. formic acid contains aldehydic functional group. Due to this methanoic acid gives Tollen's test and forms silver mirror on the inner wall of test tube.



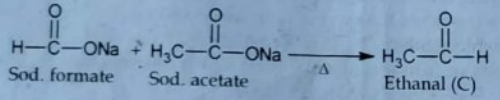
$$2\,AgNO_3 + 2\,NH_4OH \xrightarrow{\Delta} Ag_2O + 2\,NH_4NO_3 + H_2O$$



$$\underset{\text{Methanoic acid}}{H-\overset{O}{\overset{\|}{C}}-OH} + Ag_2O \xrightarrow{\Delta} H_2O + CO_2 + \underset{\text{Silver mirror}}{2\,Ag\downarrow}$$

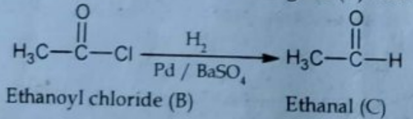
31. **2075 Set B Q.No. 29** **An aliphatic compound Ⓐ reacts with $SOCl_2$ to give Ⓑ. Ⓑ on reduction with H_2, in presence of Pd/$BaSO_4$ to give Ⓒ. When HCN is added to Ⓒ produces Ⓓ. On hydrolysis of Ⓓ in acidic medium forms Ⓔ. Compound Ⓒ can be obtained by heating a mixture of sodium formate and sodium acetate. Identify A, B, C, D, E and write reactions involved.** [5]

➣ The compound (C) is obtained by heating a mixture of sodium formate and sodium acetate.



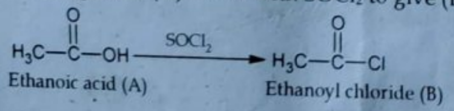
$$\underset{\text{Sod. formate}}{H-\overset{O}{\overset{\|}{C}}-ONa} + \underset{\text{Sod. acetate}}{H_3C-\overset{O}{\overset{\|}{C}}-ONa} \xrightarrow{\Delta} \underset{\text{Ethanal (C)}}{H_3C-\overset{O}{\overset{\|}{C}}-H}$$

The compound (B) on reduction gives (C). The structure of (B) must be



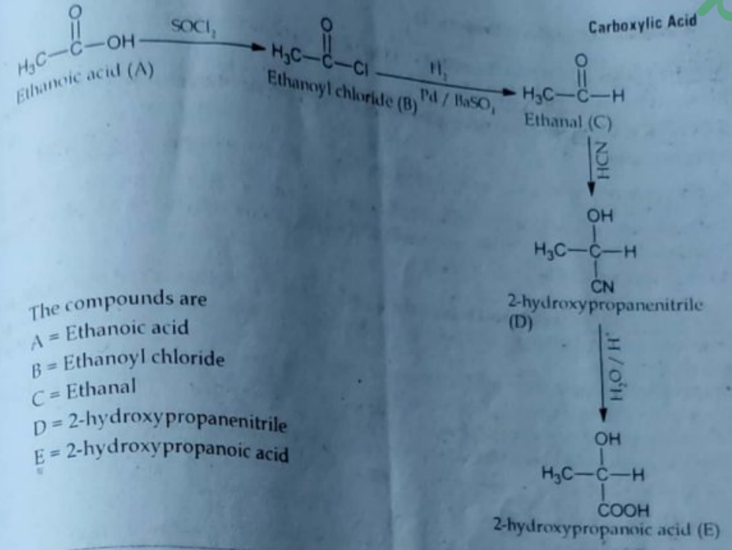
$$\underset{\text{Ethanoyl chloride (B)}}{H_3C-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[Pd\,/\,BaSO_4]{H_2} \underset{\text{Ethanal (C)}}{H_3C-\overset{O}{\overset{\|}{C}}-H}$$

The compound (A) reacts with $SOCl_2$ to give (B). The structure of (A) must be



$$\underset{\text{Ethanoic acid (A)}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride (B)}}{H_3C-\overset{O}{\overset{\|}{C}}-Cl}$$

The reaction sequence is given as:



$$\underset{\text{Ethanoic acid (A)}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride (B)}}{H_3C-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[Pd\,/\,BaSO_4]{H_2} \underset{\text{Ethanal (C)}}{H_3C-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{HCN} \underset{\text{2-hydroxypropanenitrile (D)}}{H_3C-\overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-H} \xrightarrow{H_2O\,/\,H^+} \underset{\text{2-hydroxypropanoic acid (E)}}{H_3C-\overset{OH}{\overset{|}{\underset{COOH}{\underset{|}{C}}}}-H}$$

The compounds are

A = Ethanoic acid

B = Ethanoyl chloride

C = Ethanal

D = 2-hydroxypropanenitrile

E = 2-hydroxypropanoic acid

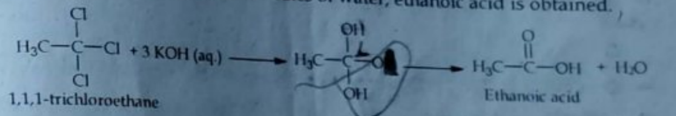
32. **2074 Supp. Q.No. 28** **2074 Set B Q.No. 28** **Give chemical reaction for the preparation of ethanoic acid from**

  i. **1,1,1-trichloroethane**
  ii. **Methyl magnesium iodide**
  iii. **Ethanenitrile**

How is ethanoic acid converted into methanoic acid? [3+2]

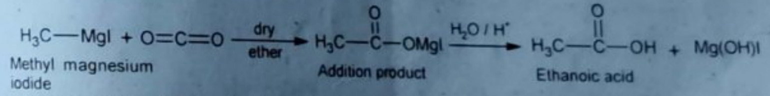
➣ **Preparation of ethanoic acid from:**

i. **1,1,1-trichloroethane:** When 1,1,1-trichloroethane is treated with aq. KOH, unstable product is obtained which loose a molecules of water, ethanoic acid is obtained.



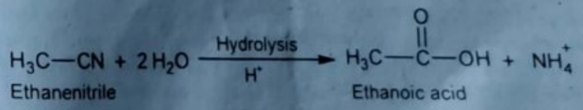
$$\underset{\text{1,1,1-trichloroethane}}{H_3C-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-Cl} + 3\,KOH\,(aq.) \longrightarrow H_3C-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OH \longrightarrow \underset{\text{Ethanoic acid}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} + H_2O$$

ii. **Methyl magnesium iodide:** When methyl magnesium iodide is treated with carbon dioxide in the presence of dry ether, an addition product is obtained which on hydrolysis to give ethanoic acid.



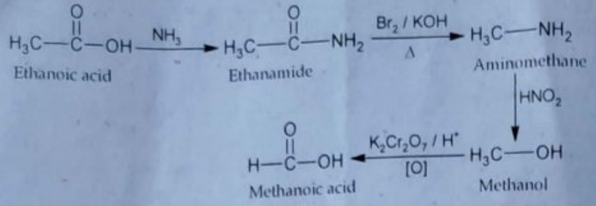
$$\underset{\text{Methyl magnesium iodide}}{H_3C-MgI} + O{=}C{=}O \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Addition product}}{H_3C-\overset{O}{\overset{\|}{C}}-OMgI} \xrightarrow{H_2O\,/\,H^+} \underset{\text{Ethanoic acid}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} + Mg(OH)I$$

iii. **Ethanenitrile:** Ethanenitrile on hydrolysis in the presence of acid, ethanoic acid is obtained.



$$\underset{\text{Ethanenitrile}}{H_3C-CN} + 2\,H_2O \xrightarrow[H^+]{\text{Hydrolysis}} \underset{\text{Ethanoic acid}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} + \overset{+}{NH_4}$$

Conversion:

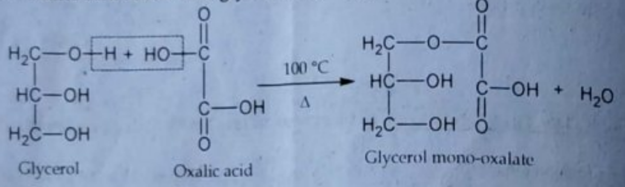


33. **2074 Set A Q.No. 28** **Give chemical reaction for the preparation of methanoic acid from oxalic acid. How is anhydrous methanoic acid obtained from hydrous methanoic acid? Convert methanoic acid into ethanoic acid.** **[1+2+2]**

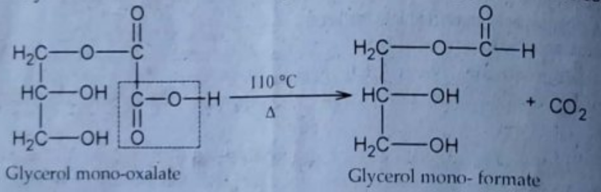
Preparation of methanoic acid from oxalic acid:

Formic acid is prepared by the decarboxylation of oxalic acid with glycerol at 110°C. Following reactions occur and formic acid is obtained.

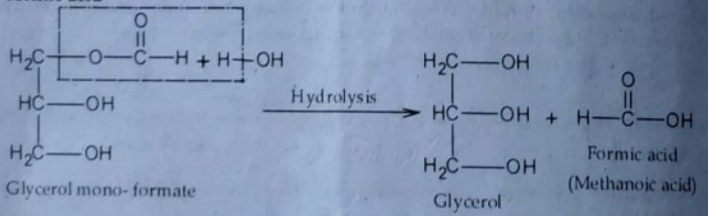
Step:- I Oxalic acid reacts with glycerol to give glycerol mono-oxalate



Step:- II Glycerol mono-oxalate is decomposed at 110°C into glycerol mono-formate



Step:- III Glycerol mono-formate is hydrolyzed with water of crystallization to give formic acid



Preparation of Anhydrous formic acid: The aqueous formic acid is neutralized with lead carbonate when lead formate is crystallized and the crystals of lead formate are filtered by means of a Buchner funnel, washed thoroughly with water and finally dried. The dry lead formate is packed in the inner tube of a Leibig's condenser and treated with dry H_2S gas. As a result of this, anhydrous formic acid is liberated which collects in the receiver.

$$\underset{\text{Lead carbonate}}{PbCO_3} + \underset{\text{Formic acid}}{2HCOOH} \longrightarrow \underset{\text{Lead formate}}{Pb(HCOO)_2} + CO_2 + H_2O$$

$$\underset{\text{Lead formate}}{Pb(HCOO)_2} + H_2S \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + \underset{\text{Anhydrous formic acid}}{2\,HCOOH}$$

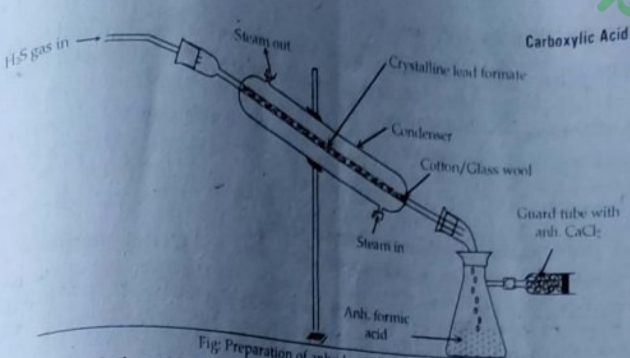
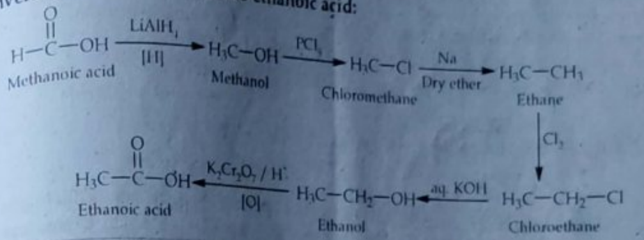


Fig: Preparation of anhydrous formic acid

Conversion: Methanoic acid into ethanoic acid:



34. **2073 Supp Q.No. 27** **2073 Set C Q.No. 27** **Describe the laboratory method of preparation of anhydrous formic acid. How does it react with Tollen's reagent?** **[4+1]**

Preparation of anhydrous formic acid: Please refer to 2074 Set A Q.No. 28

Tollen's reagent test of formic acid: Please refer to 2075 Set B Q.No. 28

35. **2072 Supp. Q.No. 27** **Write down a chemical reaction for the preparation of methanoic acid from Oxalic acid. How is methanoic acid converted into ethanoic acid?** **[2+3]**

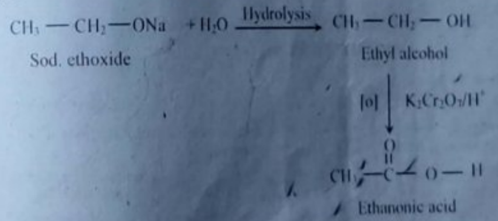
Preparation of methanoic acid from oxalic acid: Please refer to 2074 Set A Q.No. 28

Conversion: Please refer to 2074 Set A Q.No. 28

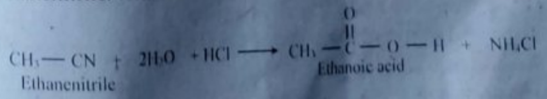
36. **2072 Set C Q.No. 28** **Give the chemical reactions for the preparation of ethanoic acid from (i) sodium ethoxide (ii) ethanenitrile (iii) methyl magnesium iodide. Why is acetic acid weaker acid than chloro acetic acid?** **[3+2]**

Preparation of ethanoic acid from

i. **Sodium ethoxide:** When sod. ethoxide on hydrolysis, ethyl alcohol is obtained. Ethyl alcohol on oxidation with acidified $K_2Cr_2O_7$, ethanoic acid is obtained.

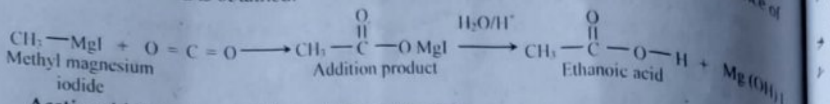


ii. **Ethanenitrile:** When ethanenitrile is boiled with HCl, ethanoic acid is obtained.



$$\underset{\text{Ethanenitrile}}{CH_3-CN} + 2H_2O + HCl \longrightarrow \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H} + NH_4Cl$$

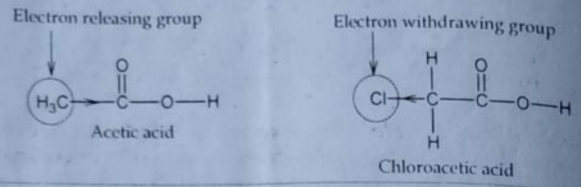
iii. **Methyl magnesium iodide:** When methyl magnesium iodide is treated with carbon dioxide, addition product is obtained. Addition product on hydrolysis in the presence of acid, ethanoic acid is obtained.


$CH_3-MgI + O=C=O \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OMgI \xrightarrow{H_2O/H^+} CH_3-\overset{O}{\overset{\|}{C}}-O-H + Mg(OH)I$

Methyl magnesium iodide; Addition product; Ethanoic acid

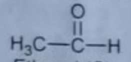
Acetic acid is weaker acid than chloroacetic acid:

The greater the tendency of acid to release proton i.e. H^+ ion, stronger the acidic character. In acetic acid, methyl group is electron releasing group, due to this proton of acid does not loose easily but in chloroacetic acid, chlorine is electron withdrawing group and withdraw the electron, due to this proton of acid loose easily. Therefore, chloroacetic acid is stronger acid than acetic acid.



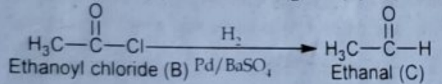
37. **2072 Set C Q.No. 29** **2072 Set D Q.No. 29** **An aliphatic compound Ⓐ reacts with $SOCl_2$ to give Ⓑ. Ⓑ on reduction with H_2 in presence of $Pd/BaSO_4$ to give Ⓒ. When HCN is added to Ⓒ produces Ⓓ. On hydrolysis of Ⓓ in acidic medium forms Ⓔ. Compound Ⓒ gives iodoform test and produces silver mirror with Tollen's reagent. Identify Ⓐ, Ⓑ, Ⓒ, Ⓓ, Ⓔ and write reactions involved.** [5]

The compound (c) gives iodoform test and produce silver mirror with Tollen's reagent. The structure of (C) must be


$H_3C-\overset{O}{\overset{\|}{C}}-H$

Ethanal (C)

The compound (B) on reduction gives (C). The structure of (B) must be


$H_3C-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} H_3C-\overset{O}{\overset{\|}{C}}-H$

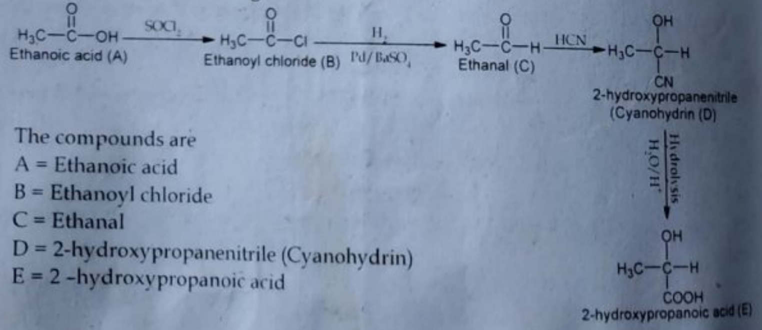
Ethanoyl chloride (B); Ethanal (C)

The compound (A) reacts with $SOCl_2$ to give (B). The structure of (A) must be


$H_3C-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} H_3C-\overset{O}{\overset{\|}{C}}-Cl$

Ethanoic acid (A); Ethanoyl chloride (B)

The sequence of reaction is given as



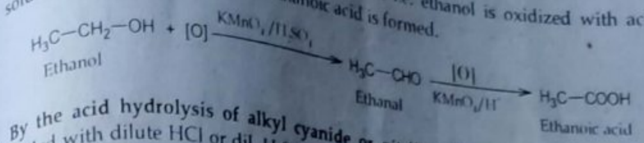
The compounds are

A = Ethanoic acid
B = Ethanoyl chloride
C = Ethanal
D = 2-hydroxypropanenitrile (Cyanohydrin)
E = 2 -hydroxypropanoic acid

2072 Set D Q.No. 28 **Suggest any three suitable chemical reactions for the preparation of ethanoic acid. How is ethanoic acid converted into methanoic acid?** [3+2]

Three methods for the preparation of ethanoic acid

From primary alcohol: When primary alcohol i.e. ethanol is oxidized with acidified solution of $K_2Cr_2O_7$ or $KMnO_4$, ethanoic acid is formed.


$H_3C-CH_2-OH + [O] \xrightarrow{KMnO_4/H_2SO_4} H_3C-CHO \xrightarrow[KMnO_4/H^+]{[O]} H_3C-COOH$

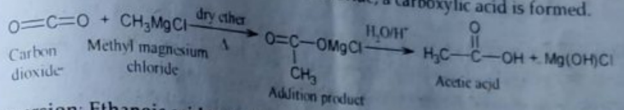
Ethanol; Ethanal; Ethanoic acid

b. **By the acid hydrolysis of alkyl cyanide or nitrile:** When alkyl cyanide or nitrile is boiled with dilute HCl or dil. H_2SO_4, the cyanide group(CN) is converted to carboxylic group(COOH) and corresponding carboxylic acid is formed.

$$\underset{\text{Alkyl cyanide}}{R-CN} + 2H_2O + HCl \xrightarrow{\text{Boil}} \underset{\text{Carboxylic acid}}{R-COOH} + NH_4Cl$$

$$\underset{\text{Methyl cyanide}}{CH_3-CN} + 2H_2O + HCl \xrightarrow{\text{Boil}} \underset{\text{Ethanoic acid}}{CH_3-COOH} + NH_4Cl$$

c. **From Grignard's reagent:** When carbon dioxide is bubbled in an ethereal solution of Grignard's reagent i.e. methyl magnesium chloride, a carboxylic acid is formed.


$O=C=O + CH_3MgCl \xrightarrow[\Delta]{\text{dry ether}} O=\underset{CH_3}{\underset{|}{C}}-OMgCl \xrightarrow{H_2O/H^+} H_3C-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)Cl$

Carbon dioxide; Methyl magnesium chloride; Addition product; Acetic acid

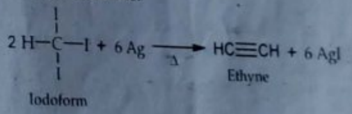
Conversion: Ethanoic acid to Methanoic acid: Please refer to **2074 Supp. Q.No. 28**

39. **2070 Supp. Q.No. 27** **Identify A, B, C, D and E in the following reaction sequence and write reactions involved.** [5]

$$A \xrightarrow{NH_3} B \xrightarrow[\Delta]{Br_2/aq.KOH} C \xrightarrow{HNO_2} D \xrightarrow[\Delta]{NaOH/I_2} E$$

The compound E produces ethyne when heated with silver powder.

The compound 'E' produces ethyne when heated with silver powder. The compound E must be iodoform i.e. tri-iodomethane.


$2\,H-\underset{I}{\underset{|}{\overset{I}{\overset{|}{C}}}}-I + 6\,Ag \xrightarrow{\Delta} HC{\equiv}CH + 6\,AgI$

Iodoform; Ethyne

The compound E is obtained from D with NaOH and I_2. The compound D must be Ethanol.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

The compound D is obtained from C with HNO_2. The compound C must be ethanamine.

$$\underset{\text{Ethanamine}}{CH_3-CH_2-NH_2}$$

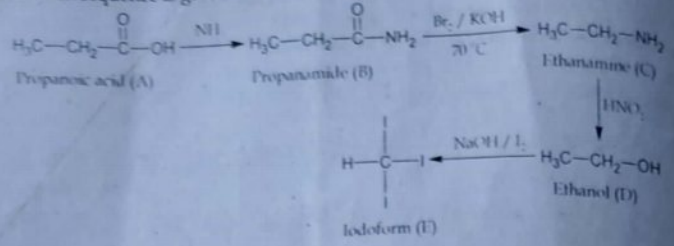
The compound C is obtained from B with Br_2 and aq. KOH, the compound B must be Propanamide.

$$\underset{\text{Propanamide}}{CH_3-CH_2-CO-NH_2}$$

The compound B is obtained from A with NH_3, the compound A must be propanoic acid.

$$\underset{\text{Propanoic acid}}{CH_3-CH_2-COOH}$$

The reation sequence is given as:



The compounds A = Propanoic acid B = Propanamide
C = Ethanamine D = Ethanol
E = Iodoform

40. **2070 Set C Q.No. 27** **Describe the method of preparation of anhydrous formic acid in the laboratory.** [5]

Please refer to 2075 GIE Q.No. 28

41. **2069 Supp. Q.No. 24** **How is anhydrous formic acid prepared in the laboratory? Why does formic acid give silver mirror with Tollen's reagent?** [5]

Laboratory preparation of anhydrous formic acid: Please refer to 2075 GIE Q No. 28

Tollen's test of methanoic acid: Please refer to 2075 Set B Q.No. 28

42. **2068 Q.No. 23** **Write any three important methods of preparation of ethanoic acid. How would you obtain anhydrous formic acid from its aqueous solution?** [5]

Three methods for the preparation of ethanoic acid: Please refer to 2072 Set D Q.No. 28

Preparation of Anhydrous formic acid: The aquous formic acid is neutralized with lead carbonate when lead formate is crystallized and the crystals of lead formate are filtered by means of a Buchner funnel, washed thoroughly with water and finally dried. The dry lead formate is packed in the inner tube of a Leibig's condenser and treated with dry H_2S gas. As a result of this, anhydrous formic acid is liberated which collects in the receiver.

$$\underset{\text{Lead carbonate}}{PbCO_3} + \underset{\text{Formic acid}}{2HCOOH} \longrightarrow \underset{\text{Lead formate}}{Pb(HCOO)_2} + CO_2 + H_2O$$

$$\underset{\text{Lead formate}}{Pb(HCOO)_2} + H_2S \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + \underset{\text{Anhydrous formic acid}}{2\,HCOOH}$$

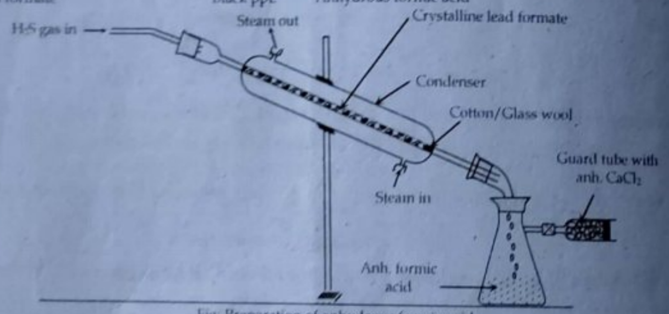


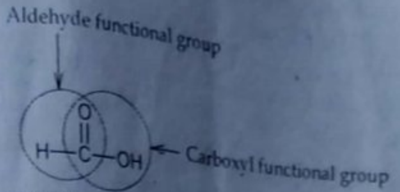
Fig: Preparation of anhydrous formic acid

43. **2065 Q.No. 31** **Describe Laboratory preparation of anhydrous methanoic acid.** [5]

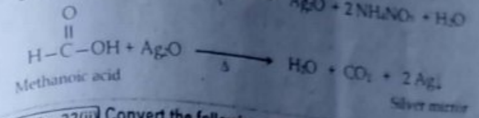
Please refer to 2075 GIE Q.No. 28

44. **2063 Q.No. 23(e)** **What happens when Methanoic acid is warmed with ammoniacal silver nitrate?** [2]

Methanoic acid contains aldehydic functional group. Due to this methanoic acid gives Tollen's test. When methanoic acid is warmed with ammoniacal silver nitrate solution i.e. Tollen's reagent, a silver mirror is seen on the inner wall of test tube.



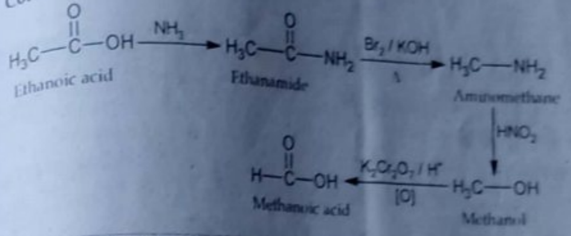
$$2AgNO_3 + 2NH_4OH \xrightarrow{\Delta} Ag_2O + 2NH_4NO_3 + H_2O$$



$$\underset{\text{Methanoic acid}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + Ag_2O \xrightarrow{\Delta} H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

45. **2062 Q.No. 22(ii)** **Convert the following organic compounds: Ethanoic acid to methanoic acid** [5]

Conversion:



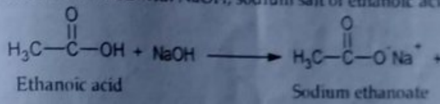
46. **2061 Q.No. 22** **What products are obtained when CH_3COOH is allowed to react with** [5]

a. NaOH b. NaOH / CaO c. PCl_5 d. P_2O_5 e. $LiAlH_4$

Also mention reaction condition where ever relevant.

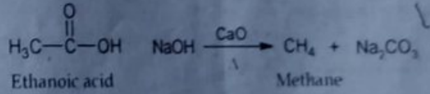
The reaction of CH_3COOH with:

a. NaOH: Ethanoic acid reacts with NaOH, sodium salt of ethanoic acid is formed.



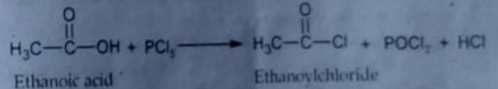
$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + NaOH \longrightarrow \underset{\text{Sodium ethanoate}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+} + H_2O$$

b. NaOH + CaO: Ethanoic acid is heated with sodalime i.e. NaOH + CaO, methane is fomed.



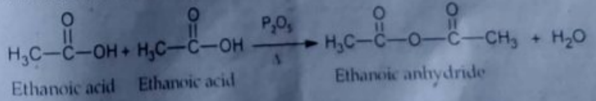
$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \quad NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

c. PCl_5: Ethanoic acid is treated with PCl_5, ethanoylchloride is formed.



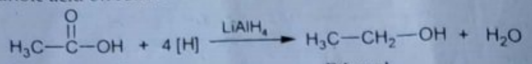
$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + PCl_5 \longrightarrow \underset{\text{Ethanoylchloride}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + POCl_3 + HCl$$

d. P_2O_5: Ethanoic acid on heating with P_2O_5, ethanoic anhydride is obtained.



$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Ethanoic anhydride}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + H_2O$$

e. **LiAlH₄:** Ethanoic acid on reduction with LiAlH$_4$, ethanol is obtained.



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + 4[H] \xrightarrow{LiAlH_4} H_3C-CH_2-OH + H_2O$$

Ethanoic acid Ethanol

47. **2059 Q.No. 23 Why is P_2O_5 not used for the preparation of anhydrous formic acid? Suggest a suitable method for the preparation of anhydrous formic acid.** [5]

Phosphorous pentoxide i.e. P_2O_5 is acidic oxide and combines with water molecules to form phosphoric acid i.e. H_3PO_4. So, P_2O_5 is not used for the preparation of anhydrous formic acid.

$$HCOOH \xrightarrow[\Delta]{P_2O_5} CO\uparrow + H_2O$$

Formic acid

$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$$

Phosphoric acid

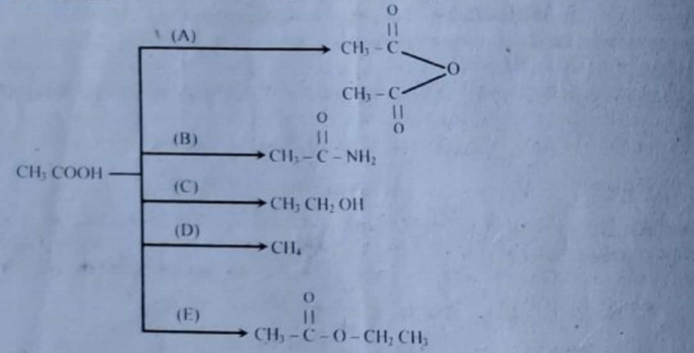
Preparation of anhydrous formic acid: Please refer to 2075 GIE Q.No. 28

48. **2056 Q.No. 26 a Convert Ethane to ethanoic acid** [2.5]

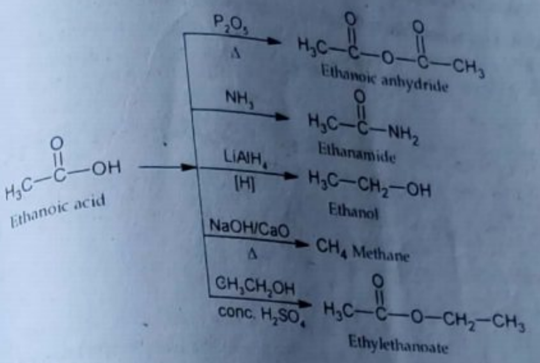
Conversion: Ethane to ethanoic acid

$$\underset{\text{Ethane}}{H_3C-CH_3} \xrightarrow{Cl_2} \underset{\text{Chloroethane}}{H_3C-CH_2-Cl} \xrightarrow{aq.KOH} \underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow[{[O]}]{K_2Cr_2O_7\,/\,H^+} \underset{\text{Ethanoic acid}}{H_3C-COOH}$$

49. **2055 Q.No. 26 How would you bring about the following conversions?** [5]



(A) Ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained.
(B) Ethanoic acid is reacted with NH_3, ethanamide is obtained.
(C) Ethanoic acid on reduction with LiAlH$_4$, ethanol is obtained.
(D) Ethanoic acid is heated with sodalime (NaOH/CaO), methane is obtained.
(E) Ethanoic acid is heated with ethanol in the presence of conc. H_2SO_4, ethyl ethanoate is obtained.

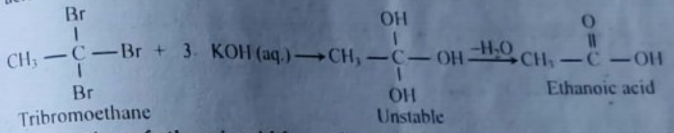


LONG ANSWER QUESTIONS [10 MARKS]

60. **2072 Set E Q.No. 31b Write any three methods of preparation of ethanoic acid. How is ethanoic acid distinguished from methanoic acid?** [3+2]

Three methods of preparation of ethanoic acid:

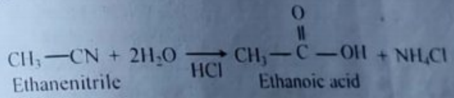
i. **Preparation of ethanoic acid from tribromoethane:** When tribomoethane is treated with aq. KOH, unstable product is formed which loose a molecule of water to form ethanoic acid.



$$CH_3-\underset{Br}{\overset{Br}{C}}-Br + 3\ KOH(aq.) \longrightarrow CH_3-\underset{OH}{\overset{OH}{C}}-OH \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Tribromoethane Unstable Ethanoic acid

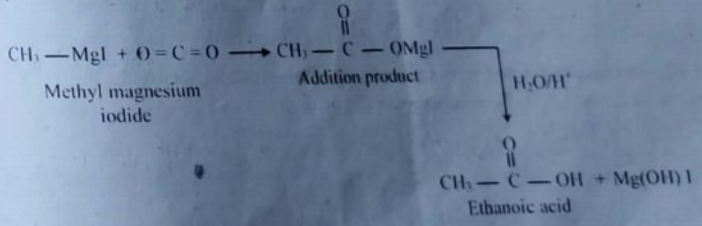
ii. **Preparation of ethanoic acid from ethanenitrile:** when ethanenitrile on hydrolysis in the presence of acid, ethnoic acid is obtained.



$$CH_3-CN + 2H_2O \xrightarrow[HCl]{} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

Ethanenitrile Ethanoic acid

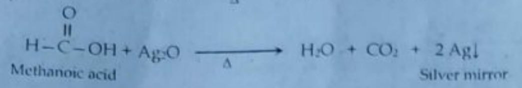
iii. **Preparation of ethanoic acid from CH_3MgI:** When methyl magnesium iodide (CH_3MgI) is treated with carbon dioxide, addition product is obtained which on hydrolysis in the presence of acid gives ethanoic acid



Distinction of ethanoic acid from methanoic acid:

Tollen's reagent test is suitable test to identify whether the given acid is methanoic i.e. formic acid or ethanoic acid i.e. acetic acid. The two acids is taken in two separate test tubes, added Tollen's reagent and boiled for a few minutes. A silver mirror is deposited on the inner wall of test tube which shows the presence of methanoic acid. Methanoic acid only gives the silver mirror test but ethanoic acid does not give. In this way ethanoic and methanoic acid is identified.

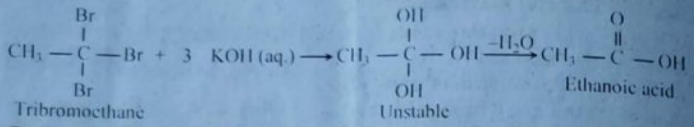
$$2AgNO_3 + 2NH_4OH \xrightarrow[\Delta]{} Ag_2O + 2NH_4NO_3 + H_2O$$



$$\underset{\text{Methanoic acid}}{H-\overset{\overset{O}{\|}}{C}-OH} + Ag_2O \xrightarrow[\Delta]{} H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

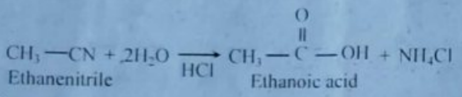
51. 2071 Supp. Q.No. 31a **How will you prepare ethanoic acid from** [5+5]
    - **i. tribromoethane** **ii. ethanenitrile**
    - **iii. CH_3 MgI. What happens when ethanoic acid is**
    - **a. heated with P_2O_5**
    - **b. treated with $SOCl_2$**

i. **Preparation of ethanoic acid from tribromoethane:** When tribomoethane is treated with aq. KOH, unstable product is formed which loose a molecule of water to form ethanoic acid.



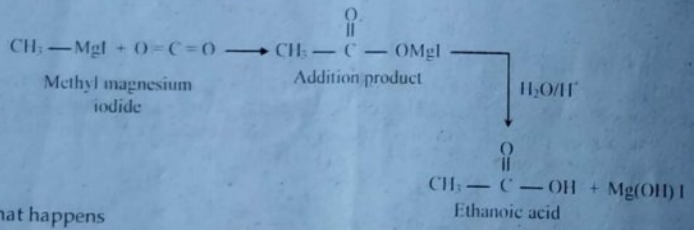
$$\underset{\text{Tribromoethane}}{CH_3-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-Br} + 3\ KOH(aq.) \longrightarrow \underset{\text{Unstable}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-OH} \xrightarrow{-H_2O} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

ii. **Preparation of ethanoic acid from ethanenitrile:** when ethanenitrile on hydrolysis in the presence of acid, ethnoic acid is obtained.



$$\underset{\text{Ethanenitrile}}{CH_3-CN} + 2H_2O \xrightarrow[HCl]{} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + NH_4Cl$$

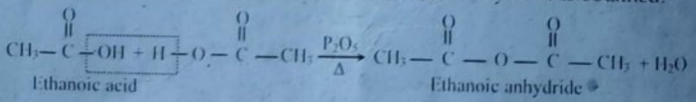
iii. **Preparation of ethanoic acid from CH_3MgI:** When methyl magnesium iodide (CH_3MgI) is treated with carbon dioxide, addition product is obtained which on hydrolysis in the presence of acid gives ethanoic acid



$$\underset{\text{Methyl magnesium iodide}}{CH_3-MgI} + O=C=O \longrightarrow \underset{\text{Addition product}}{CH_3-\overset{\overset{O}{\|}}{C}-OMgI} \xrightarrow{H_2O/H^+} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + Mg(OH)I$$

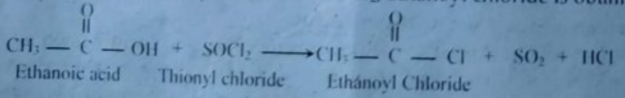
What happens

a. When ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained.



$$\underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + H-O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{P_2O_5} \underset{\text{Ethanoic anhydride}}{CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

b. When ethanoic acid is treated with $SOCl_2$, ethanoyl chloride is obtained



$$\underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{Ethanoyl Chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + SO_2 + HCl$$

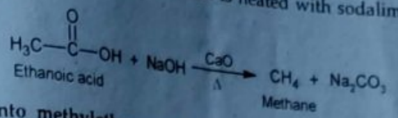
---

52. 2071 Set C Q.No. 31 a **How is anhydrous formic acid prepared from hydrous formic acid? Write suitable chemical reaction to convert ethanoic acid into:** [5]
    - **i. Methane**
    - **ii. Methylethanoate**
    - **iii. Ethanoic anhydride**

Preparation of anhydrous formic acid: Please refer to Please refer to 2075 GIE Q.No. 28

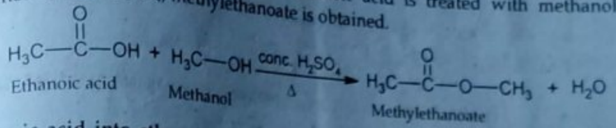
Conversion:

i. **Ethanoic acid into methane:** Ethanoic acid is heated with sodalime i.e. NaOH + CaO, methane is fomed.



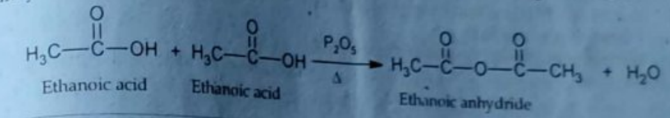
$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

ii. **Ethanoic acid into methylethanoate:** Ethanoic acid is treated with methanol in the presence of conc.H_2SO_4, methylethanoate is obtained.



$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Methanol}}{H_3C-OH} \xrightarrow[\Delta]{\text{conc. }H_2SO_4} \underset{\text{Methylethanoate}}{H_3C-\overset{\overset{O}{\|}}{C}-O-CH_3} + H_2O$$

iii. **Ethanoic acid into ethanoic anhydride:** Ethanoic acid on heating with P_2O_5, ethanoic anhydride is obtained.



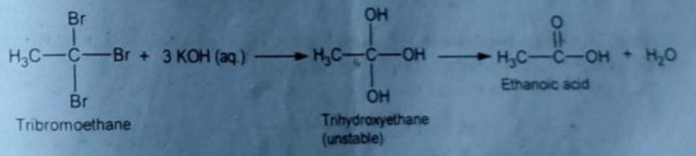
$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Ethanoic anhydride}}{H_3C-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

53. 2071 Set D Q.No. 31 a **How will you prepare ethanoic acid from** [5]
    - **i. Tribromoethane**
    - **ii. ethanenitril**
    - **iii. methyl magnesium iodide.**

What happens when ethanoic acid is:
- **a. Heated with P_2O_5**
- **b. Treated with $SOCl_2$**

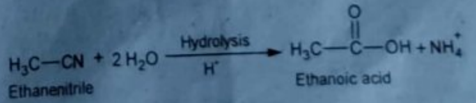
Preparation of **Ethanoic acid from:**

i. **Tribromoethane:** Tribromoethane is treated with aqueous solution of KOH, trihydroxy ethane unstable product is formed which loose a molecule of water, ethanoic acid is obtained.



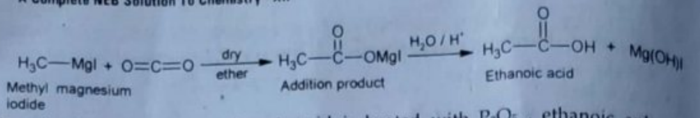
$$\underset{\text{Tribromoethane}}{H_3C-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-Br} + 3\ KOH(aq.) \longrightarrow \underset{\text{Trihydroxyethane (unstable)}}{H_3C-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-OH} \longrightarrow \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + H_2O$$

ii. **Ethanenitrile:** Ethanenitrile on hydrolysis in the presence of acid, ethanoic acid is obtained.



$$\underset{\text{Ethanenitrile}}{H_3C-CN} + 2H_2O \xrightarrow[H^+]{\text{Hydrolysis}} \underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + NH_4^+$$

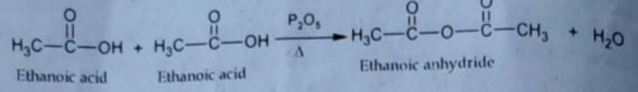
iii. **Methyl magnesium iodide:** When methyl magnesium iodide is treated with carbon dioxide in the presence of dry ether, an addition product is obtained which on hydrolysis to give ethanoic acid.



$$H_3C{-}MgI + O{=}C{=}O \xrightarrow[\text{ether}]{\text{dry}} H_3C{-}\overset{O}{\overset{\|}{C}}{-}OMgI \xrightarrow{H_2O/H^+} H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + Mg(OH)I$$

Methyl magnesium iodide; Addition product; Ethanoic acid

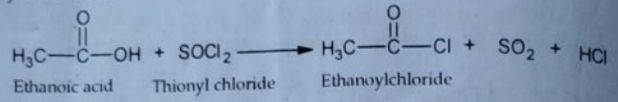
a. **Heated with P_2O_5:** When ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained.



$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow[\Delta]{P_2O_5} H_3C{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O$$

Ethanoic acid; Ethanoic acid; Ethanoic anhydride

b. **Treated with $SOCl_2$:** When ethanoic acid is treated with thionyl chloride i.e. $SOCl_2$, ethanoylchloride is obtained.



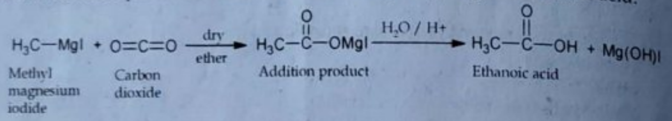
$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + SOCl_2 \longrightarrow H_3C{-}\overset{O}{\overset{\|}{C}}{-}Cl + SO_2 + HCl$$

Ethanoic acid; Thionyl chloride; Ethanoylchloride

54. 2070 Supp. Q.No. 31 b **How is ethanoic acid prepared from methyl magnesium iodide? What happens when ethanoic acid is,** **[5]**

- i. **Heated with P_2O_5.**
- ii. **Heated with HI in presence of red phosphorous.**
- iii. **Passed over heated MnO.**
- iv. **Warmed with ethanol in presence of conc. H_2SO_4.**

When methyl magnesium iodide is treated with carbon dioxide in the presence of dry ether, an addition product is obtained which on hydrolysis gives ethanoic acid.

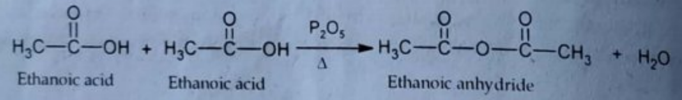


$$H_3C{-}MgI + O{=}C{=}O \xrightarrow[\text{ether}]{\text{dry}} H_3C{-}\overset{O}{\overset{\|}{C}}{-}OMgI \xrightarrow{H_2O/H^+} H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + Mg(OH)I$$

Methyl magnesium iodide; Carbon dioxide; Addition product; Ethanoic acid

What happens when

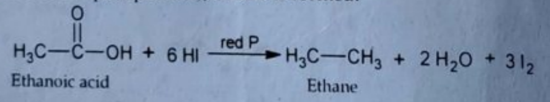
i. **Heated with P_2O_5:** When ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained.



$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow[\Delta]{P_2O_5} H_3C{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O$$

Ethanoic acid; Ethanoic acid; Ethanoic anhydride

ii. **Heated with HI in presence of red phosphorous:** When ethanoic acid is heated with HI in the presence of red phosphorous, ethane is formed.



$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + 6\,HI \xrightarrow{\text{red P}} H_3C{-}CH_3 + 2H_2O + 3I_2$$

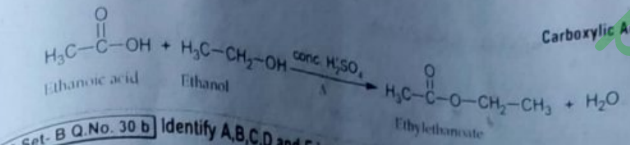
Ethanoic acid; Ethane

iii. **Passed over heated MnO:** When two molecule of ethanoic acid is passed over heated MnO at 300°C, propanone is obtained.

$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow[300\,^\circ C]{MnO} H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + CO_2 + H_2O$$

Ethanoic acid; Propanone

iv. **Warmed with ethanol in presence of conc. H_2SO_4:** When ethanoic acid is heated with ethanol in the presence of conc. H_2SO_4, ethylethanoate ester is formed.



$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + H_3C{-}CH_2{-}OH \xrightarrow[\Delta]{\text{conc. }H_2SO_4} H_3C{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3 + H_2O$$

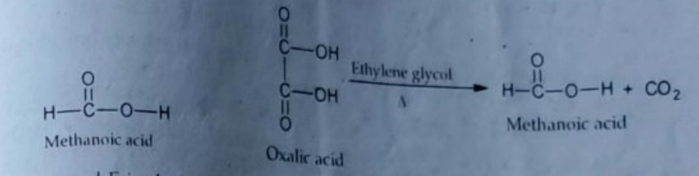
Ethanoic acid; Ethanol; Ethylethanoate

55. 2069 Set- B Q.No. 30 b **Identify A,B,C,D and E in the following sequence of reactions.**

$$A \xrightarrow{NH_3} B \xrightarrow[\Delta]{Br_2/KOH(aq.)} C \xrightarrow[\Delta]{HNO_2} D \xrightarrow{KMnO_4/H^+} E$$

The compound E can be obtained by heating oxalic acid in presence of glycol. **[5]**

The compound E can be obtained by heating oxalic acid in presence of ethylene glycol. The structure of E must be



$$\underset{\text{Methanoic acid}}{H{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}\qquad \underset{\text{Oxalic acid}}{\begin{matrix}O\\ \|\\ C{-}OH\\ |\\ C{-}OH\\ \|\\ O\end{matrix}} \xrightarrow[\Delta]{\text{Ethylene glycol}} \underset{\text{Methanoic acid}}{H{-}\overset{O}{\overset{\|}{C}}{-}O{-}H} + CO_2$$

The compound E is obtained from D on oxidation with $KMnO_4$ / H^+. The compound D must be Methanol.

$$CH_3{-}OH$$

The compound D is obtained from C with HNO_2. The compound C must be methanamine.

$$CH_3{-}NH_2$$

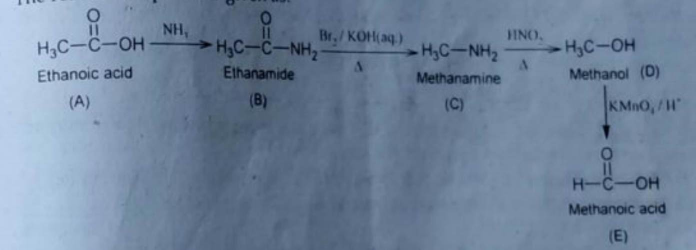
The compound C is obtained from B with Br_2 / KOH(aq.). The compound B must be Ethanamide.

$$CH_3{-}CO{-}NH_2$$

The compound B is obtained from A with NH_3.
The compound A must be Ethanoic acid.

$$CH_3{-}COOH$$

The reaction sequence is given as:



$$\underset{\text{Ethanoic acid (A)}}{H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH} \xrightarrow{NH_3} \underset{\text{Ethanamide (B)}}{H_3C{-}\overset{O}{\overset{\|}{C}}{-}NH_2} \xrightarrow[\Delta]{Br_2/KOH(aq.)} \underset{\text{Methanamine (C)}}{H_3C{-}NH_2} \xrightarrow[\Delta]{HNO_2} \underset{\text{Methanol (D)}}{H_3C{-}OH} \xrightarrow{KMnO_4/H^+} \underset{\text{Methanoic acid (E)}}{H{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

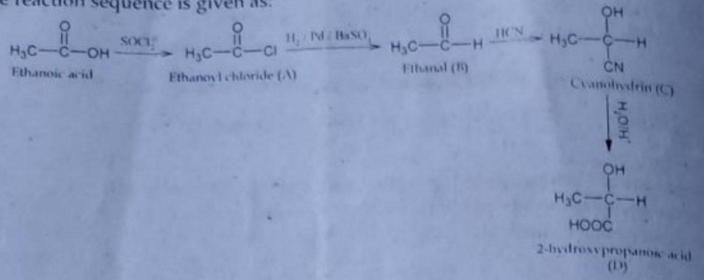
The compounds are
A = Ethanoic acid
B = Ethanamide
C = Methanamine
D = Methanl
E = Methanoic acid

56. 2068 Q.No. 28 b **Identify each lettered in the following reaction sequence:** **[5]**

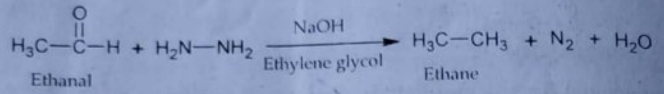
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\Delta]{H_2/Pd/BaSO_4} B \xrightarrow{HCN} C \xrightarrow{H_2O/H^+} D$$

What major product would you obtain when B is treated with alkaline solution of hydrazine and ethylene glycol?

The reaction sequence is given as:



Ethanal (B) is treated with alkaline solution of hydrazine and ethylene glycol, ethane is obtained.



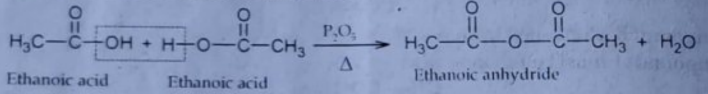
$$\underset{\text{Ethanal}}{H_3C-\overset{\overset{O}{\|}}{C}-H} + H_2N-NH_2 \xrightarrow[\text{Ethylene glycol}]{NaOH} \underset{\text{Ethane}}{H_3C-CH_3} + N_2 + H_2O$$

57. 2066 Q. No. 29 a **Write any three methods of preparation of ethanoic acid. How would you convert ethanoic acid into** **[5]**
    i. **Ethanoic anhydride**
    ii. **Methylethanoate.**

Three method of preparation of ethanoic acid: Please refer to 2072 Set E Q.No. 31b

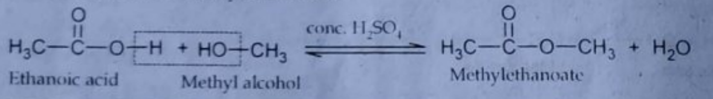
Conversion:

i. Ethanoic acid into ethanoic anhydride



$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Ethanoic acid}}{H-O-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\Delta]{P_2O_5} \underset{\text{Ethanoic anhydride}}{H_3C-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

ii. Ethanoic acid into methyl ethanoate



$$\underset{\text{Ethanoic acid}}{H_3C-\overset{\overset{O}{\|}}{C}-O-H} + \underset{\text{Methyl alcohol}}{HO-CH_3} \xrightleftharpoons{\text{conc. }H_2SO_4} \underset{\text{Methylethanoate}}{H_3C-\overset{\overset{O}{\|}}{C}-O-CH_3} + H_2O$$

58. 2064 Q.No. 29 **Describe the preparation of methanoic acid in the laboratory. How is anhydrous acid obtained from it ? How does methanoic acid act upon:** **[10]**
    i. **Fehling's solution**
    ii. **methanol / H^+**
    iii. **Conc. H_2SO_4?**

Laboratory preparation of methanoic acid: Please refer to 2075 GIE Q.No. 28

Action of methanoic acid upon:

i. **Fehling's solution**: When methanoic acid is treated with Fehling's solution, it is reduced to form carbondioxide.

$$\underset{\text{Methanoic acid}}{HCOOH} + \underset{\text{Fehling's solution}}{2Cu(OH)_2} \xrightarrow{OH^-} \underset{\text{red ppt}}{Cu_2O\downarrow} + CO_2 + 3H_2O$$

ii. **Methanol /H^+**: When methanoic acid is heated with methanol in the presence of acid, ester i.e. methylmethanoate is formed.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{H^+} \underset{\text{Methylmethanoate}}{HCOOCH_3} + H_2O$$

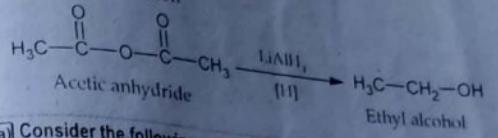
iii. Conc.H_2SO_4: When methanoic acid is heated with conc.H_2SO_4 ,it gets dehydrated to form carbon monoxide gas.

$$\underset{\text{Methanoic acid}}{HCOOH} + \text{conc. } H_2SO_4 \longrightarrow \underset{\text{Carbonmonoxide}}{CO} + [H_2O + H_2SO_4]$$

59. 2059 Q.No. 29b (v) **Predict the major products of the following reactions:**

$$CH_3COOCOCH_3 \xrightarrow[\Delta]{} \text{……………}$$

The major product of the reaction



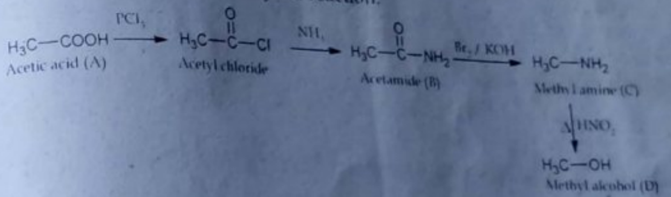
$$\underset{\text{Acetic anhydride}}{H_3C-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[{[H]}]{LiAlH_4} \underset{\text{Ethyl alcohol}}{H_3C-CH_2-OH}$$

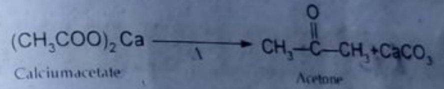
60. 2057 Q.No. 29(a) **Consider the following reaction** **[5]**

$$A \xrightarrow[\text{(ii) }NH_3]{\text{(i) }PCl_5} B \xrightarrow[\Delta]{Br_2/NaOH} C \xrightarrow[\Delta]{HNO_2} D$$

The compound, A is a carboxylic acid. Calcium salt of A on heating gives acetone. Identify A, B, C and D.

The calcium salt of 'A' i.e. carboxylic acid on heating gives acetone. So, the compound 'A' must be acetic acid because its salt i.e. calcium acetate on heating gives acetone. The reaction sequence can be shown by the reaction.





$$\underset{\text{Calciumacetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + CaCO_3$$

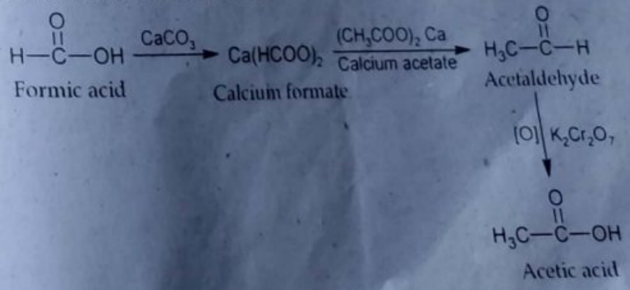
The compounds are

A = Acetic acid
B = Acetamide
C = Methyl amine
D = Methyl alcohol

61. 2057 Q.No. 28 **Describe the preparation of anhydrous formic acid in laboratory. How is it converted to acetic acid?** **[1**

Please refer to 2075 GIE Q.No. 28

Conversion: formic acid to acetic acid

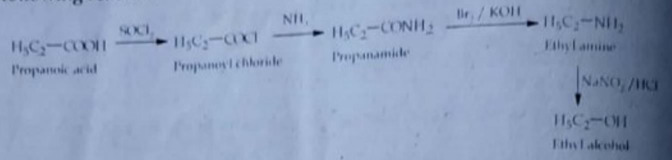


62. 2053 Q.No. 29(b) **Consider a reaction:** [5]

$$A \xrightarrow{SOCl_2} B \xrightarrow[\Delta]{NH_3} C \xrightarrow[\Delta]{Br_2/KOH} D \xrightarrow[\Delta]{NaNO_2/HCl} E$$

The compound, E is a primary alcohol which has positive iodoform test. Identify A, B, C, D and E.

The compound E is primary alcohol and gives +ve iodoform test. So, E must be ethanol which gives +ve iodoform test. This ethanol is obtained by the action of $NaNO_2$ and HCl upon the compound 'D'. So, the compound must be ethyl amine which is obtained by the action of Br_2/KOH upon the compound 'C'. So, the compound 'C' must be propanamide which is obtained by the action of NH_3 upon the compound 'B'. So, the compound 'B' must be propanoylchloride which is obtained by the action of $SOCl_2$ upon 'A'. So, the compound 'A' must be propanoic acid. The reaction sequence can be shown by following reaction.



The compounds are
A = Propanoic acid
B = Propanoyl chloride
C = Propanamide
D = Ethyl amine
E = Ethyl alcohol

WRITE SHORT NOTES ON

63. 2076 Set B Q.No. 33iii **Laboratory preparation of anhydrous formic acid.** [5]

Please refer to 2075 GIE Q.No. 28

64. 2073 Set D Q.No. 33iv **Laboratory preparation of formic acid.** [5]

Please refer to 2075 GIE Q.No. 28

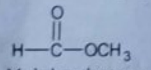
of carboxylic Acid

13.2 Derivatives o arboxylic Acid

VERY SHORT ANSWER QUESTIONS [2 MARKS]

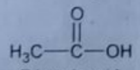
1. 2076 Set B Q.No. 15 2076 Set C Q.No. 15 **Write down the functional isomer of methyl methanoate. What product would you expect when the isomer is heated with P_2O_5?** [1+1]

The functional isomer of methyl methanoate is ethanoic acid. When ethanoic acid is heated with P_2O_5, ethanoic anhydride is obtained.



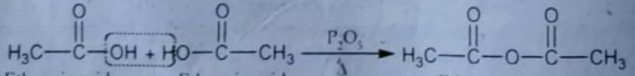
$$H-\overset{O}{\overset{\|}{C}}-OCH_3$$

Methyl methanoate



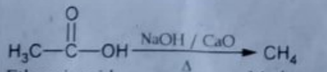
$$H_3C-\overset{O}{\overset{\|}{C}}-OH$$

Ethanoic acid



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{P_2O_5} H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Ethanoic acid Ethanoic acid Ethanoic anhydride



$$H_3C-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH / CaO} CH_4$$

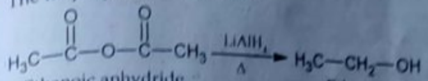
Ethanoic acid Methane

2. 2075 Set B Q.No. 13 **Predict the major products of the following reactions.** [1+1]

i. $(CH_3CO)_2O \xrightarrow[\Delta]{LiAlH_4}$

ii. $CH_3COOH \xrightarrow[\Delta]{NaOH/CaO}$

i. The major product is ethanol.



$$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{LiAlH_4} H_3C-CH_2-OH$$

Ethanoic anhydride Ethanol

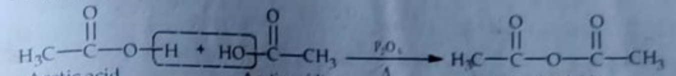
ii. The major product is methane.

3. 2073 Set C Q.No. 13 **Predict the major products of the following reactions** [1+1]

i. $CH_3COOH \xrightarrow[\Delta]{P_2O_5}$

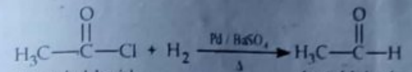
ii. $CH_3COCl \xrightarrow[\Delta]{Pd/BaSO_4}$

The major product of



i. $$H_3C-\overset{O}{\overset{\|}{C}}-O-H + HO-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{P_2O_5} H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Acetic acid Acetic acid Acetic anhydride



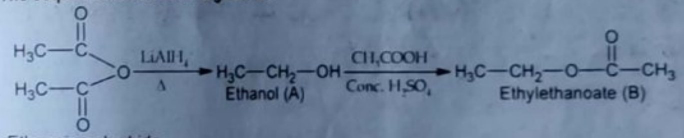
ii. $$H_3C-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\Delta]{Pd / BaSO_4} H_3C-\overset{O}{\overset{\|}{C}}-H$$

Acetyl chloride Acetaldehyde

4. 2072 Set C Q.No. 13 **Identify Ⓐ and Ⓑ in the following reaction and give their IUPAC name.**

$$(CH_3CO)_2O \xrightarrow[\Delta]{LiAlH_4} A \xrightarrow[Conc.\ H_2SO_4]{CH_3\ COOH} B$$

The sequence of reaction is given as:



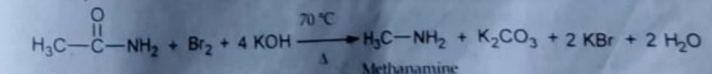
$$\left(H_3C-\overset{O}{\overset{\|}{C}}\right)_2O \xrightarrow[\Delta]{LiAlH_4} H_3C-CH_2-OH \xrightarrow[Conc.\ H_2SO_4]{CH_3COOH} H_3C-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$$

Ethanoic anhydride Ethanol (A) Ethylethanoate (B)

The compounds are
A = Ethanol
B = Ethylethanoate

5. 2069 Supp. Set B Q.No. 15 **Give an example of each of the following: Decarbonylation reaction**

The reaction in which carbonyl group (-CO-) is remeoved, is called decarbonylation. Hoffmann Hypobromite reaction is the decarbonylation reaction in which carbonyl group is removed. Whe acid amide is heated with Br_2 in the presence of KOH, decarbonylation to form primary amine.

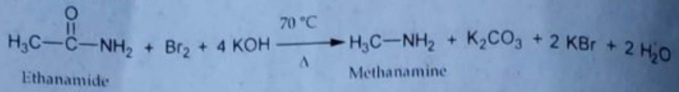


$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4\ KOH \xrightarrow[\Delta]{70\ ^\circ C} H_3C-NH_2 + K_2CO_3 + 2\ KBr + 2\ H_2O$$

Ethanamide Methanamine

6. **2064 Q.No. 6(ii)** **Write an example of each of the following reaction of Hoffmann's Bromamide Reaction.** [2]

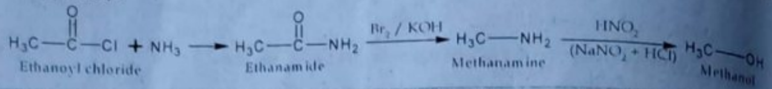
Hoffmann's bromamide reaction: Acid amide is heated with bromine in the presence of aq. KOH at 70°C, primary amine is obtained. This reaction is called Hoffmann's bromamide reaction.



$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4\,KOH \xrightarrow[\Delta]{70\,^\circ C} H_3C-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

7. **2063 Q.No. 4** **Convert ethanoyl chloride to methanol** [2]

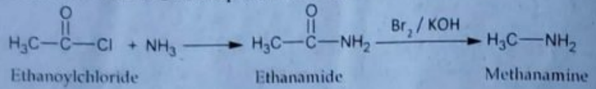
Conversion:



$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + NH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2\,/\,KOH} H_3C-NH_2 \xrightarrow[(NaNO_2\,+\,HCl)]{HNO_2} H_3C-OH$$

8. **2062 Q.No. 7** **What happens when the product obtained by the action of ethanoylchloride and ammonia is heated with Br_2 and aqueous KOH:** [2]

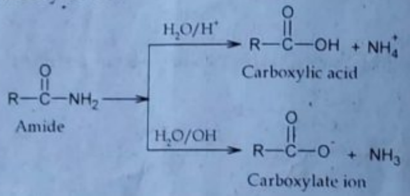
When ethanoylchloride is treated with ammonia, ethanamide is obtained which on treatment with Br_2 and aq. KOH, methamine is obtained.



$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + NH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2\,/\,KOH} H_3C-NH_2$$

9. **2057 Q.No. 7** **Write a reaction when an amide is hydrolyzed.** [2]

Amide is hydrolysed either in the presence of dilute acid or dilute base and gives carboxylic acid or carboxyale ion.

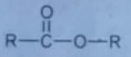


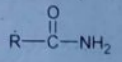
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O/H^+} R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$$

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O/OH} R-\overset{O}{\overset{\|}{C}}-O^- + NH_3$$

10. **2052 Q.No. 11** **What is functional group of (a) ester and (b) amide?** [2]

Functional group of

a. Ester:  $R-\overset{O}{\overset{\|}{C}}-O-R$

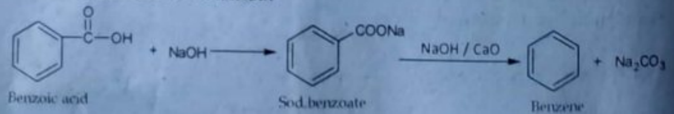
b. Amide:  $R-\overset{O}{\overset{\|}{C}}-NH_2$

13.3 Aromatic Carboxylic Acids

VERY SHORT ANSWER QUESTIONS [2 MARKS]

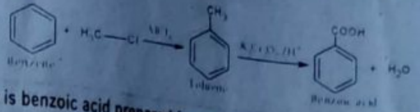
1. **2068 Q.No. 6** **Mention suitable method for the conversion of benzoic acid to benzene.** [2]

Benzoic acid on treatment with dil.NaOH, sod. benzoate is obtained which is heated with sodalime, benzene is obtained.



2. **2067 Q.No. 6** **How is benzoic acid prepared from benzene?** [2]

When benzene is treated with methyl chloride in the presence of Lewis acid , toluene is obtained which on oxidation with pot. dichromate in the presence of acid to give benzoic acid.

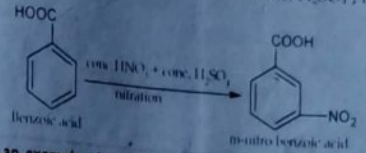


3. **2066 Q. No. 7** **How is benzoic acid prepared from benzene?** [2]

Please refer to **2067 Q.No 6**

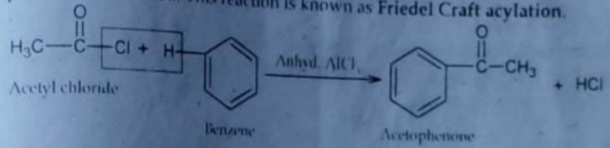
4. **2064 Q.No. 22(iv)** **What happens when benzoic acid is nitrated?**

When benzoic acid is nitrated with conc.HNO_3 and Conc. H_2SO_4 , m-nitro benzoic acid is formed.



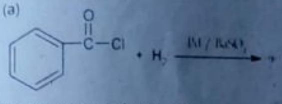
5. **2062 Q.No. 5(i)** **Write an example of each of the following reactions giving appropriate conditions: Friedal Craft acylation** [1]

When benzene is treated with acetyl chloride in the presence of Lewis acid, acetophenone is obtained. This reaction is known as **Friedel Craft acylation.**

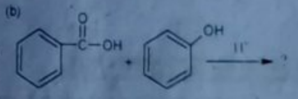


6. **2061 Q.No. 5** **Complete the following equations:**

(a)

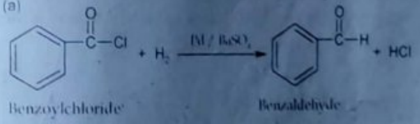


(b)

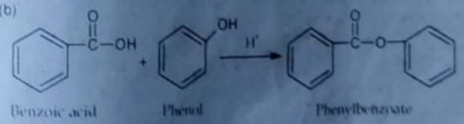


The major products are

(a)

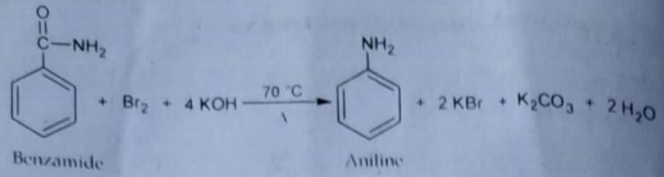


(b)



7. **2059 Q.No. 8** **What happens when benzamide is heated with bromine and aqueous KOH?** [2]

When benzamide is heated with bromine and aqueous KOH at 70°C, aniline is obtained. This reaction is called **Hoffmann bromamide reaction**.



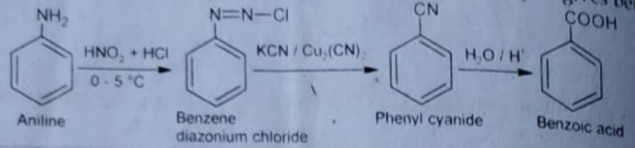
8. **2057 Q.No. 5 Write an example of Friedel Craft acylation.**

Please refer to 2062 Q.No. 5(i)

SHORT ANSWER QUESTIONS [5 MARKS]

9. **2059 Q.No. 22(b) How could you synthesize benzoic acid from aniline?** [2.5]

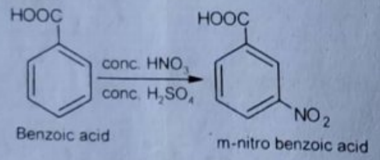
Aniline reacts with nitous acid in cold condition in the presence of mineral acid, benzene diazonium chloride is formed. Benzene diazonium chloride is treated with KCN in the presence of $Cu_2(CN)_2$, phenyl cyanide is formed which on hydrolysis gives benzoic acid.



10. **2057 Q.No. 23(b) Write the chemical equation with conditions for the following reaction. Benzoic acid is nitrated** [2.5]

Condition: conc. Nitric acid and conc. Sulphuric acid

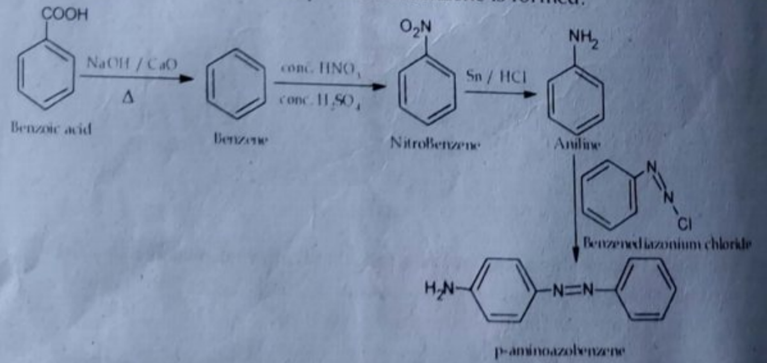
Benzoic acid on nitration with nitrating mixture i.e. conc. HNO_3 and conc. H_2SO_4, m-nitro benzoic acid is formed.



LONG ANSWER QUESTIONS [10 MARKS]

11. **2071 Set C Q.No. 32 b Benzoic acid to p-aminoazobenzene** [5]

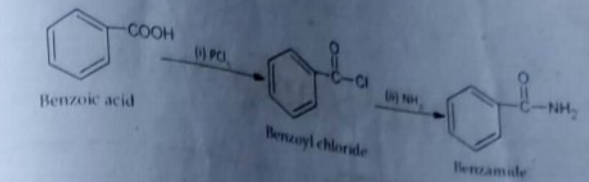
Benzoic acid is heated with sodalime benzene is obtained. Benzene on nitriation gives nitrobenzene. Nitrobenzene on reduction with Sn/HCl gives aniline. Aniline is heated with benzenediazonium chloride, p-aminoazoenzene is formed.



12. **2059 Q.No. 29b-(ii) Predict the major products of the following reactions:** [1]

$$Ar\,COOH \xrightarrow[\text{(ii) } NH_3]{\text{(i) } PCl_5} \ldots\ldots\ldots$$

The major product is



❑❑❑

Unit 14

Nitrocompounds

14.1 Aliphatic Nitrocompounds (Nitroalkane)

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2076 Set B Q.No. 13 2076 Set C Q.No. 13 **Why is nitro group called an ambident group?** [2]

The nitro group is called ambident group because the carbon atom of alkyl or aryl group can be linked with nitrogen atom as well as oxygen atom. The compounds in which the $-NO_2$ group is linked to the alkyl or aryl group through oxygen atom are called nitrites.

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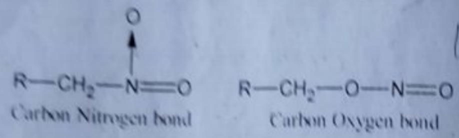


2. 2075 GIE Q.No. 14 **Give a reaction to prepare nitroalkane from haloalkane and name the test used for the detection of nitro compound.** [1+1]

When haloalkane is treated with silver nitrite, nitroalkane is obtained.

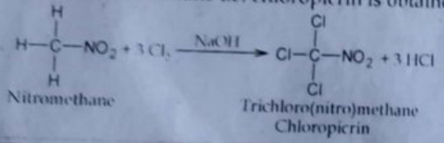
$$\underset{\text{Chloroethane}}{H_3C-CH_2-Cl} + \underset{\text{Silver nitrite}}{AgNO_2} \longrightarrow \underset{\text{Nitroethene}}{H_3C-CH_2-NO_2}$$

The ferrous hydroxide ($Fe(OH)_2$) test is used for the detection of nitro compound.

$$\underset{\text{Nitroalkane}}{R-NO_2} + 6\,Fe(OH)_2 + 4H_2O \xrightarrow[\text{KOH (alc.)}]{\text{Ferrous ammonium sulphate}} \underset{\text{Amine}}{R-NH_2} + \underset{\text{Brown ppt}}{6\,Fe(OH)_3}$$

3. 2075 Set A Q.No. 14 **How is chloropicrin obtained from nitromethane? Give an important use of chloropierin.** [1+1]

When nitromethane is treated with chlorine in the presence of NaOH, trichloronitromethane i.e. chloropicrin is obtained.



$$\underset{\text{Nitromethane}}{H-\overset{H}{\underset{H}{C}}-NO_2} + 3Cl_2 \xrightarrow{NaOH} \underset{\substack{\text{Trichloro(nitro)methane}\\ \text{Chloropicrin}}}{Cl-\overset{Cl}{\underset{Cl}{C}}-NO_2} + 3HCl$$

4. 2072 Supp. Q.No. 14 **Mention any two important uses of nitroalkane.** [2]

Two important uses of nitroalkane are

a. It is used for making explosive.

b. It is used as perfumes for soap.

2072 Set C Q.No. 14 **How are the following conversion carried out? Nitroethane into N-ethyl hydroxylamine.** [1]

Nitroethane into N-ethyl hydroxyl amine:

$$\underset{\text{Nitroethane}}{CH_3-CH_2-NO_2} + 4[H] \xrightarrow{Zn+NH_4Cl} \underset{\text{N-ethyl hydroxyl amine}}{CH_3-CH_2-NH-OH} + H_2O$$

2071 Set C Q.No. 14 **How does nitroalkane react with:**

i. **Zn/NH₄Cl** ii. **Sn/HCl** [2]

Nitroalkane react with:

i. Zn / NH_4Cl: Nitroalkane on reduction with neutral medium i.e. Zn / NH_4Cl, hydroxylamine is formed.

$$\underset{\text{Nitromethane}}{CH_3-NO_2} + 4[H] \xrightarrow{Zn+NH_4Cl} \underset{\text{N-methylhydroxylamine}}{CH_3-NH-OH} + H_2O$$

ii. Sn / HCl: Nitroalkane on reduction with acidic medium i.e. Sn / HCl, amine is formed.

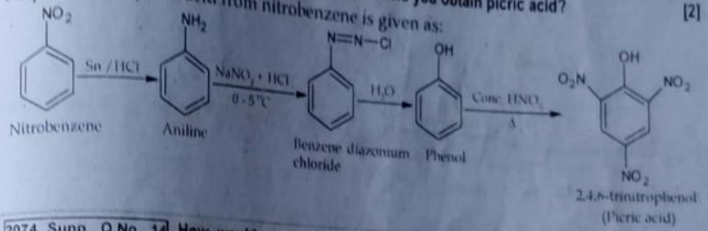
$$\underset{\text{Nitromethane}}{CH_3-NO_2} + 6[H] \xrightarrow{Sn-HCl} \underset{\text{Methylamine}}{CH_3-NH_2} + 2H_2O$$

14.2 Aromatic Nitrocompounds

VERY SHORT ANSWER QUESTIONS: [2 MARKS]

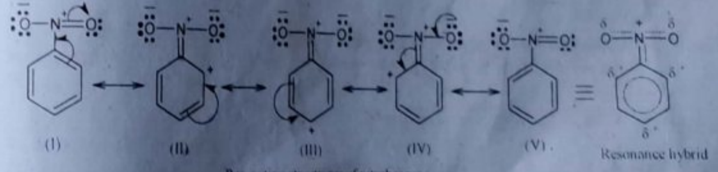
1. 2075 Set B Q.No. 14 **Starting from nitrobenzene how would you obtain picric acid?** [2]

Preparation of picric acid from nitrobenzene is given as:



2. 2074 Supp. Q.No. 14 **How would you predict that nitro group in nitrobenzene is an electron-withdrawing group?** [2]

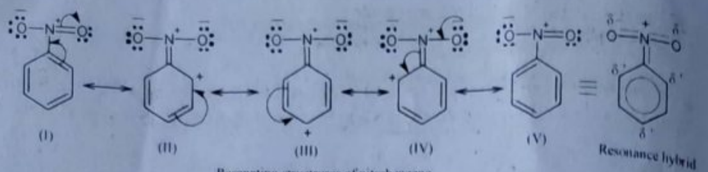
The nitro group ($-NO_2$) is electron withdrawing group and withdraws the electron from benzene ring. In the resonance structure of nitrobenzene, positive charge is developed at ortho and para position. The electron density at ortho and para postion is lower than meta position. Due to this nitro group, nitrobenzene is meta director in electrophilic aromatic substitution reaction.



Resonating structures of nitrobenzene

3. 2074 Set A Q.No. 14 **Why halogenation in nitrobenzene occurs at meta position?** [2]

The nitro group of nitrobenzene is m-directing in electrophilic substitution. This can be explained by resonance.



Resonating structures of nitrobenzene

It is observed that positive charge is developed on ortho and para position. So, electrophiles do not attack at that position. The incoming electrophile must be linked at meta-position because meta-position has relatively higher electron density than ortho and para position.

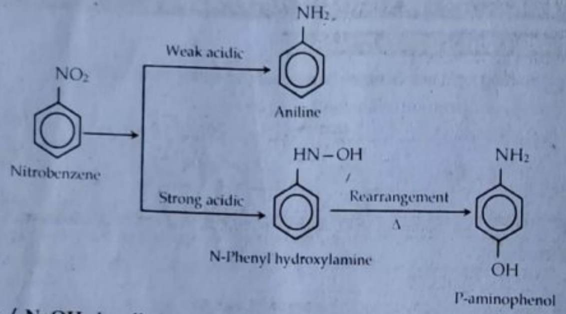
4. 2074 Set B Q.No. 14 2073 Supp Q.No. 14 2073 Set C Q.No. 14 **Why does nitrobenzene undergo electrophillic substitution at meta position?** [2]

➣ Please refer to 2074 Set A Q.No. 14

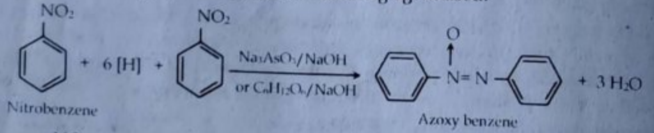
5. 2073 Set D Q.No. 14 **What happens when Nitrobenzene is** [1+1]
   i. **subjected to electrolytic reduction** ii. **treated with Zn/NaOH**

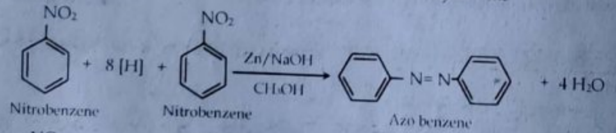
➣ **Nitrobenzene is treated with:**

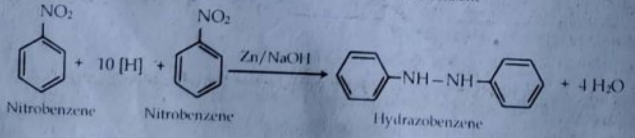
i. **Electrolytic reduction:** Nitrobenzene on electrolytic reduction gives different products in different medium.



ii. **Zn / NaOH:** In alkaline medium, nitrobenzene gives different bimolecular reduction product depending upon the nature of reducing agent used.

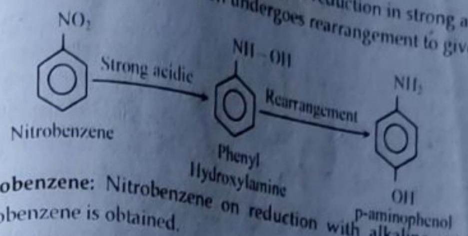




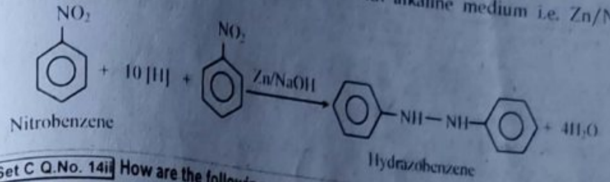


6. 2072 Set D Q.No. 14 **Convert nitrobenzene into:** [1+1]
   i. **p-aminophenol** ii. **Hydrazobenzene**

➣ i. **p-aminophenol:** Nitrobenzene on electrolytic reduction in strong acidic medium, phenyl hydroxyl amine is obtained which undergoes rearrangement to give p-aminophenol.

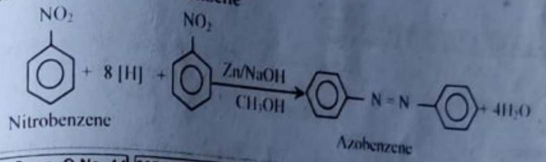


ii. **Hydrazobenzene:** Nitrobenzene on reduction with alkaline medium i.e. Zn/NaOH, hydrazobenzene is obtained.



7. 2072 Set C Q.No. 14ii **How are the following conversion carried out?** [1]
   Nitrobenzene into azobenzene.

➣ **Nitrobenzene into azobenzene** [1]

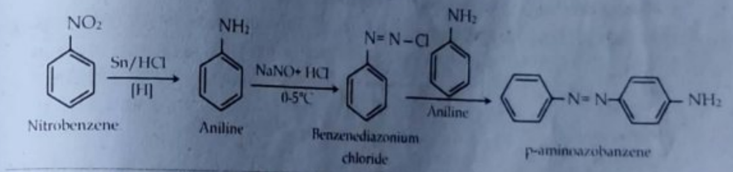


8. 2071 Supp. Q.No. 14 2071 Set D Q.No. 14 **Electrophilic substitution reaction in nitrobenzen occurs at meta position. Give reason.** [2]

➣ Please refer to 2074 Set A Q.No. 14

9. 2070 Supp. Q.No. 15 **Convert nitrobenzene to p-aminoazobenzene.** [2]

➣ **Conversion:** nitrobenzene to p-aminoazobenzene



10. 2070 Set D Q.No. 14 2057 Q.No. 8 **Why is -NO_2 group a meta directing towards electrophilic aromatic substitution?** [2]

➣ Please refer to 2074 Set A Q.No. 14

11. 2069 (Set A) Q.No. 14 2069 Supp. Set B Q.No. 14 **Why does nitrobenzene undergo electrophilic substitution reaction in meta position?**

➣ Please refer to 2074 Set A Q.No. 14

12. 2069 (Set B) Q.No. 15 **What products would you expect when Nitro benzene is treated with:**
   i. **Zn / NaOH**
   ii. **Electrolytic reduction**

➣ Please refer to 2073 Set D Q.No. 14

13. **2062 Q.No. 8** **Explain why is $-NO_2$ group a meta directing group towards electrophilic aromatic substitution?**

Please refer to 2074 Set A Q.No. 14 [2]

14. **2058 Q.No. 8** **Account for the fact that $-NO_2$ is a meta directing group towards electrophilic aromatic substitution.**

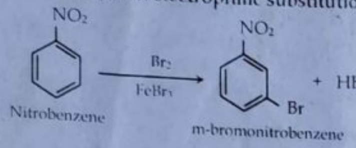
Please refer to 2074 Set A Q.No. 14 [2]

15. **2055 Q.No. 17** **Why is $-NO_2$ group meta directing in electrophilic aromatic substitution reaction?** [2]

Please refer to 2074 Set A Q.No. 14

16. **2054 Q.No. 17** **Explain with any one example of electrophilic substitution in aromatic compounds.** [2]

Electrophilic substitution reaction: The substitution reaction in which the attacking species is an electrophile in aromatic compound is called aromatic electrophilic substitution. Example: halogenations reaction in nitrobenzene. Here, halide ion is electrophile and attacks to the nitrobenzene in meta position because nitrobenzene is meta directror in electrophilic substitution reaction.

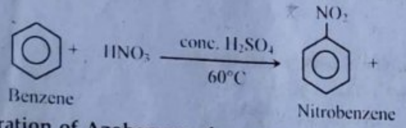


SHORT ANSWER QUESTIONS [5 MARKS]

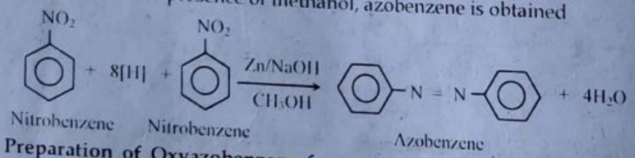
17. **2071 Supp. Q.No. 30a** **2072 Supp. Q.No. 30a** **Give a chemical reaction for the preparation of nitrobenzene from benzene, starting from nitrobenzene how will you prepare.** [1+4]

- i. **Azobenzene**
- ii. **oxyazobenzene**
- iii. **hydrazobenzene**
- iv. **TNT**

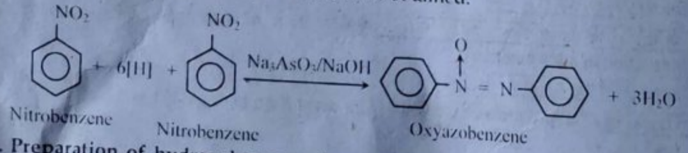
Preparation of nitrobenzene from benzene: When benzene is heated with nitrating mixture i.e. conc. HNO_3 + conc. H_2SO_4 at 60°C, nitrobenzene is obtained.



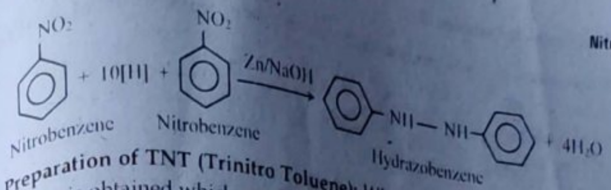
i. **Preparation of Azobenzene from nitrobenzene:** When nitrobenzene on reduction with Zn/NaOH in the presence of methanol, azobenzene is obtained



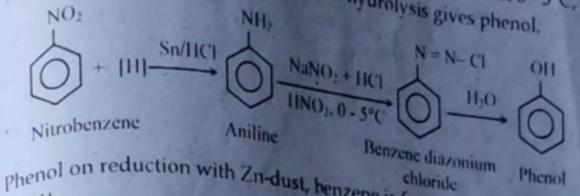
ii. **Preparation of Oxyazobenzene from nitrobenzene:** When nitrobenzene on reduction with Na_3AsO_3/NaOH, oxyazobenzene is obtained.



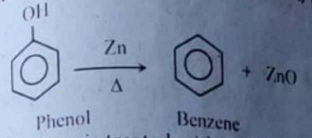
iii. **Preparation of hydrazobenzene from nitrobenzene:** When nitrobenzene on reduction with Zn/NaOH, hydrazobenzene is obtained.



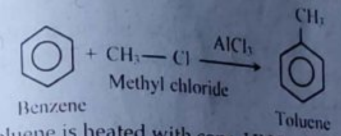
iv. **Preparation of TNT (Trinitro Toluene):** When nitrobenzene on reduction with Sn/HCl, aniline is obtained which on treatment with $NaNO_2$ + HCl at 0 - 5°C, benzene diazonium chloride is obtained. Diazonium salt on hydrolysis gives phenol.



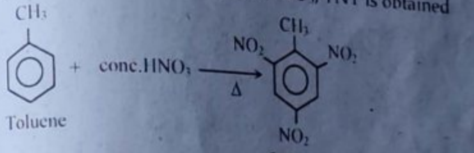
Phenol on reduction with Zn-dust, benzene is formed



Benzene is treated with methyl chloride in the presence of $AlCl_3$, Toluene is formed



Toluene is heated with conc. HNO_3, TNT is obtained

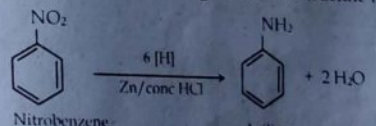


2, 4, 6-trinitrotoluene (TNT)

18. **2070 Set D Q.No. 25** **What happens when nitrobenzene is reduced in acidic, neutral, alkaline and, electrolytic conditions?** [5]

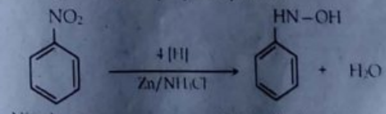
Reduction of nitrobenzene:

i. **In Acidic medium:** Nitrobenzene gives aniline in acidic medium.



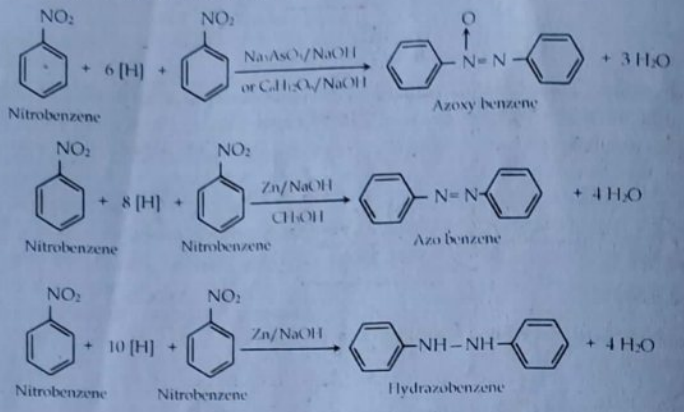
Nitrobenzene Aniline

ii. **In Neutral medium:** In neutral medium i.e. in the presence of Zn + NH_4Cl, nitrobenzene on reduction to give N-phenylhydroxylamine.

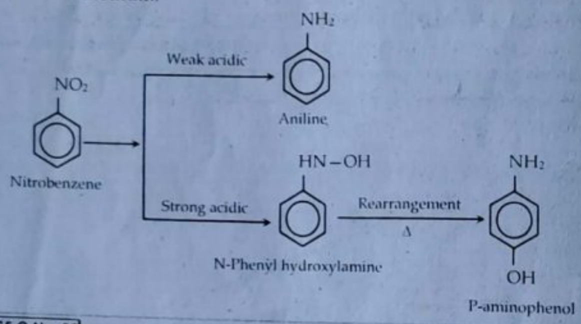


Nitrobenzene N-phenylhydroxylamine

iii. **In Alkaline medium:** In alkaline medium, nitrobenzene gives different bimolecular reduction product depending upon the nature of reducing agent used.



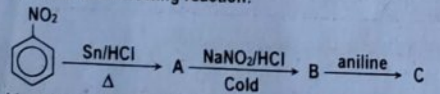
vi. **In electrolytic reduction**: Nitrobenzene on electrolytic reduction gives different products in different medium.



19. **2065 Q.No. 28**

a. **How is dry and pure nitrobenzene prepared in laboratory?**

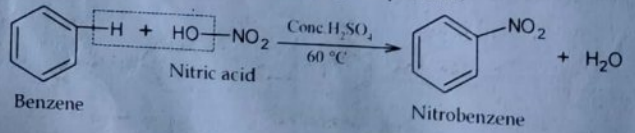
b. **Consider the following reaction:** **[5]**



Identify compounds A, B and C and write the reactions involved.

a. **Laboratory preparation of nitrobenzene:**

Theory: It is prepared in the laboratory by the nitration of benzene with a mixture of conc.HNO_3 and conc.H_2SO_4 at ordinary temperature.



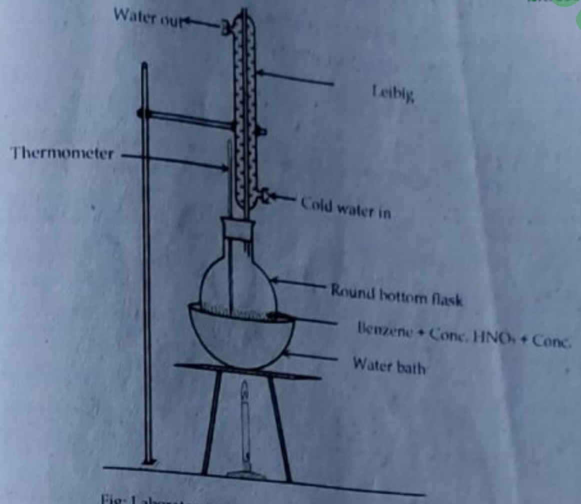


Fig: Laboratory preparation of nitrobenzene (reflux)

Procedure: 60 mL of conc. H_2SO_4 and 60 mL conc. HNO_3 is taken in a round bottom flask and the flask is cooled by immersing in cold water then 50 mL benzene is added in small amount and the mixture is shaked in every addition. The mixture is heated in water bath at 60°C for 60 minutes, pale yellow oily layer with bitter almond odour appears on the surface the flask is cooled and the mixture is transferred into cold water. The layer of nitrobenzene is separated by using separating funnel.

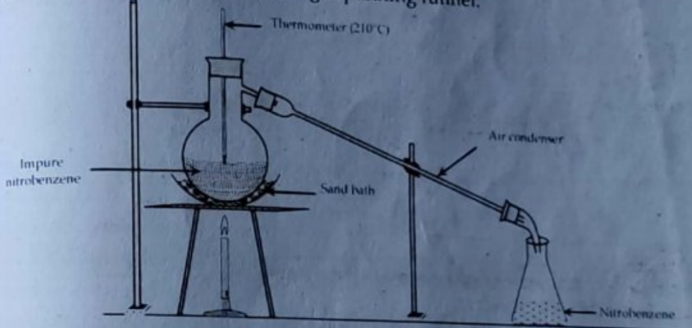
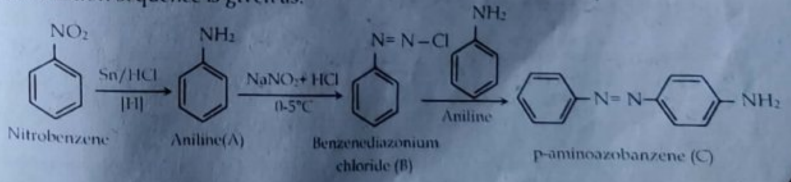


Figure: Distillation of nitrobenzene (for purification)

Purification: Thus the obtained nitrobenzene is washed with Na_2CO_3 and water several times and dried over anhydrous $CaCl_2$ and nitrobenzene is distilled by using air condenser to get pure nitrobenzene. Thus, the obtained pure nitrobenzene has boiling point 210°C.

b. The reaction sequence is given as:



The compounds are

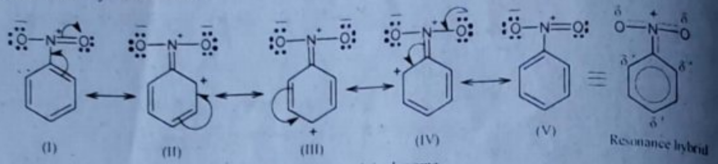
A = Aniline

B = Benzenediazoniumchloride

C = p-aminoazobenzene

20. **2063 Q.No. 21 Write the reasonating structures of nitrobenzene and explain why does it give meta substituted product during electrophilic substitution? How is nitrobenzene converted to p-hydroxyazobenzene?** **[5]**

➣ The nitro group of nitrobenzene is m-directing in electrophilic substitution. This can be explained by resonance.

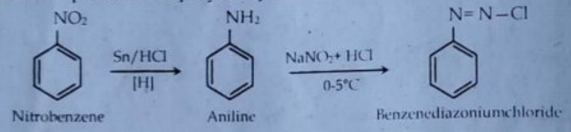


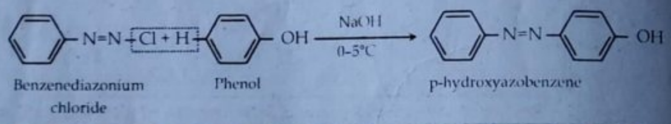
Resonating structures of nitrobenzene

It is observed that positive charge is developed on ortho and para position. So, electrophiles do not attack at that position. The incoming electrophile must be linked at meta-position because meta-position has relatively higher electron density than ortho and para position.

Conversion:

Nitrobenzene to p-hydroxyazobenzene: When nitrobenzene is reduced with Sn/HCl then aniline is formed which on treatment with nitrous acid ($NaNO_2$ + HCl), benzenediazoniumchloride is obtained. Thus the formed benzenediazoniumchloride is treated with phenol then p-hydroxy azobenzene is formed.

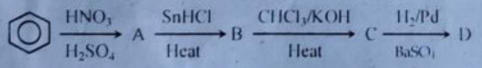




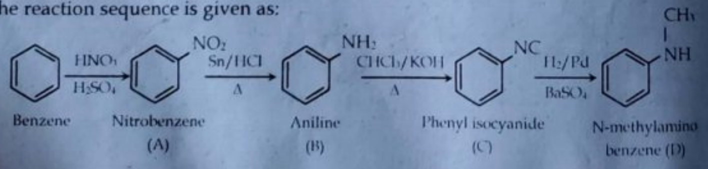
21. **2057 Q.No. 23(d) Write the chemical equation with conditions for the following reaction:** **[1]**
Nitrobenzene is reduced in neutral medium.

➣ Please refer to 2070 Set D Q No. 25

22. **2056 Q.No. 25 Write the structures of organic compound A, B, C and D in the following sequence of reactions.** **[5]**



➣ The reaction sequence is given as:



The compounds are

A = Nitobenzene

B = Aniline

C = Phenyl isocyanide

D = N-methylaminobenzene

23. **2056 Q.No. 27 How is nitrobenzene prepared in laboratory?** **[5]**

➣ Please refer to 2065 Q.No 28

LONG ANSWER QUESTIONS [10 MARKS]

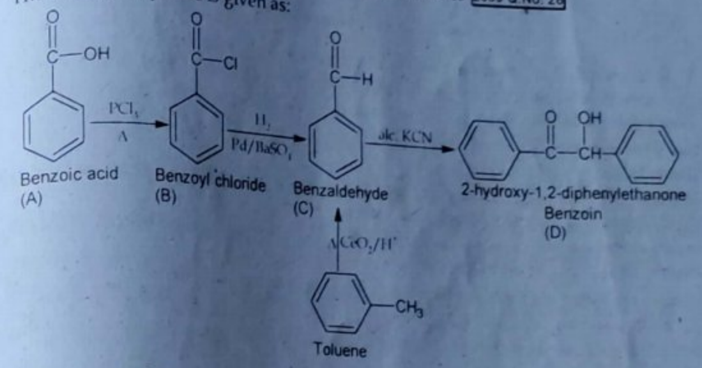
24. **2076 Set B Q.No. 30 2076 Set C Q.No. 30 Describe laboratory method of preparation of pure and dry nitrobenzene. Identify the major products Ⓐ, Ⓑ, Ⓒ and Ⓓ in the following reaction sequence:**

$$Ⓐ \xrightarrow[\Delta]{PCl_3} Ⓑ \xrightarrow[Pd/BaSO_4]{H_2} Ⓒ \xrightarrow{alc.KCN} Ⓓ$$

The compound Ⓒ can be obtained by heating toluene in presence of CeO_2/H^+ **[6+1+1+1+1]**

➣ **Laboratory preparation of nitrobenzene:** Please refer to 2065 Q.No. 28

The reaction sequence is given as:



The compounds are

Ⓐ = Benzoic acid

Ⓑ = Benzoyl chloride

Ⓒ = Benzaldehyde

and Ⓓ = Benzoin

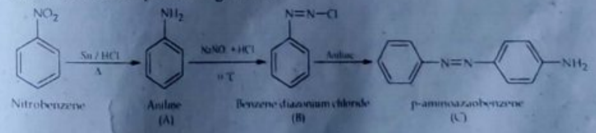
25. **2074 Set A Q.No. 30 How is pure nitrobenzene prepared in the laboratory? Identify (A), (B) and (C) in the reaction sequence.**

$$\text{Nitrobenzene} \xrightarrow[\Delta]{Sn/HCl} (A) \xrightarrow[0\,^\circ C]{NaNO_2 + HCl} (B) \xrightarrow{\text{Aniline}} (C)$$

Give an use of (C). **[6+4]**

➣ **Laboratory preparation of nitrobenzene:** Please refer to Please refer to 2065 Q.No. 28

The reaction sequence is given as:



The compounds are

A = Aniline

B = Benzene diazonium chloride

C = p-aminoazobenzene

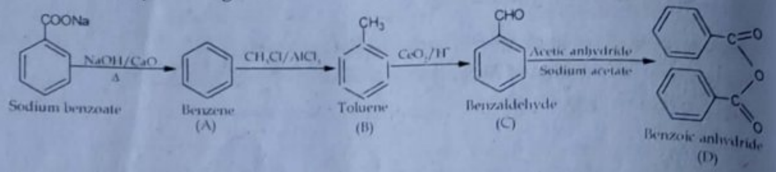
Use of C (p-aminoazobenzene): It is used in the form of its salt as a dye and as an intermediate in manufacture of acid yellow, diazo dyes and indulines.

26. **2074 Supp. Q.No. 30 How is pure nitrobenzene prepared in the laboratory? Identify (A), (B), (C) and (D) in the following reaction sequence.** **[6+4]**

$$\text{Sodium benzoate} \xrightarrow[\Delta]{NaOH/\ CaO} (A) \xrightarrow{CH_3Cl/\ AlCl_3} (B) \xrightarrow{CeO_2/H^+} (C) \xrightarrow[\text{Sodium acetate}]{\text{Acetic anhydride}} (D)$$

Laboratory preparation of nitrobenzene: Please refer to 2056Q.No. 27

The reaction sequence is given as:



The compounds are

A = Benzene C = Benzaldehyde

B = Toluene D = Benzoic anhydride

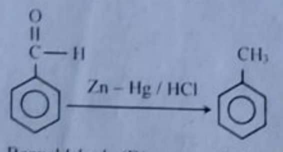
27. **2072 Set C Q.No. 31 How is dry and pure nitrobenzene prepared in the laboratory. Identify A, B and C and D in the following reaction sequence:**

$$A \xrightarrow[\Delta]{Zn} B \xrightarrow[AlCl_3]{CH_3\,Cl} C \xrightarrow{CeO_2/H^+} D$$

Compound D when react with zinc amalgam in presence of acid to give toluene. **[6+4]**

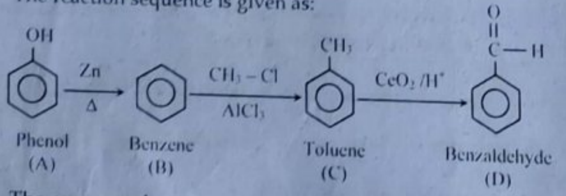
Laboratory preparation of Nitrobenzene: Please refer to 2065 Q.No. 28

Second part: The compound D reacts with Zn - Hg in presence of acid to give toluene. The compound (D) must be



Benzaldehyde (D) Toluene

The reaction sequence is given as:



The compounds are

A = Phenol

B = Benzene

C = Toluene

D = Benzaldehyde

28. **2071 Set C Q.No. 32 (a) How is pure nitrobenzene prepared in the laboratory? Perform the following conversions: nitrobenzene to p-hydroxyazobenzene**

Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

Conversion: Nitrobenzene to p-hydroxyazobenzene: Please refer to 2063 Q.No. 21

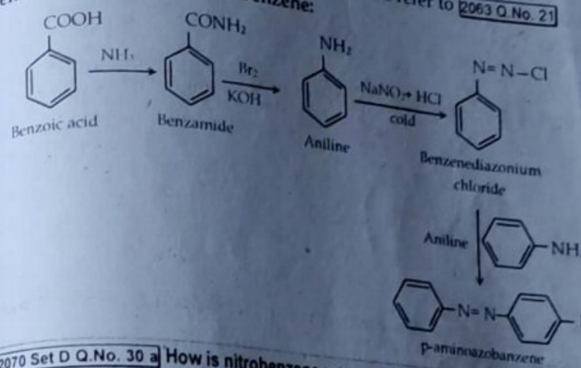
29. **2071 Set D Q.No. 30 How is pure nitrobenzene prepared in the laboratory? Perform the following conversions.**
    a. **nitrobenzene to p-hydroxyazobenzene.**
    b. **Benzoic acid to p-aminoazobenzene**

Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

Conversions:

a. **Nitrobenzene to p-hydroxyazobenzene:** Please refer to 2063 Q.No. 21

b. **Benzoic acid to p-aminoazobenzene:**



30. **2070 Set D Q.No. 30 a How is nitrobenzene prepared in the laboratory in pure and dry state?**

Please refer to 2065 Q.No. 28

31. **2069 Supp. Set B Q.No. 31 a Sketch a well-labelled diagram for the preparation of nitrobenzene in the laboratory.**

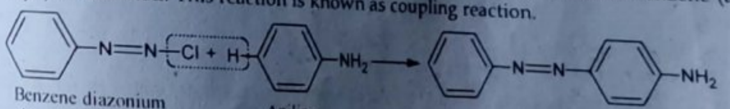
Please refer to 2065 Q.No. 28

32. **2069 (Set B) Q.No. 31**
    a. **How is nitrobenzene prepared in the laboratory?**
    b. **Convert the following:**
        i. **Aniline into azo dye**
        ii. **Benzaldehyde into Cinnamic acid.**

a. **Laboratory preparation of nitrobenzene:** Please refer to 2065 Q.No. 28

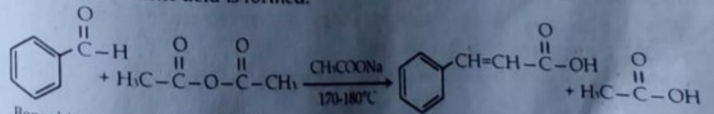
b. **Conversion:**

i. When aniline is treated with benzene diazonium chloride, p-aminoazobenzene (azo dye) is obtained. This reaction is known as coupling reaction.



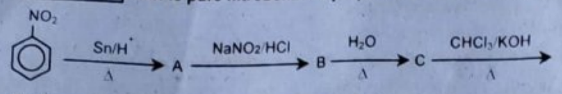
Benzene diazonium chloride Aniline p-aminoazobenzene

ii. When benzaldehyde is heated with acetic anhydride in the presence of sodium acetate, Cinnamic acid is formed.



Benzaldehyde Acetic anhydride Cinnamic acid Acetic acid

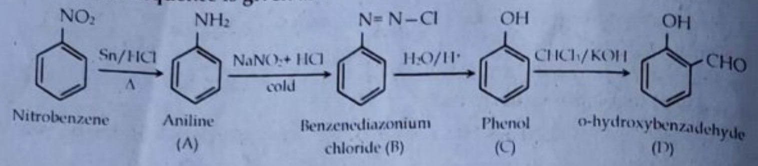
33. **2067 Q. No. 30** **How is pure nitrobenzene prepared in the laboratory?**



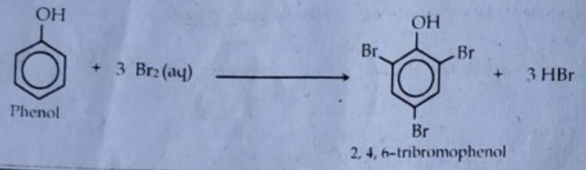
What happens when C is treated with aqueous bromine?

Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

The reaction sequence is given as:



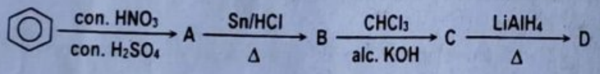
When 'C' i.e. phenol is treated with aqueous bromine, 2, 4, 6-tribromo phenol is obtained.



34. **2066 Q. No. 28**

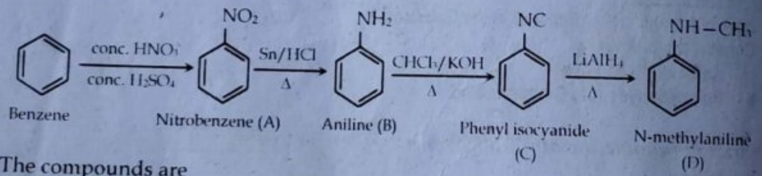
(a) How is dry and pure nitrobenzene prepared in laboratory?

(b) Identify compounds A, B, C and D in the followings and write the reactions involved: **[10]**



a. **Laboratory preparation of nitrobenzene**: Please refer to 2065 Q.No. 28

b. The reaction sequence is given as:



The compounds are

A = Nitrobenzene

B = Aniline

C = Phenyl isocyanide

D = N-methylaniline

35. **2059 Q.No. 28** **How is nitrobenzene prepared in laboratory in pure and dry state? How is it converted to p-hydroxyazobenzene?** **[10]**

Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

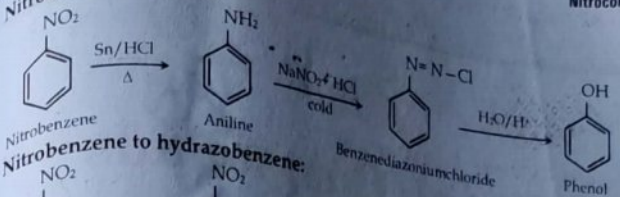
Conversion: Please refer to 2063 Q.No. 21

36. **2058 Q.No. 28** **Describe the preparation of pure and dry nitrobenzene in laboratory. How is it converted to (i) phenol and (ii) hydrazobenzene?** **[10]**

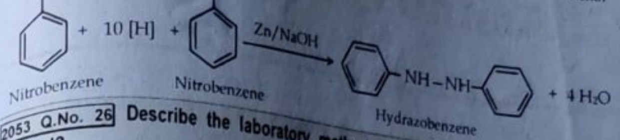
Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

Conversion:

i. **Nitrobenzene to phenol:**



ii. **Nitrobenzene to hydrazobenzene:**



37. **2053 Q.No. 26** **Describe the laboratory method for the preparation of Nitrobenzene. How is it purified?**

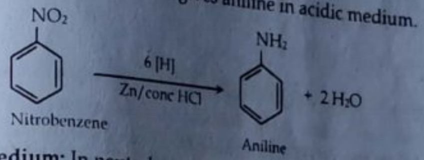
What happens when Nitrobenzene is subjected to reduction in

a. Acidic medium **b. Neutral medium** **[10]**

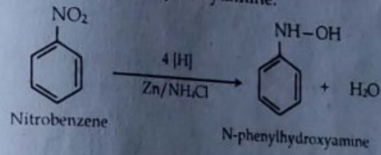
Laboratory preparation of nitrobenzene: Please refer to 2065 Q.No. 28

Recuction of nitrobenzene:

a. **Acidic medium:** Nitrobenzene gives aniline in acidic medium.



b. **Neutral medium:** In neutral medium i.e. in the presence of Zn + NH_4Cl, nitrobenzene on reduction to give N-phenylhydroxylamine.



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Unit 15

Amino Compounds

15.1 Aliphatic Amines

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2075 GIE Q.No. 15 Write down two isomeric amines and their names from C_2H_7N. What chemical test is used to distinguish them?** [1+1]

The possible isomers of C_2H_7N are

$H_3C—CH_2—NH_2$ Ethanamine $H_3C—NH—CH_3$ N-methylmethanamine

Nitrous acid test: This test can distinguish ethanamine from N-methylmethanamine. Nitrous test can distinguish ethanamine from N-methylmethanamine.

Ethanamine i.e. primary amine reacts with nitrous acid to form alcohol and nitrogen gas.

$$\underset{\text{Ethanamine}}{H_3C—CH_2—NH_2} \xrightarrow[HNO_2,\ 0-5\ °C]{NaNO_2\ /\ HCl} \underset{\text{Ethanol}}{H_3C—CH_2—OH} + N_2 + H_2O$$

N-methyl methanamine i.e. secondary amine reacts with nitrous acid to form water insoluble N-nitrosoamine.

$$H_3C—\overset{CH_3}{\overset{|}{N}}H + HNO_2 \longrightarrow H_3C—\overset{CH_3}{\overset{|}{N}}—N{=}O + H_2O$$

N-methylmethanamine   Dimethyl-N-nitrosoamine

2. **2075 Set A Q.No. 15 2073 Supp Q.No. 15 2073 Set C Q.No. 15 2073 Set D Q.No. 15 2072 Set E Q.No. 14 2070 Supp. Q.No. 14 Give a chemical test to distinguish ethanamine from N-methylmethanamine.** [2]

Please refer to 2075 GIE Q.No. 15

3. **2075 Set B Q.No. 15ii Write an example of Carbylamine reaction** [1]

Carbylamine reaction:

$$\underset{\text{Methyl amine}}{H_3C—NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3\,KOH\,(alc.) \xrightarrow{\Delta} \underset{\text{Methyl isocyanide}}{H_3C—NC} + 3\,KCl + 3\,H_2O$$

4. **2074 Supp. Q.No. 15 Write down the structure of a primary amine and a secondary amine from C_3H_9N and give their IUPAC name.** [1+1]

The structure of primary amine of molecular formula C_3H_9N is

$H_3C—CH_2—CH_2—NH_2$

Propan-1-amine

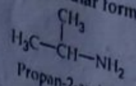
The structure of secondary amine of molecular formula C_3H_9N is

$H_3C—NH—CH_3$

N-methylmethanamine

2074 Set A Q.No. 15 Write down the structure of a secondary amine and a tertiary amine from C_3H_9N and give their IUPAC name. [1+1]

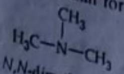
The structure of secondary amine of molecular formula C_3H_9N is



$$H_3C—\overset{CH_3}{\overset{|}{C}}H—NH_2$$

Propan-2-amine

The structure of tertiary amine of molecular formula C_3H_9N is

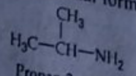


$$H_3C—\overset{CH_3}{\overset{|}{N}}—CH_3$$

N,N-dimethylmethanamine

6. **2074 Set B Q.No. 15 Write down the structure of a secondary amine and a tertiary amine from C_3H_9N and give their IUPAC name.** [1+1]

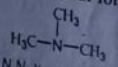
The structure of secondary amine of molecular formula C_3H_9N is



$$H_3C—\overset{CH_3}{\overset{|}{C}}H—NH_2$$

Propan-2-amine

The structure of tertiary amine of molecular formula C_3H_9N is



$$H_3C—\overset{CH_3}{\overset{|}{N}}—CH_3$$

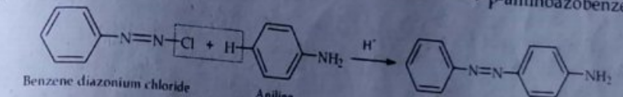
N,N-dimethylmethanamine

7. **2072 Supp. Q.No. 15 Write a chemical test to distinguish aliphatic amine from aromatic amine.** [2]

Azo dye formation test: Aliphatic amine does not react with benzene diazonium chloride to form azo dye but aromatic amine react with benzene diazonium chloride to for azo dye. This test distinguishes aliphatic amine from aromatic amine.

Aliphatic amine + Benzene diazonium chloride ⟶ no reaction

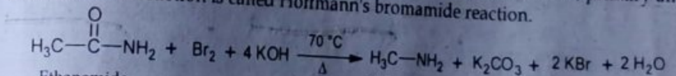
Aromatic amine (Aniline)+Benzene diazonium chloride ⟶ p-aminoazobenzene (azo dye)



Benzene diazonium chloride   Aniline   p-aminoazobenzene (azo dye)

8. **2072 Set E Q.No. 15i Define and give an example of Hoffmann's hypobromite reaction.** [1]

Acid amide is heated with bromine in the presence of aq. KOH at 70°C, primary amine is obtained. This reaction is called Hoffmann's bromamide reaction.



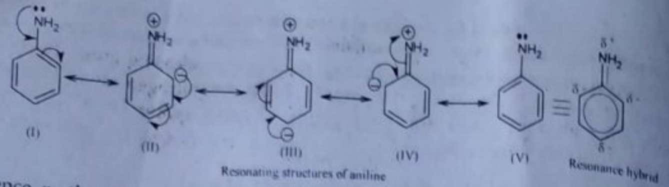
$$H_3C—\overset{O}{\overset{\|}{C}}—NH_2 + Br_2 + 4\,KOH \xrightarrow[\Delta]{70\ °C} H_3C—NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Ethanamide   Methanamine

9. **2071 Supp. Q.No. 15 Why is methanamine more basic than aniline?** [2]

Methanamine contains one alkyl group i.e. electron releasing group. The electron releasing group increases the basicity of animes by increasing the electron density on nitrogen atom.

In the case of aniline, the electron withdrawing group benzene is linked to the nitrogen atom of amine. This group decreases the availability of lone pair of electron due to resonance.



Hence, methanamine is more basic than aniline.

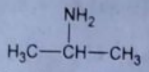
10. **2071 Set C Q.No. 15 (i) Give an example of each of the following reaction: Hoffman's bromamide reaction.** [2]

Please refer to 2072 Set E Q.No. 15

11. **2071 Set D Q.No. 15 Write the structure of isomeric amines of propanamine and their IUPAC name.** [2]

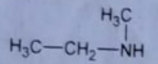
The isomers of propanamine are

$H_3C-CH_2-CH_2-NH_2$
1-aminopropane
or propanamine



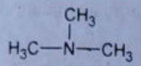
$H_3C-\underset{}{\overset{NH_2}{CH}}-CH_3$

2-aminopropane



$H_3C-CH_2-\overset{H_3C}{NH}$

N-methylaminoethane

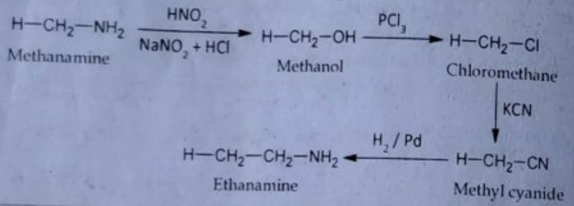


$H_3C-\overset{CH_3}{N}-CH_3$

N,N-dimethylaminomethane

12. **2070 Set C Q.No. 15 Convert methanamine into ethanamine.** [2]

Conversion:

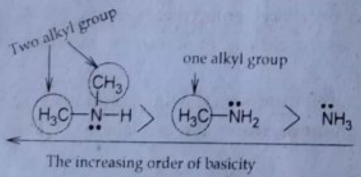


$$H-CH_2-NH_2 \xrightarrow[NaNO_2 + HCl]{HNO_2} H-CH_2-OH \xrightarrow{PCl_3} H-CH_2-Cl \xrightarrow{KCN} H-CH_2-CN \xrightarrow{H_2 / Pd} H-CH_2-CH_2-NH_2$$

Methanamine, Methanol, Chloromethane, Methyl cyanide, Ethanamine

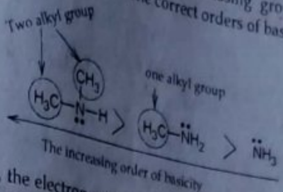
13. **2069 (Set A) Q.No. 15 Why is amine more basic than ammonia?** [2]

We know that amines are the derivatives of ammonia. So, basicity of amines are given with respect to ammonia. The lone pair of electron present in the nitrogen atom is responsible for basicity. Higher the availability of lone pair and ease of donation of lone pair of electon, more the basicity of amines. The electron releasing group increases the basicity of amines by increasing the electron density on nitrogen atom. Primary and secondary amines have one and two electron releasing group i.e. alkyl group but ammonia does not contain alkyl group. The correct orders of basicity of amines are:

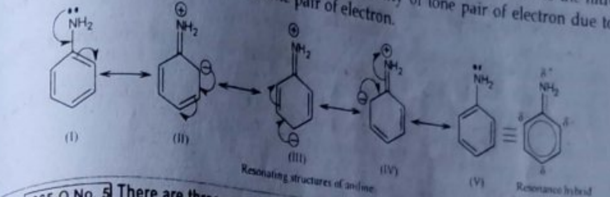


14. **2069 (Set B) Q.No. 14 Why are aliphatic amines more basic than aniline?** [2]

We know that amines are the derivatives of ammonia. So, basicity of amines are given with respect to ammonia. The lone pair of electron present in the nitrogen atom is responsible for basicity. Higher the availability of lone pair and ease of donation of lone pair of electon, more the basicity of amines. The electron releasing group increases the basicity of amines by increasing the electron density on nitrogen atom. Primary and secondary amines have one and two electron releasing group i.e. alkyl group but ammonia does not contain alkyl group. The correct orders of basicity of amines are:



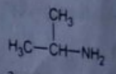
In the case of aniline, the electron withdrawing group benzene is linked to the nitrogen atom of amine. This group decrease the availability of lone pair of electron due to the resonance i.e. delocalization of lone pair of electron.



15. **2065 Q.No. 5 There are three possible isomeric amines of C_3H_9N. One of them is propanamine. Write other two isomers and give their IUPAC name.** [2]

The three possible isomers of C_3H_9N are

$H_3C-CH_2-CH_2-NH_2$
1-aminopropane
or propanamine



$H_3C-\overset{CH_3}{CH}-NH_2$

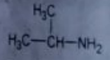
2-aminopropane

$H_3C-CH_2-NH-CH_3$
N-methylaminoethane

16. **2063 Q.No. 8 Write the possible isomeric amines of C_3H_9N and give their IUPAC names.** [2]

Following are the isomer of molecular formula C_3H_9N

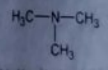
$H_3C-CH_2-CH_2-NH_2$
1-aminopropane



$H_3C-\overset{H_3C}{CH}-NH_2$

2-aminopropane

$H_3C-CH_2-NH-CH_3$
N-methylaminoethane

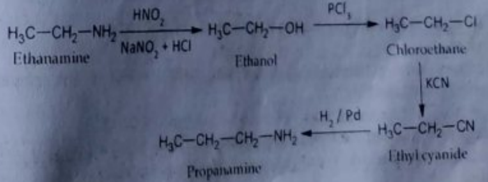


$H_3C-\underset{CH_3}{N}-CH_3$

N,N-dimethylaminomethane

17. **2055 Q.No. 14 Convert $CH_3-CH_2-NH_2$ into $CH_3-CH_2-CH_2-NH_2$** [2]

Conversion:



$$H_3C-CH_2-NH_2 \xrightarrow[NaNO_2 + HCl]{HNO_2} H_3C-CH_2-OH \xrightarrow{PCl_3} H_3C-CH_2-Cl \xrightarrow{KCN} H_3C-CH_2-CN \xrightarrow{H_2 / Pd} H_3C-CH_2-CH_2-NH_2$$

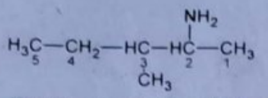
Ethanamine, Ethanol, Chloroethane, Ethyl cyanide, Propanamine

18. [2054 Q.No. 15] **Which of the following has most basic character? Explain.** [2]
a. NH_3 b. $(CH_3)_2NH$ c. CH_3NH_2 d. $C_6H_5NH_2$

Please refer to [2069 (Set B) Q.No. 14]

19. [2052 Q.No. 10(a)] **Name: $CH_3-CH_2-CH(CH_3)CH(NH_2)-CH_3$** [2]

The IUPAC name of



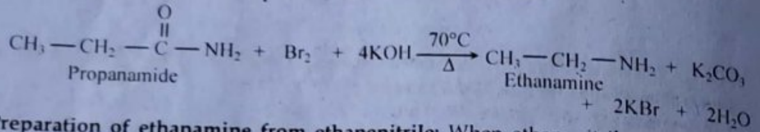
IUPAC = 2-amino-3-methylpentane

SHORT ANSWER QUESTIONS [5 MARKS]

20. [2072 Supp. Q.No. 29] **Write down a chemical reaction to distinguish ethanamine from N-methyl methanamine. How is ethanamine prepared from:**
i. propanamide ii. ethanenitrile
Covert ethanamine into methamine. [1+1+1+2]

Chemical reaction to distinguish ethanamine from N-methylmethanamine: Please refer to [2075 GIE Q.No. 15]

i. **Preparation of ethanamine from propanamide:** When propanamide is heated with bromine in the presence of aq. KOH, ethanamine is obtained



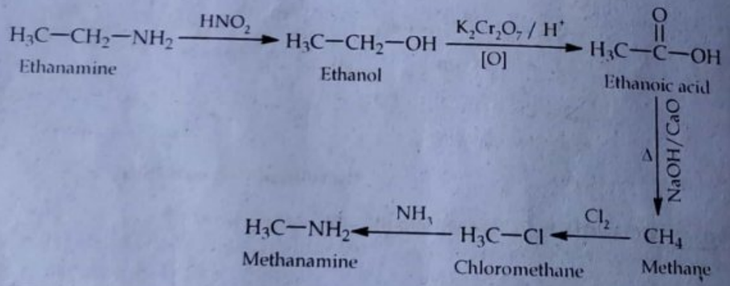
$$\underset{\text{Propanamide}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4KOH \xrightarrow[\Delta]{70°C} \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

ii. **Preparation of ethanamine from ethanenitrile:** When ethanenitrile on reduction with $LiAlH_4$, ethanamine is obtained.

$$\underset{\text{Ethanenitrile}}{CH_3-CN} \xrightarrow[{[H]}]{LiAlH_4} \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2}$$

Conversion:

Ethanamine into methanamine:



21. [2071 Supp. Q.No. 29] **How will you prepare ethanamine from**
i. propanamide ii. ethanenitrile
What happens when ethanamine is treated with $NaNO_2$ + HCl at low temperature convert methanamine into ethanamine? [1+1+1+2]

i. **Preparation of ethanamine from Propanamide:** Please refer to [2072 Supp. Q.No. 29]

ii. **Preparation of ethanamine from Ethanenitrile:** Please refer to [2072 Supp. Q.No. 29]

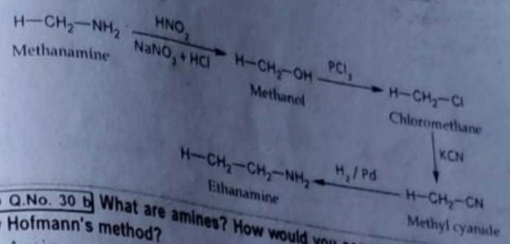
What happens:

When ethanamine is treated with $NaNO_2$ + HCl at low temperature, ethanol is obtained.

$$\underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} \xrightarrow[HNO_2,\ 0\text{-}5°C]{NaNO_2 + HCl} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + N_2 + H_2O$$

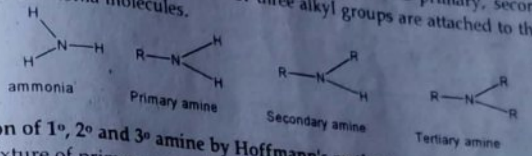
Conversion:

Methanamine to ethanamine:



22. [2070 Set D Q.No. 30 b] **What are amines? How would you separate 1°, 2° and 3° amines from their mixture by Hofmann's method?** [5]

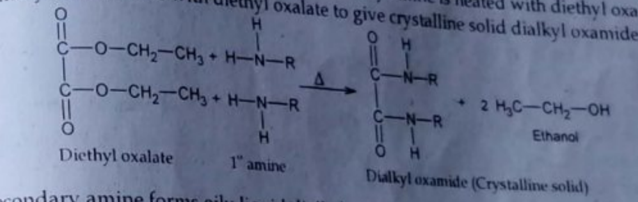
Amines: Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl groups. They are classified as primary, secondary and tertiary amines according as one, two or three alkyl groups are attached to the nitrogen atom of the ammonia molecules.



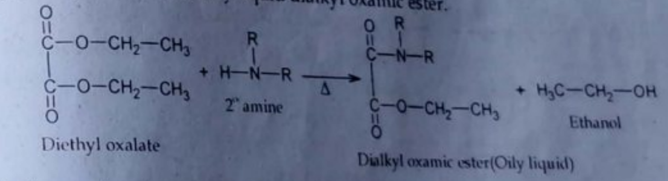
Separation of 1°, 2° and 3° amine by Hoffmann's method:

Given mixture of primary, secondary and tertiary amine is heated with diethyl oxalate.

i. Primary amine reacts with diethyl oxalate to give crystalline solid dialkyl oxamide.

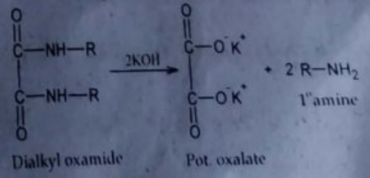


ii. Secondary amine forms oily liquid dialkyl oxamic ester.

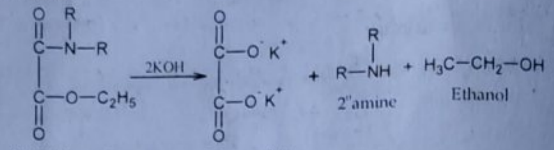


iii. Tertiary amine does not react with diethyl oxalate.

The reaction mixture containing dialkyl oxamide, dialkyl oxamic ester, tertiary amine, and ethyl alcohol is first filtered and solid product of dialkyl oxamide is separated. Dialkyl oxamide is heated with aq. KOH to recover primary amine.



The remaining mixture of dilakyl oxamic ester, tertiary amine and ethyl alcohol is subjected to fractional distillation. Tertiary amine is distilled out first. The residual dialkyl oxamic ester is heated with aq.KOH to recover secondary amine and alcohol in different fractions:



Dialkyl oxamic ester Pot. oxalate

In this way, the given mixture of 1°,2°,3° amines are separated out by Hoffmann's method.

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23. 2065 Q.No. 29 a **Mention any three suitable methods of preparation of Primary amine. How would you convert methenamine into ethanamine?** [5]

Three method of preparation of primary amines are

a. **From alkylhalide:** When alkyl halide is treated with ammonia at low temperature, primary amine is obtained.

$$R-X + 2NH_3 \longrightarrow \underset{1^\circ\ \text{amine}}{R-NH_2} + NH_4X$$

$$\underset{\text{Chloromethane}}{CH_3-Cl} + 2NH_3 \longrightarrow \underset{\text{Aminomethane}}{CH_3-NH_2} + NH_4Cl$$

b. **From alkane nitrile:** Alkane nitrile on reduction with $LiAlH_4$ gives primary amine.

$$\underset{\text{Alkanenitrile}}{R-CN} + 4[H] \xrightarrow{LiAlH_4} \underset{1^\circ\ \text{amine}}{R-CH_2-NH_2}$$

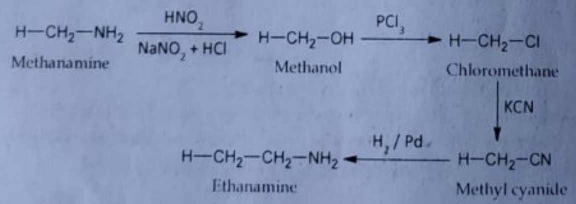
$$\underset{\text{Ethanenitrile}}{CH_3CN} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Aminoethane}}{CH_3-CH_2-NH_2}$$

c. **From Nitroalkane:** Nitroalkane on reduction with Sn/HCl gives primary amine.

$$R-NO_2 + 6[H] \xrightarrow{Sn/HCl} \underset{1^\circ\ \text{amine}}{R-NH_2} + 2H_2O$$

$$\underset{\text{Nitromethane}}{CH_3-NO_2} \xrightarrow{Sn/HCl} \underset{\text{Aminomethane}}{CH_3-NH_2} + 2H_2O$$

Conversion: Methanamine to Ethanamine:



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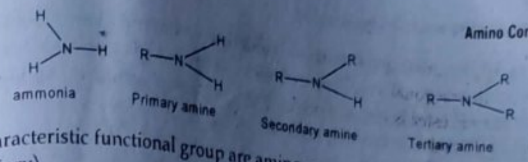
24. 2058 Q.No. 23 **What are amines? How are they classified? How do different classes of amines react with diethyl oxalate?** [5]

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl groups. They are classified as primary, secondary and tertiary amines according as one, two or three alkyl groups are attached to the nitrogen atom of the ammonia molecules.

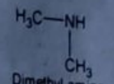


Their characteristic functional group are amino group $-NH_2$ (primary), $>NH$(secondary), $-N<$ (tertiary).

Primary amine: It is formed when one hydrogen atom of ammonia is replaced by alkyl group.

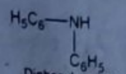
H_3C-NH_2 Methanamine $H_3C-CH_2-NH_2$ Ethanamine

Secondary amine: It is formed when two hydrogen atom of ammonia is replaced by alkyl group.



$H_3C-NH-CH_3$

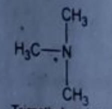
Dimethyl amine



$H_5C_6-NH-C_6H_5$

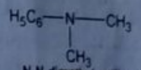
Diphenyl amine

Tertiary amine: It is formed when three hydrogen atom of ammonia is replaced by alkyl group.



$H_3C-N(CH_3)_2$

Trimethyl amine

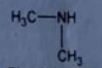


$H_5C_6-N(CH_3)-CH_3$

N,N-dimethyl aniline

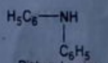
In the case of secondry and tertiary amines, the alkyl groups attached to nitrogen may be same or different giving simple and mixed amines respectively. Thus,

Simple amines: Alkyl groups attached to the nitrogen atom are same.



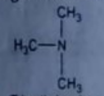
$H_3C-NH-CH_3$

Dimethyl amine



$H_5C_6-NH-C_6H_5$

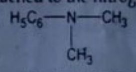
Diphenyl amine



$H_3C-N(CH_3)-CH_3$

Trimethyl amine

Mixed amines: Alkyl groups attached to the nitrogen atom are different.

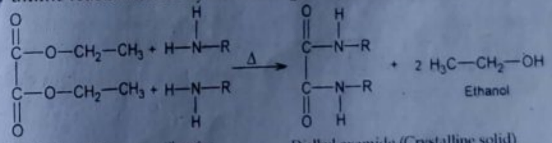


$H_5C_6-N(CH_3)-CH_3$

N,N-dimethylaniline

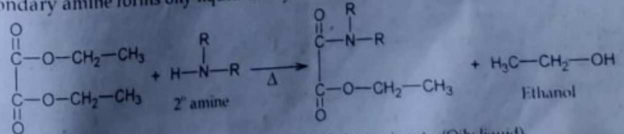
Reaction of difference class of amine with diethyl oxalate:

i. Primary amine reacts with diethyl oxalate to give crystalline solid dialkyl oxamide.



Diethyl oxalate 1° amine Dialkyl oxamide (Crystalline solid)

ii. Secondary amine forms oily liquid dialkyl oxamic ester.



Diethyl oxalate Dialkyl oxamic ester(Oily liquid)

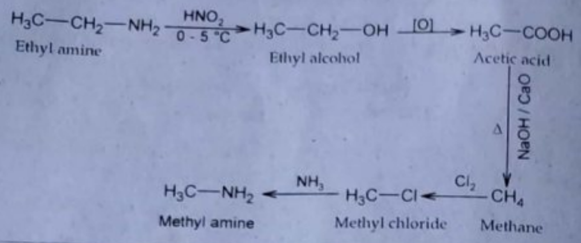
iii. Tertiary amine does not react with diethyl oxalate.

25. **2057 Q.No. 22 How would you separate 1°, 2° and 3° amines from their mixture by Hoffmann's method?** [5]

Please refer to 2070 Set D Q.No. 30 b

26. **2056 Q.No. 26 b Convert Ethylamine to methylamine** [2.5]

Conversion:



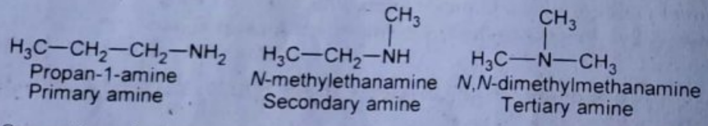
27. **2054 Q.No. 20 Discuss any one method that can be used for separation of primary, secondary and tertiary amines.** [5]

Please refer to 2070 Set D Q.No. 30 b

LONG ANSWER QUESTIONS [10 MARKS]

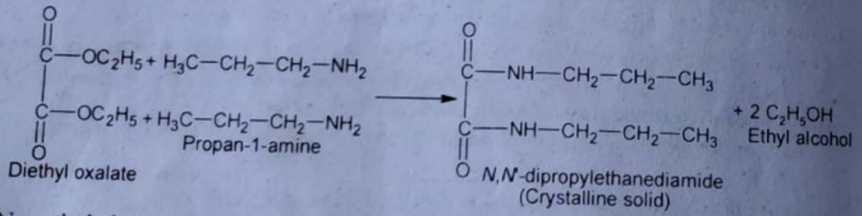
28. **2076 Set B Q.No. 31b 2076 Set C Q.No. 31b Write down a structural formula of primary, secondary and tertiary amine of each from C_3H_9N. How is Hoffmann's method applied to separate them from their mixture?**

The structural formulae of C_3H_9N are [4]

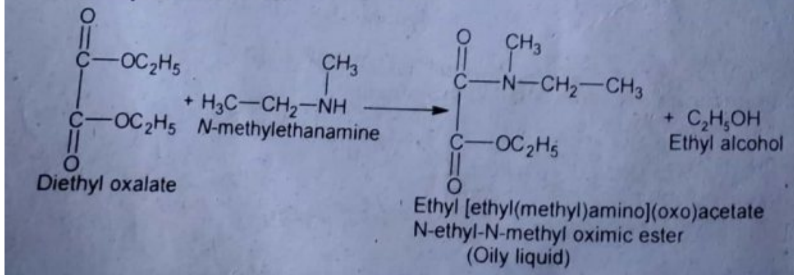


Separation of primary, secondary and tertiary amines by Hoffman's method:

a. Propan-1-amine reacts with diethyl oxalate to give crystalline solid N,N-dipropylethanediamide.

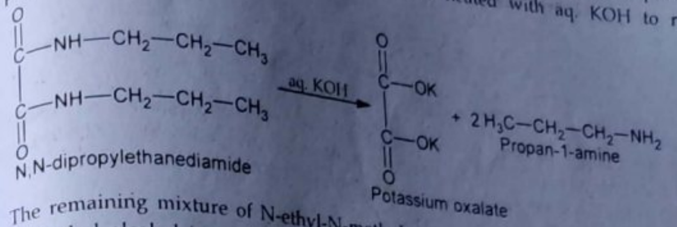


b. N-methylethanamine reacts with diethyl oxalate to give oily liquid product of N-ethyl-N-methyl oxamic ester.

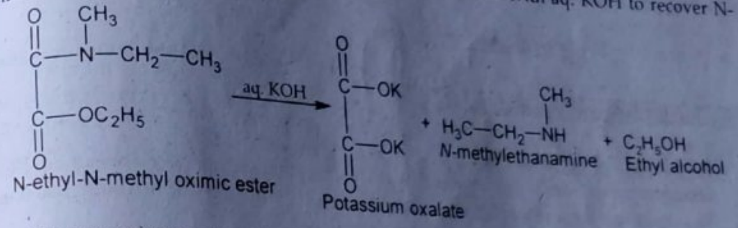


N,N-dimethylmethanamine does not react with diethyl oxalate.

The reaction mixture containing N,N-dipropylethanediamide, N-ethyl-N-methyl oxamic ester, N,N-dimethylmethanamine and ethyl alcohol is first filtered and solid product of N,N-propylethanediamide is separated which is heated with aq. KOH to recover propan-1-amine.



The remaining mixture of N-ethyl-N-methyl oxamic ester, N,N-dimethylmethanamine and ethyl alcohol is subjected to fractional distillation. N,N-dimethylmethanamine is distilled out first. N-ethyl-N-methyl oxamic ester is heated with aq. KOH to recover N-methlyethanamine.



In this way primary, secondary and tertiary amines are separated from their mixture by Hoffmann's method.

29. **2071 Set C Q.No. 29 Write down a chemical reaction to distinguish ethanamine from N-methyl methanamines? How is ethanamine prepared from:** [10]

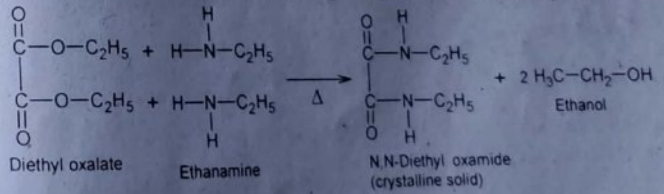
i. **propanamide**
ii. **ethanenitril**

Convert ethanamine into methanamine.

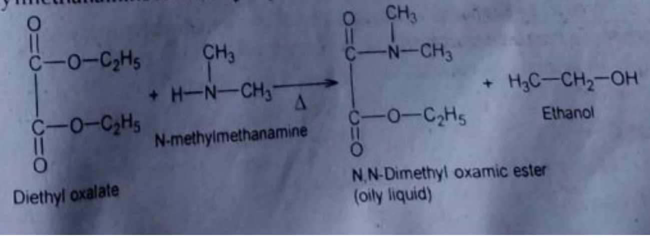
Hoffmann's method distinguishes ethanamine from N-methyl methanamine:

Given mixture of ethanamine and N-methyl methanamine is heated with diethyl oxalate.

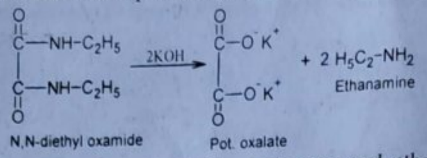
i. Ethanamine reacts with diethyl oxalate to give crystalline solid diethyl oxamide.



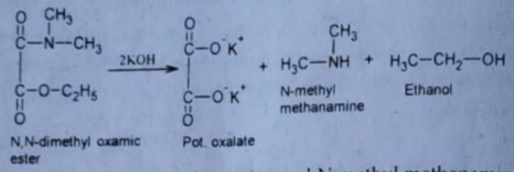
ii. N-methylmethanamine forms oily liquid dimethyl oxamic ester.



The reaction mixture containing N,N-diethyl oxamide, N,N-dimethyl oxamic ester and ethanol is first filtered and solid product of N,N-diethyl oxamide is separated. N,N-diethyl oxamide is heated with aq. KOH to recover ethanamine.



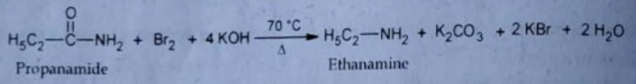
The remaining mixture of N,N-dimethyl oxamic ester and ethanol is subjected to fractional distillation. The N,N-dimethyl oxamic ester is heated with aq.KOH to recover N-methylmethanamine and alcohol in different fractions.



In this way, the given mixture of ethanamine and N-methyl methanamine are separated out by Hoffmann's method.

Preparation of Ethanamine:

i. **From propanamide:** Propanamide is heated with bromine in the presence of aq. KOH at 70°C, ethanamine is obtained. This reaction is called Hoffmann's bromamide reaction.



$$H_5C_2-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4\,KOH \xrightarrow[\Delta]{70\,°C} H_5C_2-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Propanamide Ethanamine

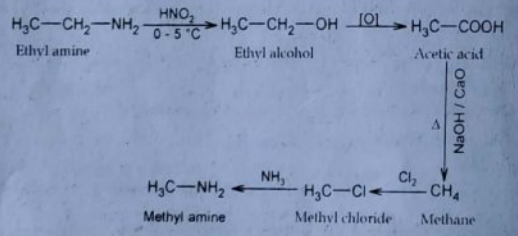
ii. **From Ethane nitrile:** Ethane nitrile on reduction with $LiAlH_4$, ethanamine is obtained.

$$H_3C-CN \xrightarrow[\text{[H]}]{LiAlH_4} H_3C-CH_2-NH_2$$

Ethanenitrile Ethanamine

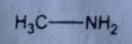
Conversion:

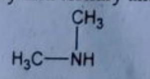
Ethanamine or ethyl amine to methanamine or methyl amine:

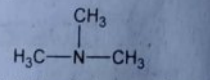


30. 2071 Set- D Q.No. 29 **Mention an example of each of primary, secondary and tertiary amine. How are they separated from their mixture by Hoffmann's method? [10]**

Example of primary, secondary and tertiary amines are:

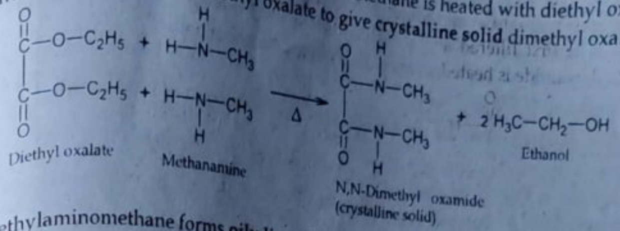

Aminomethane
Primary


N-methylaminomethane
Secondary

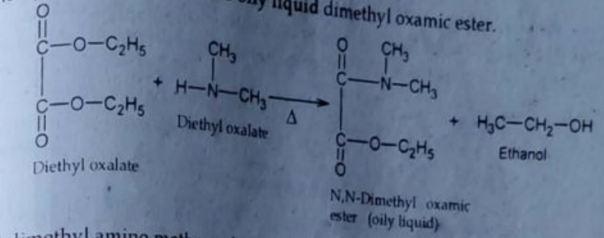

N,N-dimethylaminomethane
Tertiary

Separation by Hoffmann's Method: Given mixture of aminomethane, N-methylaminomethane and N,N-dimethylaminomethane is heated with diethyl oxalate.

i. Aminomethane reacts with diethyl oxalate to give crystalline solid dimethyl oxamide.

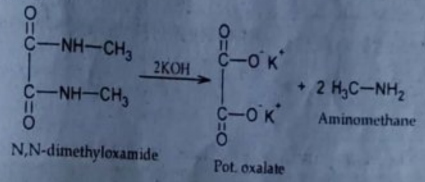


ii. N-methylaminomethane forms oily liquid dimethyl oxamic ester.

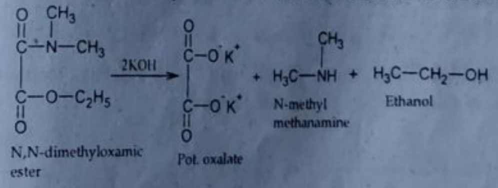


iii. N,N-dimethyl amino methane does not react with diethyl oxalate.

The reaction mixture containing N, N-dimethyloxamide, N,N-dimethyl oxamic ester, N,N-dimethylaninomethane and ethanol is first filtered and solid product of N,N-dimethyloxamide is separated. N,N-dimethyl oxamide is heated with aq. KOH to recover aminomethane.



The remaining mixture of N,N-dimethyloxamic ester, N,N-dimethyl aminomethane and ethanol is subjected to fractional distillation. Tertiary amine i.e. N,N-dimethylaminomethane is distilled out first. The N,N-dimethyl oxamic ester is heated with aq.KOH to recover N-methylamino methane and alcohol in different fractions.



In this way, the given mixture of aminomethane, N-methylaminomethane and N,N-dimethylaminomethane are separated out by Hoffmann's method.

31. 2069 Supp. Set B Q.No. 32 a **Explain the method of separation of 1°, 2°, 3° amines from their mixture. [5]**

Please refer to 2070 Set D Q No. 30 b

32. 2066 Q. No. 29 b **Describe the chemical method of separation of 1°, 2° and 3° amines from their mixture. [5]**

Please refer to 2070 Set D Q No. 30 b

33. 2064 Q.No. 28(i) **What are amines? How are they classified? Describe a suitable method for the separation of amines from their mixtures.** [5]

Amines: Please refer to 2058 Q.No. 23

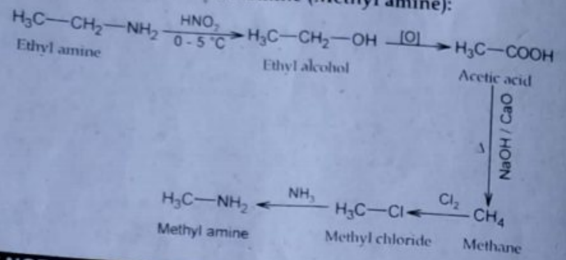
Separation of 1°,2° and 3° amine by Hoffmann's method:
Please refer to 2070 Set D Q.No. 30 b

34. 2064 Q.No. 28(ii) **How could you convert methanamine to ethanamine and vice versa?** [5]

Conversion:

Methanamine to ethanamine: Please refer to 2070 Set C Q.No. 15

Ethanamine (Ethyl amine) to methanamine (Methyl amine):



WRITE SHORT NOTES ON [5 MARKS]

35. 2075 GIE Q.No. 33ii 2075 Set A Q.No. 33ii 2074 Supp. Q.No. 33(iv) 2073 Supp Q.No. 33iii 2073 Set C Q.No. 33iv 2072 Set C Q.No. 33d **Separation of 1°, 2° and 3° amines by Hoffman's method/ Process.** [5]

Please refer to 2070 Set D Q.No. 30 b

36. 2075 Set B Q.No. 33iv 2069 Set A Q.No. 33 d **Separation of amine by Hoffmann's method.** [5]

Please refer to 2070 Set D Q.No. 30 b

37. 2074 Set B Q.No. 33b **Separation of 1°, 2°, 3° amines from their mixture.** [5]

Please refer to 2070 Set D Q.No. 30 b

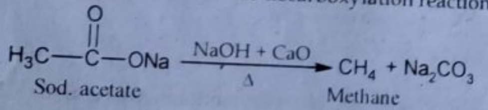
15.2 Aromatic Amine (Aniline)

VERY SHORT ANSWER QUESTIONS: [2 MARKS]

1. 2076 Set B Q.No. 14 **Write an example of each of the following reactions:**
   - i. Decarboxylation
   - ii. Coupling reaction

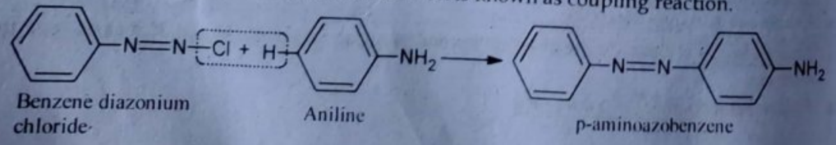
[1+1]

i. **Decarboxylation:** When sodium acetate is heated with sodalime, methane is obtained. This reaction is known as decarboxylation reaction.



$$H_3C-\overset{\overset{O}{\parallel}}{C}-ONa \xrightarrow[\Delta]{NaOH + CaO} CH_4 + Na_2CO_3$$

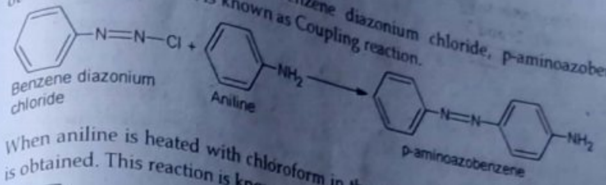
ii. **Coupling reaction:** When aniline is treated with benzene diazonium chloride, p-aminoazobenzene is obtained. This reaction is known as coupling reaction.



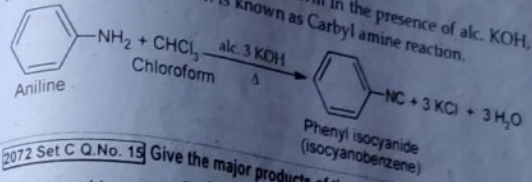
2. 2076 Set C Q.No. 14 **What happens when aniline is**
   - i. **Treated with benzene diazonium chloride.**
   - ii. **Heated with chloroform in presence of alc. KOH.**

[1+1]

i. When aniline is treated with benzene diazonium chloride, p-aminoazobenzene is obtained. This reaction is known as Coupling reaction.



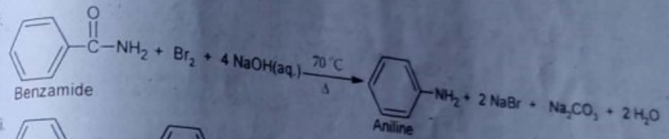
ii. When aniline is heated with chloroform in the presence of alc. KOH, phenyl isocyanide is obtained. This reaction is known as Carbyl amine reaction.



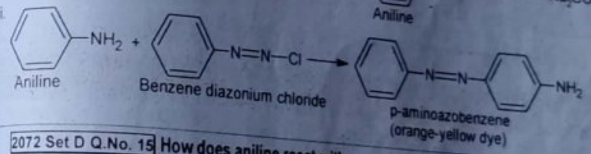
3. 2072 Set C Q.No. 15 **Give the major products of the following reactions:**
   - i. Benzamide + $Br_2 \xrightarrow[\Delta]{aq.\ NaOH}$
   - ii. Aniline + Benzenediazonium chloride $\xrightarrow{warm}$

[1+1]

i.



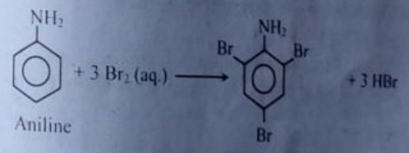
ii.



4. 2072 Set D Q.No. 15 **How does aniline react with:**
   - i. aqueous bromine
   - ii. $NaNO_2$+ HCl at low temperature

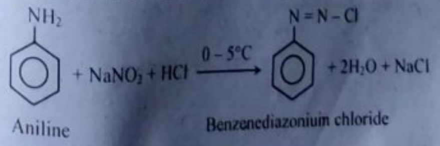
[1+1]

i. **Aqueous bromine:** Aniline reacts with aq.bromine, white ppt. of 2, 4, 6 – tribromoaniline is obtained.



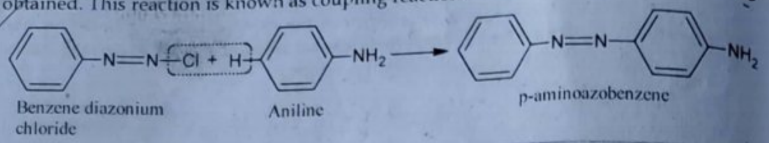
2, 4, 6 – tribromoaniline

ii. **$NaNO_2$+ HCl at low temperature:** Aniline reacts with $NaNO_2$ and HCl at 0 - 5°C, benzenediazonium chloride is obtained. This reaction is called diazotization reaction



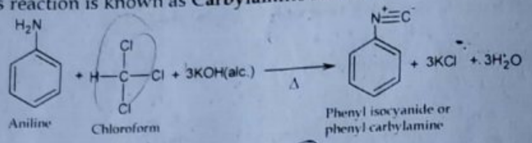
5. 2072 Set E Q.No. 15ii **Define and give an example of Coupling reaction.** [1]

When aniline is treated with benzene diazonium chloride, p-aminoazobenzene is obtained. This reaction is known as coupling reaction.



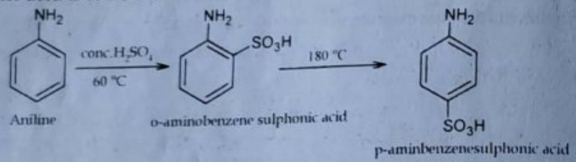
6. 2071 Set C Q.No. 15 (ii) **Give an example of each of the following reaction: Carbylamine reaction** [1]

When a mixture of chloroform and aniline is heated with alc. KOH, phenyl isocyanide is formed. This reaction is known as **Carbylamine reaction**.

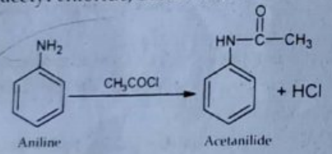


7. 2070 Set D Q.No. 15 **How are sulphanilic and acetanilide prepared from aniline?** [2]

Aniline on heating with conc. H_2SO_4 for 4 - 5 hours, p-aminobenzene sulphonic acid or sulphanilic acid is formed.



Aniline is treated with acetyl chloride, acetanilide is obtained.



8. 2069 Supp. Set B Q.No. 15 ii **Give an example of each of the following: Coupling reaction** [2]

Please refer to 2072 Set E Q.No. 15ii

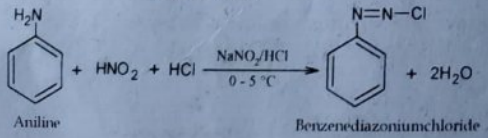
9. 2068 Q.No. 7b **Write an examples of each of the followings: Diazotization reaction.** [1]

Diazotization (Formation of diazonium salt)

Aniline reacts with nitrous acid at 0 - 5°C then diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

Sod. Nitrite   Nitrous acid

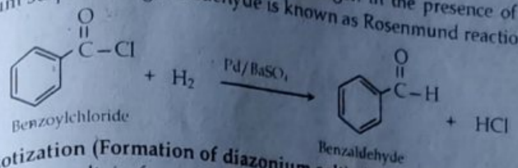


2065 Q.No. 7 **Mention one example of each of the following:** [2]

i. **Rosenmund's reduction**

ii. **Diazotization reaction**

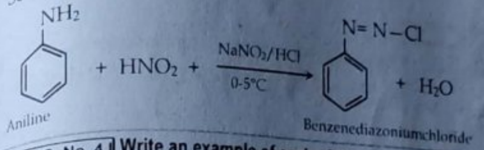
i. The reaction of acid chlorides with hydrogen in the presence of palladium metal and barium sulphate, to give aldehyde is known as Rosenmund reaction.



ii. **Diazotization (Formation of diazonium salt):** Aniline reacts with nitrous acid at 0 - 5°C, diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

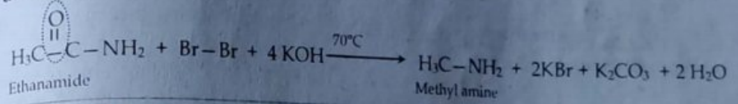
$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

Sodium nitrite   Nitrous acid



11. 2066 Q. No. 4 I **Write an example of each of the followings: Decarbonylation reaction** [2]

Decarbonylation reaction: The reaction of removal of carbonyl group (-CO-) is known as decarbonylation reaction. Hoffmann-Bromamide reaction is an example of decarbonylation reaction.



$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + Br-Br + 4\,KOH \xrightarrow{70°C} H_3C-NH_2 + 2KBr + K_2CO_3 + 2\,H_2O$$

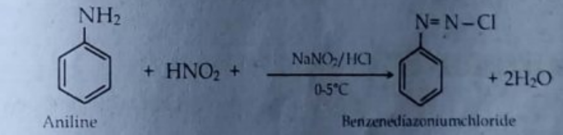
12. 2064 Q.No. 6(i) **Write an example of each of the following reaction of Diazotisation.** [2]

Diazotization:

Aniline reacts with nitrous acid at 0 - 5°C, diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

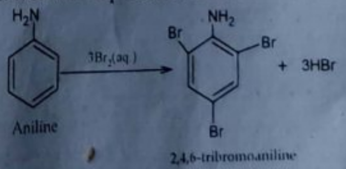
$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

Sodium nitrite   Nitrous acid



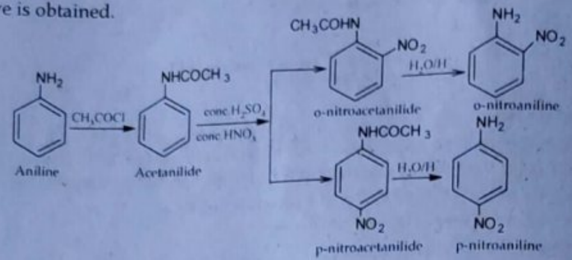
13. 2063 Q.No. 6(i) **What happens when: Aniline is shaken well with aq. Br_2?** [2]

When aniline is shaken well with aq. Br_2, 2,4,6-tribromoaniline of white ppt is formed.



14. 2061 Q.No. 6 **Why is – NH_2 group of aniline protected before nitration?** [2]

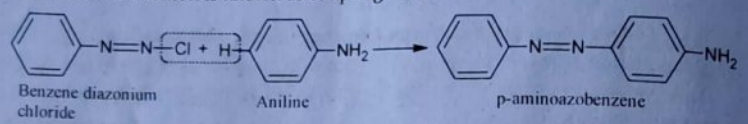
Nitration: When aniline is treated with conc. HNO_3, it yields a complex mixture of mono-, di- and tri-nitro compound and unexpected oxidation products. If the amino group ($-NH_2$) is protected by acetylation followed by hydrolysis then only mono nitro derivative is obtained.



SHORT ANSWER QUESTIONS [5 MARKS]

15. 2062 Q.No. 23(c) **What happens when Aniline is coupled with benzene diazonium chloride.** [5]

When aniline is treated with benzene diazonium chloride, p-aminoazobenzene is obtained. This reaction is known as coupling reaction.

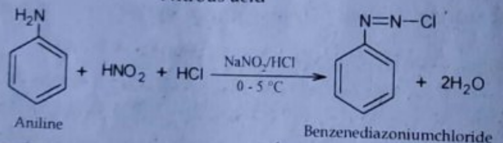


16. 2057 Q.No. 23(a) **Write the chemical equation with conditions for the following reaction. Aniline is diazotised.** [2.5]

Aniline reacts with nitrous acid at 0 - 5°C, diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

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

Sod. Nitrite Nitrous acid



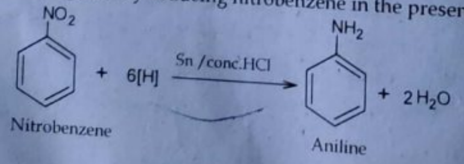
LONG ANSWER QUESTIONS [10 MARKS]

17. 2075 GIE Q.No. 31 **How is dry and pure aniline prepared in laboratory? Identify Ⓐ, Ⓑ, Ⓒ and Ⓓ in the following reaction sequence.** [6+4]

$$\text{Aniline} \xrightarrow[\text{Cold}]{NaNO_2+HCl} \text{Ⓐ} \xrightarrow[\Delta]{H_2O} \text{Ⓑ} \xrightarrow[\Delta]{Zn} \text{Ⓒ} \xrightarrow[\Delta/AlCl_3]{CH_3Cl} \text{Ⓓ}$$

Laboratory preparation of aniline:

Principle: Aniline is prepared by reducing nitrobenzene in the presence of Sn/HCl.



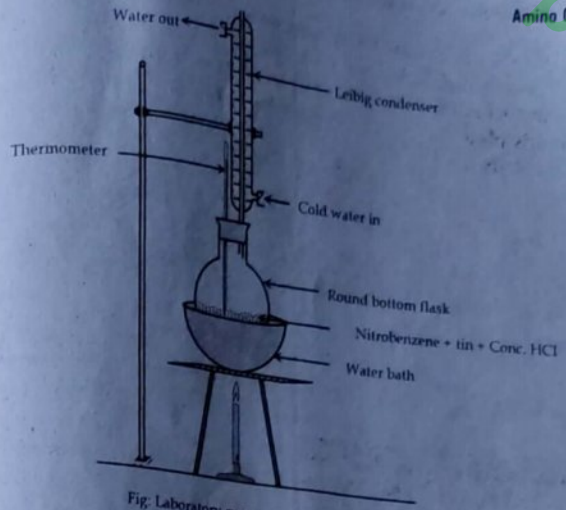


Fig: Laboratory preparation of aniline (reflux)

Procedure: 20 g of nitrobenzene and 40 g of granulated tin are placed in the 250 mL round bottom flask fitted with a reflux condenser. Conc. HCl of 100 mL is added gradually with constant shaking. After each addition, the round bottom flask is cooled so that temperature may not go above 90°C. Then reaction mixture is heated on a boiling water bath for about an hour until the reaction is completed which is indicated by smell of nitrobenzene, the disappearance of smell indicates the completion of the reaction. On cooling, a solid mass separates out.

$$Sn + 4HCl \longrightarrow SnCl_4 + 4H$$

$$C_6H_5NO_2 + 6H \longrightarrow C_6H_5NH_2 + 2H_2O$$

$$2C_6H_5NH_2 + 2HCl + SnCl_4 \longrightarrow [C_6H_5NH_3Cl]_2SnCl_4$$

Phenyl ammonium chloride stannic chloride (solid)

The crystalline solid mass is treated with conc. NaOH until the solution is cleared and becomes strongly alkaline. Aniline is separated out and is floated on the surface as dark brown oil. The mixture obtained is then subjected to the process of steam distillation until clear distillate is obtained.

$$[C_6H_5NH_3Cl]_2SnCl_4 + 8NaOH \rightarrow 2C_6H_5NH_2 + Na_2SnO_3 + 6\,NaCl + 5H_2O$$

Phenyl ammonium chloride stannic chloride (solid)

Purification: Aniline is extracted by shaking the distillate several times with ether. The ethereal layer is separated each time with the help of separating funnel. The ethereal aniline is placed for the evaporation where ether is evaporated out. Thus the pure aniline is obtained having boiling point about 182-184°C.

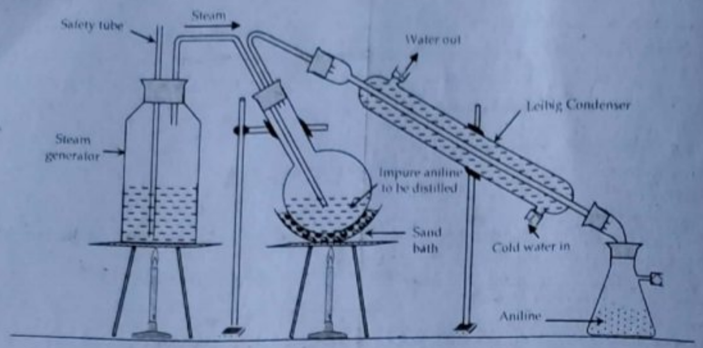
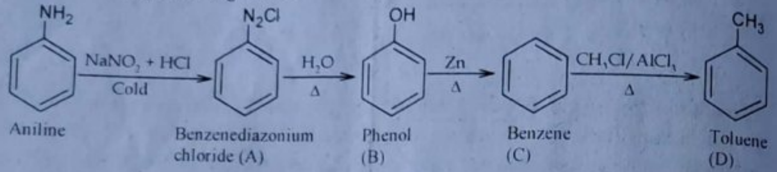


Figure: Steam distillation of aniline.

The reaction sequence is given as



The compounds are

(A)= Benzenediazonium chloride (B) = Phenol

(C) = Benzene (D) = Toluene

---

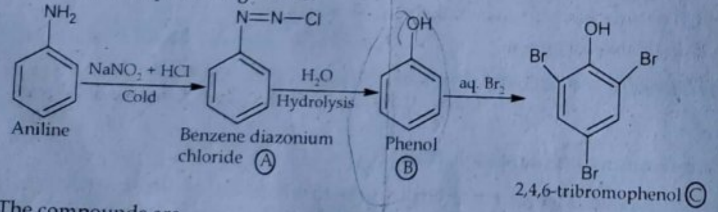
18. **2075 Set A Q.No. 31 How is dry and pure aniline prepared in laboratory? Identify Ⓐ, Ⓑ and Ⓒ in the following reaction sequence.**

$$\text{Aniline} \xrightarrow[\text{Cold}]{NaNO_2+HCl} Ⓐ \xrightarrow[\Delta]{H_2O} Ⓑ \xrightarrow{aq.Br_2} Ⓒ$$

What product would you expect when Ⓐ is treated with phenol in alkaline condition? **[6+3+1]**

Laboratory preparation of Aniline: Please refer to 2075 GIE Q.No. 31

The reaction sequence is given as:



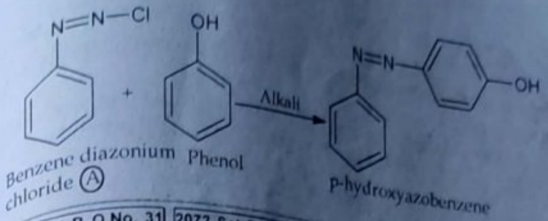
The compounds are

Ⓐ = Benzene diazonium chloride

Ⓑ = Phenol

Ⓒ = 2,4,6-tribromophenol

When benzene diazonium chloride is treated with phenol in alkaline condition, p-hydroazobenzene is obtained. This reaction is known as coupling reaction.



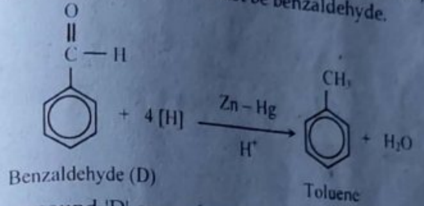
19. **2075 Set B Q.No. 31 2072 Set D Q.No. 31 How is pure and dry aniline prepared in the laboratory? Identify A, B, C, D in the following reaction sequences**

$$A \xrightarrow[\Delta]{Zn} B \xrightarrow[AlCl_3]{CH_3Cl} C \xrightarrow{CeO_2/H^+} D$$

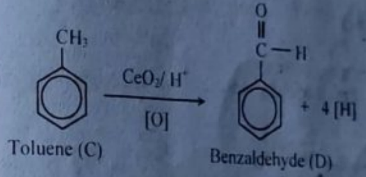
Compound D when react with zinc amalgam in presence of acid to give toluene. **[6+4]**

Laboratory preparation of aniline: Please refer to 2075 GIE Q.No. 31

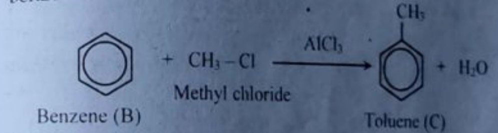
Reaction Sequence: The compound 'D' reacts with Zn/Hg in the presence of acid gives toluene. The compound 'D' must be benzaldehyde.



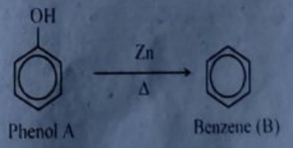
The compound 'D' comes from 'C' by oxidation with CeO$_2$/ H$^+$. The compound 'C' must be toluene.



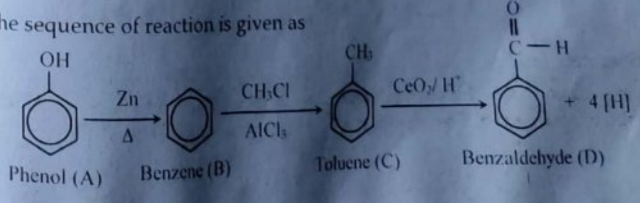
The compound 'C' comes from 'B' by Friedel-Craft alkylation. The compound 'B' must be benzene.



The compound 'B' comes from 'A' by reduction with Zn. The compound 'A' must be phenol.



The sequence of reaction is given as



The compounds are

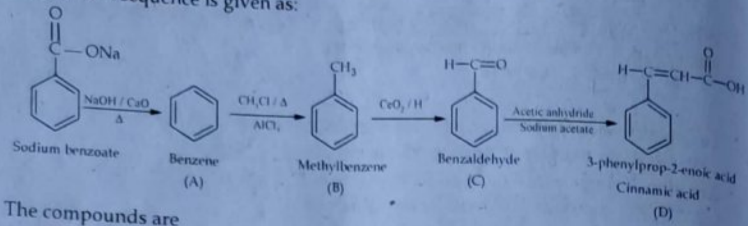
A = Phenol B = Benzene C = Toluene D = Benzaldehyde

20. 2074 Set B Q.No. 30 **How is pure aniline prepared in the laboratory? Identify (A), (B), (C), and (D) in the following reaction sequences.** [6+4]

$$\text{Sodium benzoate} \xrightarrow[\Delta]{NaOH\,/\,CaO} (A) \xrightarrow[AlCl_3]{CH_3Cl\,/\,\Delta} (B) \xrightarrow{CeO_2\,/\,H} (C) \xrightarrow[\text{Sodium acetate}]{\text{Acetic anhydride}} (D)$$

Laboratory preparation of aniline: Please refer to 2075 GIE Q.No. 21

The reaction sequence is given as:



The compounds are

A = Benzene

B = Methylbenzene (Toluene)

C = Benzaldehyde

D = Cinnamic acid (3-phenylprop-2-enoic acid)

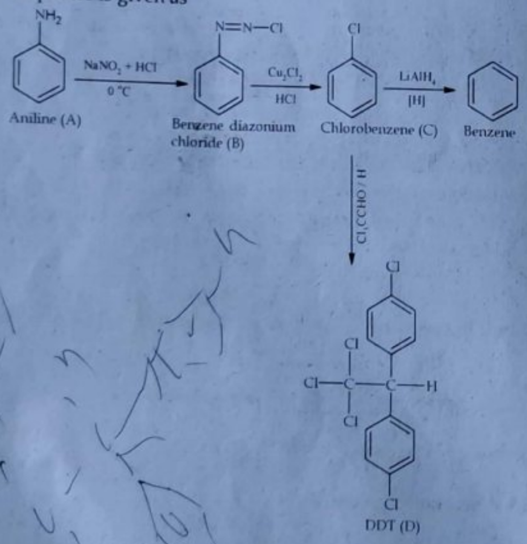
21. 2073 Supp Q.No. 30 **How is pure and dry aniline prepared in the laboratory? Identify the major products Ⓐ, Ⓑ, Ⓒ and Ⓓ in the following reaction sequence.** [6+4]

$$A \xrightarrow[0^\circ C]{NaNO_2 + HCl} B \xrightarrow[HCl]{Cu_2Cl_2} C \xrightarrow[H^+]{Cl_3CCHO} D$$

The compound Ⓒ undergoes reduction with $LiAlH_4$ to give benzene.

Laboratory preparation of aniline: Please refer to 2075 GIE Q.No. 31

The reaction sequence is given as



2073 Set C Q.No. 30 **How is pure aniline prepared in the laboratory? Identify the major products A, B, C and D in the following reaction sequence.** [6+4]

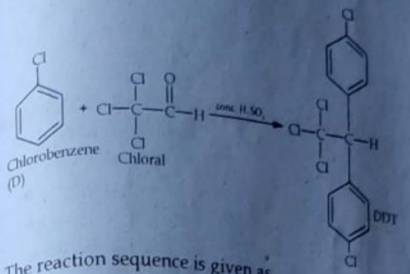
$$A \xrightarrow{Aq.NaOH + Br_2} B \xrightarrow[0^\circ C]{NaNO_2 + HCl} C \xrightarrow[HCl]{CuCl} D$$

The compound D if heated with chlorol in presence of acid gives DDT.

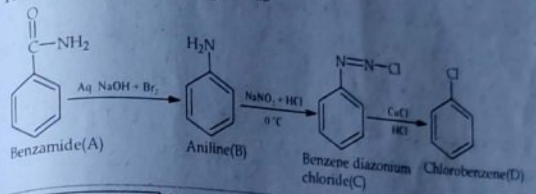
Laboratory preparation of Aniline: Please refer to 2075 GIE Q.No. 31

The reaction sequence is given as:

The compound (D) is treated with chloral in presence of acid to give DDT. The compound (D) must be chlorobenzene.



The reaction sequence is given as



23. 2073 Set D Q.No. 30 **How is pure and dry aniline prepared in the laboratory? Identify the major products Ⓐ, Ⓑ, Ⓒ and Ⓓ in the following reaction sequences.** [6+4]

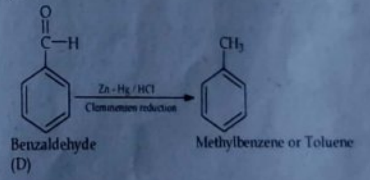
$$Ⓐ \xrightarrow[HCl]{CuCl} Ⓑ \xrightarrow[\text{dry ether}/\Delta]{Na/CH_3Br} Ⓒ \xrightarrow[\Delta]{CeO_2/H^+} Ⓓ$$

The compound D undergoes Clemmensen's reduction to give Toluene.

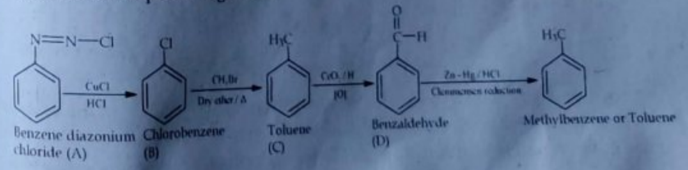
Laboratory preparation of Aniline: Please refer to 2075 GIE Q.No. 31

The reaction sequence is given as:

The compound D undergoes Clemmensen's reduction to give Toluene. The compound D must be benzaldehyde.



The reaction sequence is given as



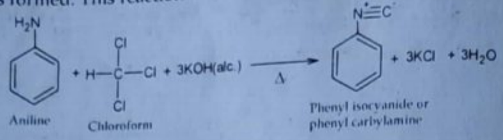
24. 2072 Set E Q.No. 30 **How is aniline prepared in the laboratory in pure and dry state? How does aniline react with.** **[7+3]**

i. Chloroform. ii. benzene diazonium chloride iii. aq. Br_2

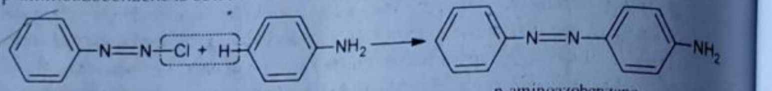
✍ **Laboratory preparation of aniline**: Please refer to 2075 GIE Q.No. 31

Reaction of aniline with

i. **Chloroform**: When a mixture of chloroform and aniline is heated with alc. KOH, phenyl isocyanide is formed. This reaction is known as **Carbylamine reaction**.

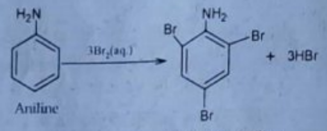


ii. **Benzene diazonium chloride**: When aniline is treated with benzene diazonium chloride, p-aminoazobenzene is obtained. This reaction is known as coupling reaction.



Benzene diazonium chloride Aniline p-aminoazobenzene

iii. **Aq. Br_2**: When aniline is shaken well with aq. Br_2, 2,4,6-tribromoaniline of white ppt is formed.



2,4,6-tribromoaniline

25. 2070 Supp. Q.No. 30 b **Explain why,** **[5]**

i. **Amino group of aniline is ortho or para directing.**

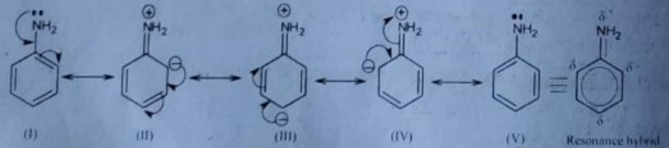
ii. **Amino group of aniline is protected before nitration.**

iii. **Aniline is a weaker base than aliphatic amine.**

✍

i. **Amino group of aniline is ortho or para directing:** The electron releasing group $-NH_2$ is directly linked on the benzene ring and the presence of lone pair of electron on N-atom gives electron to benzene ring. This decrease the availability of the lone pair of electron on nitrogen atom for protonation. This makes aniline a weaker base than aliphatic amine.

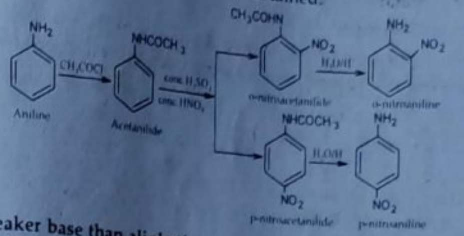
Resonance structure of aniline is



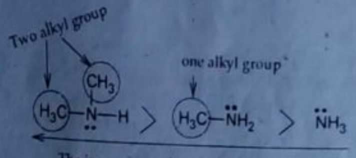
Resonating structures of aniline

The negative charge is developed on ortho and para position of aniline in the resonance structure. The incoming electrophile attacks to the ortho and para position. Therefore, amino group of aniline is ortho and para director in electrophilic substitution reaction.

ii. **Amino group of aniline is protected before nitration:** When aniline is treated with conc. HNO_3, it yields a complex mixture of mono-, di- and tri-nitro compound and unexpected oxidation products. If the amino group $(-NH_2)$ is protected by acetylation followed by hydrolysis then only mono nitro derivative is obtained.

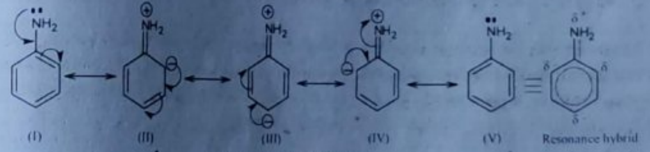


iii. **Aniline is weaker base than aliphatic amine:** We know that amines are the derivatives of ammonia. So, basicity of amines are given with respect to ammonia. The lone pair of electron present in the nitrogen atom is responsible for basicity. Higher the availability of lone pair and ease of donation of lone pair of electon, more the basicity of amines. The electron releasing group increases the basicity of amines by increasing the electron density on nitrogen atom. Primary and secondary amines have one and two electron releasing group i.e. alkyl group but ammonia does not contain alkyl group. The correct orders of basicity of amines are:



The increasing order of basicity

In the case of aniline, the electron withdrawing group benzene is linked to the nitrogen atom of amine. This group decrease the availability of lone pair of electron due to the resonance i.e. delocalization of lone pair of electron.



Resonating structures of aniline

26. 2070 Supp. Q.No. 30 a **Sketch a well-labelled diagram for the preparation of pure aniline in laboratory. Write the principle and process involved in it.** **[5]**

✍ Please refer to 2075 GIE Q.No. 31

27. 2070 Set C Q.No. 30 a **How is pure aniline prepared in the laboratory?** **[10]**

✍ Please refer to 2075 GIE Q.No. 31

28. 2069 (Set A) Q.No. 31

a. **How is pure aniline prepared in the laboratory?**

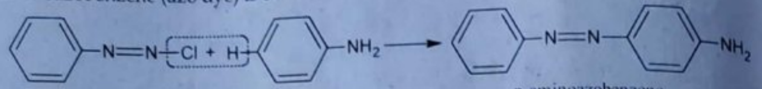
b. **Convert aniline into:**

i. azodye ii. N-methylaniline **[10]**

a. **Laboratory preparation of aniline:** Please refer to 2075 GIE Q No. 31

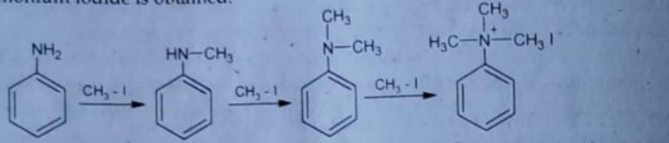
b. **Conversion:**

i. **Aniline into Azo dye:** When aniline is treated with benzene diazonium chloride, p-aminoazobenzene (azo dye) is obtained. This reaction is known as coupling reaction.



Benzene diazonium chloride Aniline p-aminoazobenzene

ii. **Methyl iodide:** Aniline is treated with methyl iodide, N-methylaniline is obtained. Excess of methyl iodide gives N'N-dimethylaniline and ultimetly quarternary ammonium iodide is obtained.

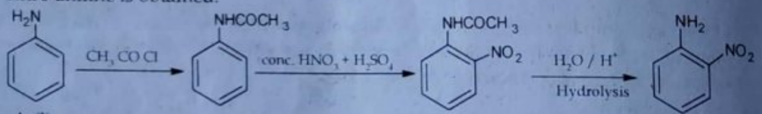


Aniline N-methylaniline N,N-dimethylaniline Quarternary ammonium iodide

29. 2068 Q.No. 29 **How is pure aniline prepared in the laboratory? Starting from aniline, how would you obtain:**
   - i. **Ortho-nitro aniline**
   - ii. **N-methylaniline** [10]

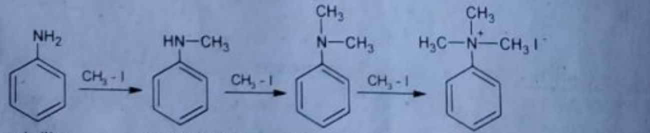
Laboratory preparation of aniline: Please refer to 2075 GIE Q No. 31

i. **Preparation of o-nitro aniline:** When aniline is treated with acetyl chloride, acetanilide is formed which on nitration with nitrating agent i.e. conc. HNO_3 and conc. H_2SO_4 then o-nitro acetanilide is obtained. Thus, the formed o-nitro acetanilide is hydrolyzed, o-nitro aniline is obtained.



Aniline Acetanilide o-nitroacetanilide o-nitroaniline

ii. **Preparation of N-methyl aniline from aniline:** Aniline is treated with methyl iodide, N-methylaniline is obtained. Excess of methyl iodide gives N'N-dimethylaniline and ultimetly quarternary ammonium iodide is obtained.



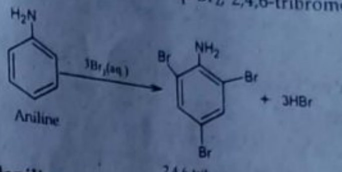
Aniline N-methylaniline N,N-dimethylaniline Quarternary ammonium iodide

30. 2062 Q.No. 28 **Describe the preparation of pure and dry aniline in the laboratory. Give its action upon:**
   - i. aq. Br_2 ii. methyl iodide [10]

Laboratory preparation of aniline: Please refer to 2075 GIE Q No. 31

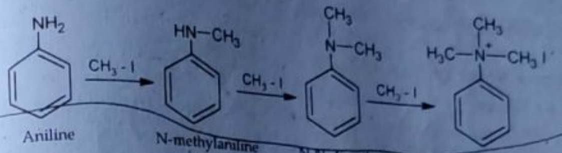
Action of aniline up on:

i. **Aq. Br_2 :** When aniline is shaken well with aq. Br_2, 2,4,6-tribromoaniline of white ppt is formed.

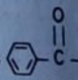


Aniline 2,4,6-tribromoaniline

ii. **Aniline into N-methylaniline:** Aniline is treated with methyl iodide, N-methylaniline is obtained. Excess of methyl iodide gives N'N-dimethylaniline and ultimetly quarternary ammonium iodide is obtained.



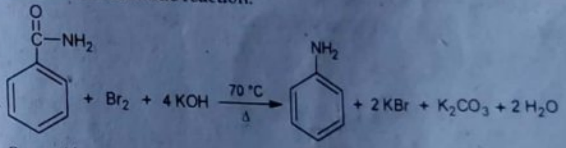
Aniline N-methylaniline N,N-dimethylaniline Quarternary ammonium iodide

31. 2061 Q.No. 29 **How is aniline prepared in the laboratory? What happens when**
   - a. **Benzamide,**  **– NH_2, is allowed to react with bromine in presence of KOH solution**
   - b. **Aniline is warmed with chloroform and ethanolic potassium hydroxide?**

Why is aniline less basic than methylamine? [10]

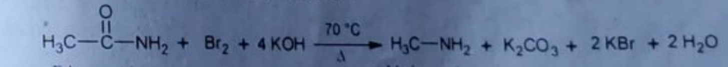
Laboratory preparation of aniline: Please refer to 2075 GIE Q No. 31

a. **Benzamide is allowed to react with bromine in presence of KOH:** When benzamide is heated with bromine and aqueous KOH at 70°C, aniline is obtained. This reaction is called Hoffmann's bromamide reaction.



Benzamide Aniline

b. **Aniline is warmed with chloroform and ethanolic KOH:** Acid amide is heated with bromine in the presence of aq. KOH at 70°C, primary amine is obtained. This reaction is called Hoffmann's bromamide reaction.



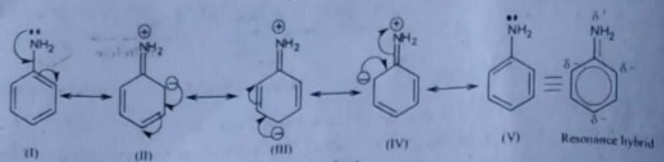
$$H_3C-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4\,KOH \xrightarrow[\Delta]{70\,^\circ C} H_3C-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Ethanamide Methanamine

c. **Aniline is less basic than methylamine**

We know that amines are the derivatives of ammonia. So, basicity of amines are given with respect to ammonia. The lone pair of electron present in the nitrogen atom is responsible for basicity. Higher the availability of lone pair and ease of donation of lone pair of electon, more the basicity of amines. The electron releasing group increases the basicity of amines by increasing the electron density on nitrogen atom. Methylamine amines has one electron releasing group i.e. methyl group.

In the case of aniline, the electron withdrawing group benzene is linked to the nitrogen atom of amine. This group decrease the availability of lone pair of electron due to the resonance i.e. delocalization of lone pair of electron.



Resonating structures of aniline

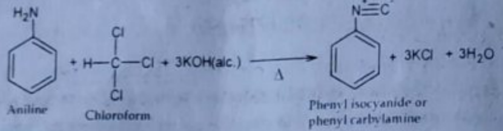
Therefore, methyl amine is more basic than aniline.

32. **2060 Q.No. 28** **How is aniline prepared in laboratory? Give its action upon** **[10]**
   a. **$CHCl_3$ / alc. KOH**
   b. **$NaNO_2$ / HCl under ice cold condition**
   c. **aq. Br_2**

✍ Laboratory preparation of aniline: Please refer to 2075 GIE Q.No. 31

Action of aniline up on:

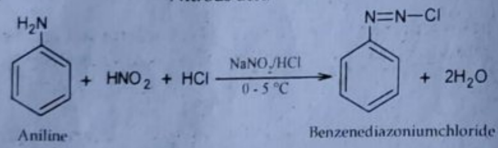
a. **$CHCl_3$ / alc.KOH:** When a mixture of chloroform and aniline is heated with alc. KOH, phenyl isocyanide is formed. This reaction is known as **Carbylamine reaction.**



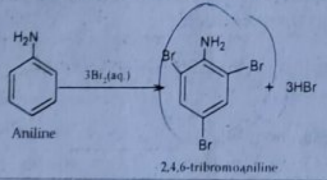
b. **$NaNO_2$ / HCl:** Aniline reacts with nitrous acid at 0 - 5°C, diazonium salt is formed. This reaction is known as **diazotization**. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

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

Sod. Nitrite Nitrous acid



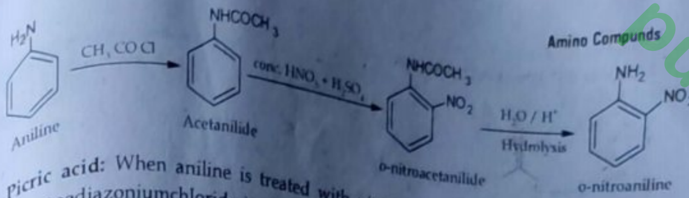
c. **Aq. Br_2:** When aniline is shaken well with aq. Br_2, 2,4,6-tribromoaniline of white ppt is formed.



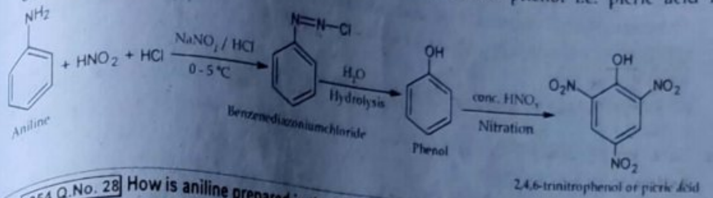
33. **2057 Q.No. 29(b)** **Starting from aniline how would you obtain** **[5]**
   i. **o-nitroaniline and** ii. **picric acid?**

✍

i. **o-nitro aniline:** When aniline is treated with acetyl chloride, acetanilide is formed which on nitration with nitrating agent i.e. conc. HNO_3 and conc. H_2SO_4 then o-nitro acetanilide is obtained. Thus, the formed o-nitro acetanilide is hydrolyzed, o-nitro aniline is obtained.



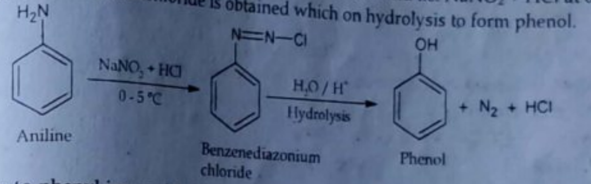
ii. **Picric acid:** When aniline is treated with nitrous acid i.e. $NaNO_2$ + HCl at 0 - 5°C, benzenediazoniumchloride is obtained which on hydrolysis to form phenol. Thus, the formed phenol is nitrated with conc. HNO_3, 2,4,6-trinitro phenol i.e. picric acid is obtained.



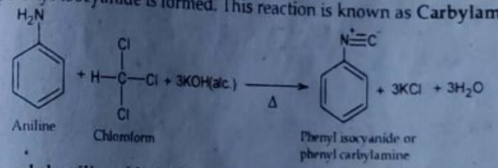
34. **2054 Q.No. 28** **How is aniline prepared in the laboratory? How would you convert aniline into:** **[10]**
   a. **Phenol**
   b. **Phenyl isocyanide**
   c. **Sulphanilic acid**
   d. **p-benzoquinone**
   e. **Benzene diazonium chloride**

✍ Laboratory preparation of aniline: Please refer to 2075 GIE Q.No. 31

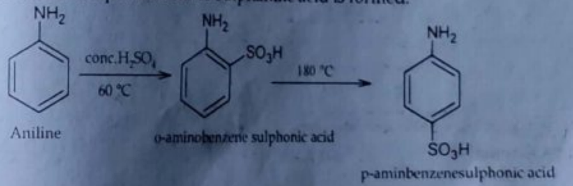
a. **Aniline to phenol:** When aniline is treated with nitrous acid i.e. $NaNO_2$ + HCl at 0 - 5°C then benzenediazoniumchloride is obtained which on hydrolysis to form phenol.



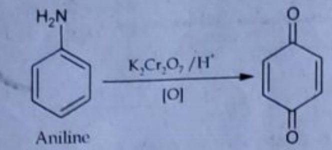
b. **Aniline to phenyl isocyanide:** When a mixture of chloroform and aniline is heated with alc. KOH, phenyl isocyanide is formed. This reaction is known as **Carbylamine reaction.**



c. **Aniline to sulphanilic acid:** Aniline on heating with conc. H_2SO_4 for 4 - 5 hours, p-aminobenzene sulphonic acid or sulphanilic acid is formed.



d. **Aniline to p-benzoquinone:** When aniline is oxidized with pot.dichromate in the presence of acid, p-benzoquinone is obtained.

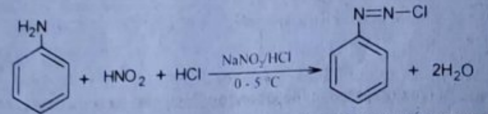


Aniline

p-benzoquinone

e. **Aniline to benzenediazoniumchloride:** Aniline reacts with nitrous acid at 0 - 5°C, diazonium salt is formed. This reaction is known as diazotization. Nitrous acid is prepared by the action of sodium nitrite and mineral acid.

$$\underset{\text{Sod. Nitrite}}{NaNO_2} + HCl \longrightarrow NaCl + \underset{\text{Nitrous acid}}{HNO_2}$$



Aniline

Benzenediazoniumchloride

□□□

Unit 16

Molecules of Life

VERY SHORT ANSWER QUESTIONS [2MARKS]

1. 2076 Set B Q.No. 16 **How does DNA differ from RNA in respect of sugar and base units present in it? [1+1]**

DNA consists of deoxyribose sugar where as RNA consists of ribose sugar. DNA consists nitrogenous base adenine, guanine, cytosine and thymine where as RNA consists nitrogenous base adenine, guanine, cytosine and uracil.

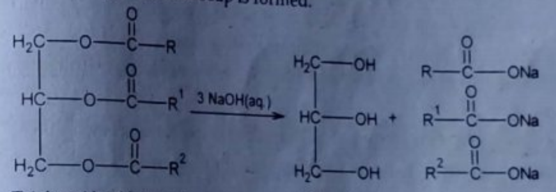
2. 2076 Set B Q.No. 17 **Define sugar and non-sugar giving an example of each. [1+1]**

Sugar: The carbohydrates which are sweet in taste and dissolve in water are called sugar. They are generally crystalline. Examples: glucose, fructose, sucrose, lactose etc.

Non-sugar: The carbohydrates which are not sweet in taste and are insoluble in water are called non-sugar. They are generally amorphous. Examples- starch, cellulose etc.

3. 2076 Set C Q.No. 16 **What are lipids? Name the products formed when simple lipids undergo hydrolysis. [1+1]**

Triglyceride of fatty acid is simple lipid. When simple lipid gets hydrolysed in the presence of NaOH, glycerol and soap is formed.



Triglyceride of fatty acid

Glycerol

Soap

4. 2076 Set C Q.No. 17 **What is meant by (i) invert sugar and (ii) non-reducing sugar? [1+1]**

i. **Invert sugar:** Invert(ed) sugar (syrup) is an edible mixture of sugars made by heating up table sugar (sucrose) with water. As invert sugar is thought to be sweeter than table sugar and foods that contain it hold in moisture and crystallize less easily, bakers, who call it invert syrup, may use it more than other sweeteners.

ii. **Non-reducing sugar:** Those sugars which do not reduce Fehling's solution or Tollen's reagent are called non-reducing sugar. Example: Starch.

5. 2075 GIE Q.No. 19 2070 Set D Q.No. 16 **Distinguish between sugar and non-sugar with an example of each. [1+1]**

Following are the difference between sugar and non-sugars:

Sugar	Non-sugar
It has sweet taste.	It does not have sweet taste.
It is soluble in water.	It is insoluble in water.

6. 2075 GIE Q.No. 18 **How are DNA differed from RNA in respect of (i) sugar (ii) Base, unit present on them?** [1+1]

Following are the difference between DNA and RNA

DNA	RNA
i. **Sugar:** It contains deoxyribose sugar	i. **Sugar:** It contains ribose sugar.
ii. **Base:** It contains thymine	ii. **Base:** It contains uracil

7. 2075 Set A Q.No. 18 **Name the chemical components which constitute nucleotides. Give a biological function of nucleotides.** [1+1]

The chemical components of nucleotides are pentose sugar (ribose and deoxyribose), nitrogenous base and phospahate group. It carries genetic information from parent to offspring.

8. 2075 Set A Q.No. 19 **Distinguish between reducing and non-reducing sugar with an example of each.** [1+1]

Following are the difference between reducing sugar and non-reducing sugar:

Reducing Sugar	Non-reducing Sugar
It reduces Fehling's solution or Tollen's reagent.	It does not reduce Fehling's solution or Tollen's reagent.
Example: Glucose	Example: Starch

9. 2075 Set B Q.No. 16 **Define the terms** [1+1]
   i. **invert sugar**
   ii. **reducing sugar**

i. **Invert sugar**: Invert(ed) sugar (syrup) is an edible mixture of sugars made by heating up table sugar (sucrose) with water. As invert sugar is thought to be sweeter than table sugar and foods that contain it hold in moisture and crystallize less easily, bakers, who call it invert syrup, may use it more than other sweeteners.

ii. **Reducing sugar**: The sugar which reduce Fehling's solution or Tollen's reagent are reducing sugar.

10. 2075 Set B Q.No. 17 **What are nitrogen bases? Name the nitrogen bases present in DNA.** [1+1]

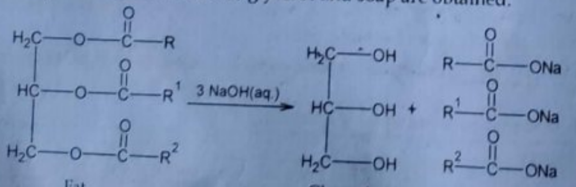
A nitrogenous base is simply a nitrogen-containing molecule that has the same chemical properties as a base. The nitrogen bases that present in DNA are adenine, guanine, cytosine, thymine.

11. 2074 Supp. Q.No. 16 **Define non-reducing sugar and give an example of it.** [1+1]

Non-reducing sugar: Those sugars which do not reduce Fehling's solution or Tollen's reagent are called non-reducing sugar. Example: Starch.

12. 2074 Supp. Q.No. 17 **What are fats? What happens when fats get hydrolyzed?** [1+1]

Ester of glycerol i.e. triglycerides are fats. When fats are hydrolysed in the presence of strong base i.e. conc. NaOH, glycerol and soap are obtained.



Fat Glycerol Soap

13. 2074 Set A Q.No. 16 **How is sugar differed from non-sugar? Give an example of each.** [1+1]

Difference between sugar and non-sugar: Please refer to 2075 GIE Q.No. 19

Example: Sugar = Glucose and Non-sugar = Starch

14. 2074 Set A Q.No. 17 **What are protein? What happens when protein get heated?** [1+1]

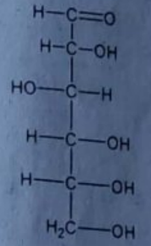
Protein: The complex nitrogenous organic compounds which are essential for the growth and maintenance of life are called protein. They are macromolecules in which large number of α -amino acid molecules are linked together by peptide bond (-CONH-). Proteins are polymer of α-amino acids.

Protein is heated: When protein is heated, it gets precipitated known as denatured protein.

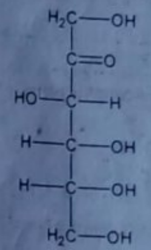
15. 2074 Set B Q.No. 16 2059 Q.No. 9 **Write down the structural formula of monosacharides obtained by the hydrolysis of sucrose.** [2]

The monosaccharides which are produced by the hydrolysis of cane sugar($C_{12}H_{22}O_{11}$) are glucose and fructose. The structrure are given below:

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



Glucose (aldohexose)



Fructose (ketohexose)

16. 2074 Set B Q.No. 17 **Define denaturation of protein. Mention the factors which are responsible for denaturation.** [1+1]

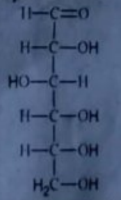
Denaturation is a process in which proteins or nucleic acids lose the quaternary structure, tertiary structure and secondary structure which is present in their native state, by application of some external stress or compound such as a strong acid or base, a concentrated inorganic salt, an organic solvent.

Following are the factors which are responsible for denaturation:

i. Heat
ii. Radiations
iii. Strong acid, base and salt.

17. 2073 Supp Q.No. 19 **What are monosaccharides? Give a structure formula of it.** [1+1]

The carbohydrate which cannot be hydrolyzed further into any small simpler molecules is called monosaccharide. Example: Glucose

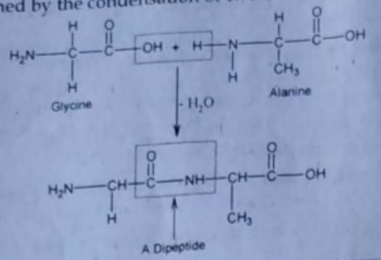


2,3,4,5,6-pentahydroxyhexanal

Glucose

18. **2073 Set C Q.No. 18 Illustrate the formation of peptide bond with an example.** [2]

Peptide bond is formed by the condensation of two or more α- amino acids. Example:



19. **2073 Set C Q.No. 19 What are reducing sugars? Write an example of it.** [1+1]

Reducing sugar: The sugars which reduce Fehling's solution or Tollen's reagent are called recucing sugar. Example: glucose

20. **2073 Set D Q.No. 18 Illustrate the formation of peptide bond with an example.** [2]

Please refer to 2073 Set C Q.No. 18

21. **2073 Set D Q.No. 19 What are non-reducing sugars? Write an example of it.** [1+1]

Please refer to 2074 Supp. Q.No. 16

22. **2072 Supp. Q.No. 16 What are carbohydrates? Write molecular formula of disaccharides.** [1+1]

Carbohydrates: Polyhydroxy aldehydes, polyhydroxy ketones or large polymeric molecules of organic compounds which on hydrolysis produce polyhydroxy aldehydes or ketones are called carbohydrates. Molecular formula of disaccharide i.e. sucrose is $C_{12}H_{22}O_{11}$.

23. **2072 Supp. Q.No. 17 Define the terms:** [1+1]

i. Co-enzyme **ii. Protein**

i. **Co-enzyme**: The catalytic activity of enzymes is enhanced in the presence of some other non-protein substances. This non-protein substance is called co-enzyme.

ii. **Protein**: The complex nitrogenous organic compounds of high molecular weight are called protein. It is the polymer of α-amino acids.

24. **2072 Set C Q.No. 16 What are disaccharides? What happens when they get hydrolysed?** [1+1]

Disaccharides: Carbohydrate which on hydrolysis produces two molecules of monosaccharides of same or different types is called disaccharides.

Example:

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

When disaccharide is hydrolysed then glucose and fructose are produced.

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

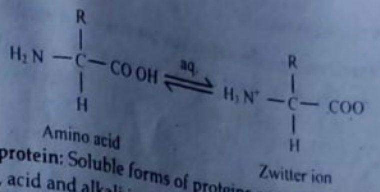
25. **2072 Set C Q.No. 17 Write an example of simple lipid. What happens when lipid gets hydrolysed?**[1+1]

Please refer to 2076 Set C Q.No. 16

26. **2072 Set D Q.No. 16 Define the terms:** [1+1]

i. Zwitter ions
ii. Denaturation of protein

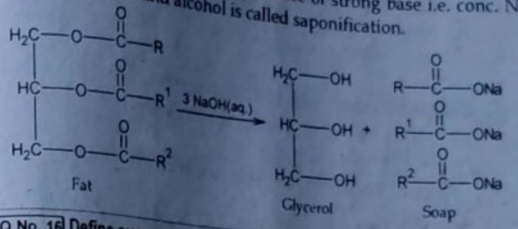
i. **Zwitter ion:** The ion in which two charges i.e. the +ve and -ve are present in the same in molecule is called zwitter ion.



ii. **Denaturation of protein:** Soluble forms of proteins are coagulated into insoluble form by the action of heat, acid and alkali is called denaturation of protein.

27. **2072 Set D Q.No. 17 What is saponification? Give an example of it.** [1+1]

The hydrolysis of an ester i.e. fat in the presence of strong base i.e. conc. NaOH to give sod. salt of carboxylic acid and alcohol is called saponification.



28. **2072 Set E Q.No. 16 Define sugar and non-sugar with an example of each.** [2]

Please refer to 2076 Set B Q.No. 17

29. **2072 Set E Q.No. 17 What are essential and non-essential amino acids? Give examples in each case.** [1+1]

Essential amino acid: Those amino acids which cannot be produced in sufficient quantity by human body. Example: valine, phenylalanine

Non-essential amino acid: Those amino acids which can be synthesized from other compound by the human body. Example: glycine, calamine

30. **2071 Supp. Q.No. 16 Distinguish between monosaccharides and diasaccharides with an example of each.** [1+1]

Distinction between monosaccharides and disaccharides are:

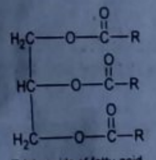
Monosaccharides	Disaccharides
1. The simplest carbohydrate which cannot be hydrolysed into any smaller simpler molecules is called monosaccharide.	1. The carbohydrate which on hydrolysis produces two molecules of monosaccharide of same or different types is called disacchharide.
2. Example - Glucose ($C_6H_{12}O_6$)	2. Example - Sucrose ($C_{12}H_{22}O_{11}$)

31. **2071 Set C Q.No. 16 Write an example of each of the following** [2]

i. reducing sugar **ii. simple lipid**
iii. non-sugar **iv. disaccharide**

i. **Reducing sugar:** Glucose (aldehydic functional group acts as reducing agent)

i. **Simple lipid:**



Triglyceride of fatty acid

iii. **Non-sugar:** Starch

iv. **Disaccharide:** Sucrose

32. 2071 Set C Q.No. 17 **Name a simple lipid. What happens when simple lipid gets hydrolysed?** [2]

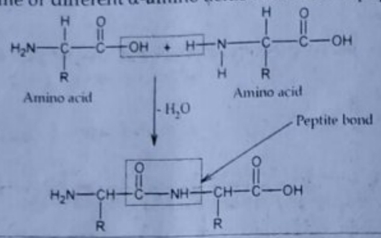
Please refer to 2076 Set C Q.No. 16

33. 2071 Set D Q.No. 16 **Distinguish between sugar and non-sugar with an example of each.** [2]

Please refer to 2076 Set B Q.No. 17

34. 2071 Set D Q.No. 17 2058 Q.No. 10 2057 Q.No. 9 2063 Q.No. 11 **What is meant by peptide bond? Write an example of dipeptide.** [2]

The linkage or bond which is formed by the condensation of two or more amino acid through their amino and carboxylic group involving elimination of water molecules is called peptide bond. During condensation a bond of the type -CONH– is formed between the two amino acids. The peptide formed due to the condensation of two molecules of the same or different α-amino acids are called dipeptide.

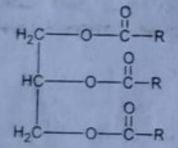


35. 2070 Supp. Q.No. 16 **Write molecular formula of each of the followings.** [2]

i. **Simple lipid**
ii. **Dipeptide**

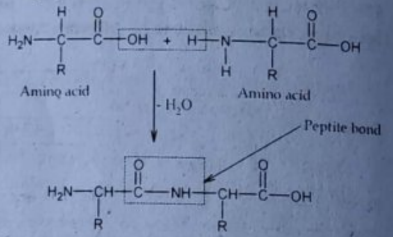
Molecular formula of

i. **Simple lipid:**



Triglyceride of fatty acid

ii. **Dipeptide:**



A peptide containing two amino acids called dipeptide.

36. 2070 Supp. Q.No. 18 **Name the products obtained by the hydrolysis of cane sugar. What is meant by invert sugar?** [2]

The product which is obtained by the hydrolysis of cane sugar is glucose and fructose.

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

Invert Sugar: A mixture of equal parts of glucose and fructose resulting from inversion of sucrose. It is found naturally in fruits and honey and produced artificially for use in food industry.

37. 2070 Set C Q.No. 16 **Define essential and non-essential amino-acid with an example of each.** [2]

Please refer to 2072 Set E Q.No. 17

38. 2070 Set C Q.No. 17 **What are disaccharides? What happens when they get hydrolysed?** [2]

Disaccharides: Carbohydrates which on hydrolysis produce two molecules of monosaccharides of same or different types. Examples: sucrose, maltose, lactose etc.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

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

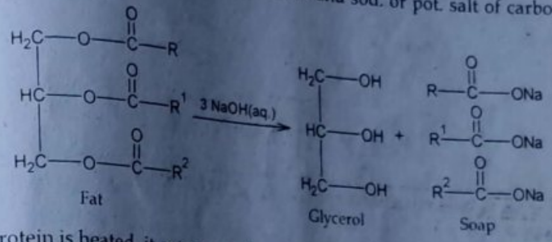
39. 2070 Set D Q.No. 17 **What is a peptide linkage? Give an example of dipeptide.** [2]

Please refer to 2071 Set D Q.No. 17

40. 2069 Supp. Set B Q.No. 18 **What happens when;** [2]

i. **fats get hydrolysed**
ii. **Protein is heated**

i. Fat is hydrolyzed in alkaline medium, alcohol and sod. or pot. salt of carboxylic acid is obtained.



ii. When protein is heated, it gets precipitated known as denatured protein.

41. 2069 Supp. Set B Q.No. 19 **What are disachharides? Write an example of non-sugar.** [2]

Disaccharides: Carbohydrates which on hydrolysis produce two molecules of monosaccharides of same or different types. Examples: sucrose, maltose, lactose etc.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

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

Non-sugar: The carbohydrates which are not sweet in taste and are insoluble in water are called non-sugar. They are generally amorphous. Examples- starch, cellulose etc.

42. 2069 (Set A) Q.No. 16 **What happens when fat gets hydrolysed?** [2]

Please refer to 2069 Supp. Set B Q.No. 18

43. 2069 Set A Q.No. 17 **What is denaturation of protein? Give an example:** [2]

When a protein is denatured, it changes its physical as well as biological change without changing the chemical composition of protein. Example: solidification of white part of egg upon heating.

44. 2069 (Set B) Q.No. 18 **What are lipids? Give one example of it.** [2]

Lipids: Waxy or oily substance which are present in all living organism as a main constituent of all cell membrane are called lipids. Lipids are the ester of long chain fatty acids and alcohols. Example of lipid is wax

45. 2069 (Set B) Q.No. 19 **Mention one example of each of sugar and non-sugar.** [2]

Please refer to 2076 Set B Q.No. 17

46. 2068 Q.No. 8 **What is meant by simple protein? Give an example of it.** [2]

The protein which gives only one mixture of α-amino acids on hydrolysis is called simple protein. Example: albumin in white of egg, oxyzenin in rice, keratin in hair, nails and horns and glutenin in wheat.

47. 2068 Q.No. 12 **How would you obtain glucose from cane sugar?** [2]

By hydrolyzing cane sugar with an enzyme i.e. invertase, glucose is obtained.

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

48. 2067 Q.No. 10 **Define following terms with correct example of each.** [2]

(i) **Sugar** (ii) **Non-sugar**

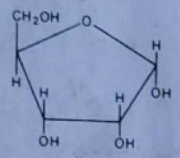
Please refer to 2076 Set B Q.No. 17

49. 2067 Q.No. 11 **What are the constituent of nucleic acid?** [2]

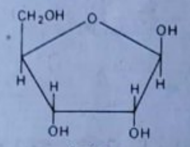
Nucleic acids are composed of the following three components:

1. Pentose sugar (ribose or deoxyribose)
2. Nitrogenous base (purine or pyridine)
3. Phosphate group

Ribose sugar

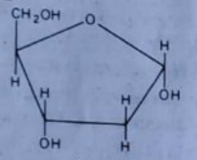


α-ribose

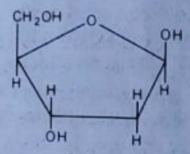


β-ribose

Deoxyribose sugar

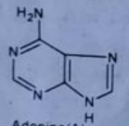


α-deoxyribose

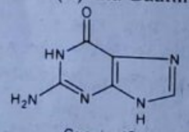


β-deoxyribose

Purine: The base derived from purine are Adenine (A) and Guanine (G)

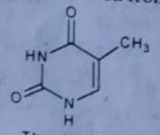


Adenine(A)

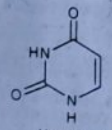


Guanine(G)

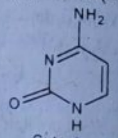
Pyridine: The base derived from pyridine are Thymine (T), Uracil(U) and Cytocine (C)



Thymine (T)



Uracil(U)



Cytocine (C)

50. 2066 Q. No. 3 **How would you obtain ethanol from Cane sugar? Write reaction only.** [2]

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

$$\underset{\text{Glulose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

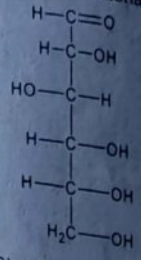
51. 2066 Q. No. 11 **What is different between essential and non-essential amino acids?** [2]

Following are the difference

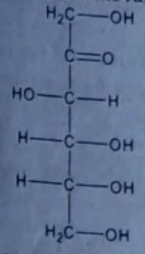
Essential amino acid	Non-essential amino acid
Those amino acids which cannot be produced in sufficient quantity by human body.	Those amino acids which can be synthesized from other compound by the human body.
Example: valine, phenylalanine	Example: glycine, calamine

52. 2066 Q. No. 12 **How do glucose and fructose differ in their functional group?** [2]

Glucose has aldehydic functional group but fructose has ketonic functional group.



Glucose (aldohexose)



Fructose (ketohexose)

53. 2065 Q.No. 11 **Name any four nitrogen bases present in nucleic acid.** [2]

Four nitrogen bases are (i) Adenine (ii) Guanine (iii) Thymine (iv)Cytosine

54. 2065 Q.No. 12 **What are the essential conditions of denaturation of Protein?** [2]

At normal pH and temperature, each protein takes a shape that is energetically most stable. This shape is specific to a given amino acid and is called its native conformation. The process which changes the native conformation of a protein is called denaturation. So, the process that brings about changes in physical as well as biological properties of the proteins without effecting its chemical composition is called denaturation of protein. Proteins are very sensitive to the action of heat, mineral acids, alkalies, change in P^{H} and exposure of uv and x-rays. Some important features of denaturation are:

i. Chemically, denaturation does not change the primary structure but changes the secondary and tertiary structure of proteins.
ii. Denaturation of proteins can be caused by changes in pH, temperature or by adding other denaturating agent.
iii. Denatured protein loses its biological activity.
iv. During denaturation, the protein molecules uncoil from an ordered and specific conformation into a more random conformation leading to precipitation.
v. Denaturation may or may be reversible.

55. 2064 Q.No. 9(i) **Define lipid.** [1]

Lipid: Waxy or oily substances which are present in all living organism as a main constituent of all cell membrane are called lipids. Lipids are the ester of long chain fatty acids and alcohols.

56. 2064 Q.No. 9(ii) **Name the pyrimidine bases found in RNA.** [2]

Uracil (U), Thymine (T) and Cytosine (C) are three pyramidine bases which are present in both DNA and RNA.

57. 2064 Q.No. 10(i) **What happens when a disaccharide is hydrolysed?** [1]

When a disaccharide is hydrolysed then glucose and fructose are produced.

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

58. 2064 Q.No. 10(ii) **What happens when a protein is denatured?** [1]

When a protein is denatured, its physical and biological properties are changed and the protein precipitates from the solution.

59. 2063 Q.No. 12 2062 Q.No. 12 **Point out any two differences between RNA and DNA molecules.** [2]

Difference between DNA and RNA are

DNA	RNA
It is deoxyribonucleic acid	It is ribonucleic acid
It is mainly found in chromosome.	It is mainly found in cytoplasm.
It consists nucleotides and deoxyribose sugar.	It consists nucleotides and ribose sugar.
The nitrogenous base are adenine,guanine,cytosine and thymine	The nitrogenous bases are adenine, guanine, cytosine and uracil.
It is found in double strand helix.	It is found in single strand.
It is genetic material.	It is not genetic material.

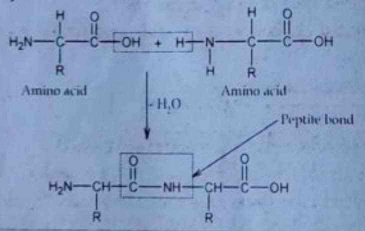
60. 2062 Q.No. 11 **Define protein. What is meant by denaturation of protein?** [2]

The complex nitrogenous organic compounds which are essential for the growth and maintenance of life are called protein. They are macromolecules in which large number of α -amino acid molecules are linked together by peptide bond (-CONH-). Proteins are polymer of α-amino acids.

At normal P^H and temperature, each protein takes a shape that is energetically most stable. This shape is specific to a given amino acid and is called its native conformation. The process which changes the native conformation of a protein is called denaturation. So, the process that brings about changes in physical as well as biological properties of the proteins without effecting its chemical composition is called denaturation of protein.

61. 2061 Q.No. 8 **Explain how amino acids are combined to form a protein molecule?** [2]

Proteins are formed by the combination of a number of α-amino acids with the peptide linkage. The $-NH_2$ group of one α-amino acid condences with the carbonyl group -COOH of another molecule of same or different amino acid with the liberation of H_2O molecule is called peptide bond.



62. 2061 Q.No. 9 **Distinguish both chemically and physically between a fat and a vegetable oil.** [2]

Fat and vegetable oil both are triglycerides of long chain of fatty acids. The difference between fat and vegetable oil are as follows:

i. **Physically**: Fat is solid at room temperature where as vegetabe oil is liquid at room temperature.

ii. **Chemically**: Fat contains large proportion of saturated fatty acid whereas vegetabe oil contains large proportion of unsaturated fatty acids.

63. 2061 Q.No. 10 **What is the role of hydrogen bonding in the structure of DNA?** [2]

In the double helical structure of DNA purine base i.e. Adinine(A) is bonded with one pyridine base Thymine(T) of another strand by two hydrogen bond (A=T). Similarly purine base i.e. Guanine(G) is bonded with pyridine base i.e. Cytocine(C) of another strand by three hydrogen bonds (G≡C). The hydrogen bonds between the pairs of two strands provide the particular structure of DNA.

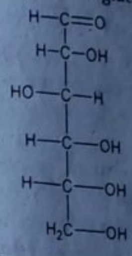
64. 2060 Q.No. 10 **Define Protein and Lipid.** [2]

Protein: The complex nitrogenous organic compounds which are essential for the growth and maintenance of life are called protein. They are macromolecules in which large number of α -amino acid molecules are linked together by peptide bond(-CONH-). Proteins are polymer of α-amino acids.

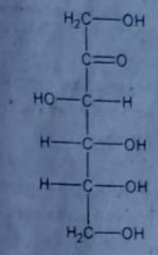
Lipids: Waxy or oily substance which are present in all living organism as a main constituent of all cell membrane are called lipids. Lipids are the ester of long chain fatty acids and alcohols.

65. 2060 Q.No. 12 **Write the open chain structure of glucose and fructose.** [2]

The open chain structure of glucose and fructose are:



Glucose (aldohexose)



Fructose (ketohexose)

66. 2059 Q.No. 10 **What happens when a protein is denatured?** [2]

Please refer to 2069 Set A Q.No. 17

67. 2058 Q.No. 9 **Write the names of two pyrimidine bases present in RNA and DNA molecules.** [2]

Please refer to 2064 Q.No. 9(ii)

68. 2057 Q.No. 10 **What happens when an oil is hydrogenated?** [2]

When oil is hydrogenated, it changes into solid mass which is called vegetable ghee or vanaspati ghee.

$$\text{Oil} + H_2 \xrightarrow[\text{Ni}]{450°C,200\text{ atm}} \text{Vegetable ghee}$$

69. 2055 Q.No. 19 **What are enzymes and what are their role in the body?** [2]

The biological catalysts which are produced by the living cells and catalyse many biochemical reactions in living system are called Enzymes. It prevents disease and cures the disease.

70. 2055 Q.No. 20 **What are two differences between DNA and RNA?** [2]

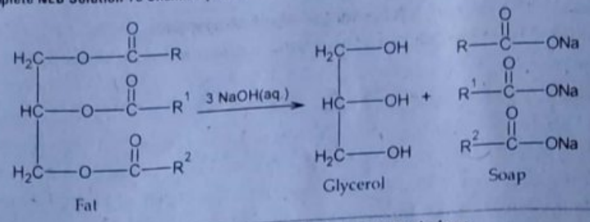
Please refer to 2063 Q.No. 12

71. 2054 Q.No. 18 **What are carbohydrates? Give two examples.** [2]

Carbohydrates are defined as the polyhydroxy aldehydes, polyhydroxy ketones or large polymeric molecules which on hydrolysis produce polyhydroxy aldehydes or ketones. Examples: glucose and fructose.

72. 2053 Q.No. 8 **What is soap? How is soap obtained from fat?** [2]

Sodium or potassium salt of long chain fatty acids are called soap. Soap is obtained from fat of animal or vegetable by the process of saponification. Fat is heated with conc.NaOH to form soap.



73. 2053 Q.No. 9 **Give the main functions of carbohydrates for living beings.** [2]

Function of carbohydrate:

1. It supports plants structure constituent of cell membrane(cellulose)
2. It stores chemical energy in plants.
3. It acts as the major source of energy for animals and human beings.
4. It acts as energy storage in the form of glycogen in human body.

74. 2052 Q.No. 13 **Classify carbohydrates and give an example for each.** [2]

Classification of carbohydrates: On the basis of hydrolysis there are three types of carbohydrates:

a. **Monosaccharides:** The simplest carbohydrate which cannot be hydrolysed further into any smaller simpler molecules is called monosaccharides. The general formula is $(CH_2O)_n$ where, n = 3 to 7. Example: glucose $(C_6H_{12}O_6)$, fructose $(C_6H_{12}O_6)$, glactose $(C_6H_{12}O_6)$, ribose $(C_5H_{10}O_5)$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O \xrightarrow{H^+} \text{No reaction}$$

b. **Oligosaccharides:** The carbohydrates which on hydrolysis give two or more i.e. 2 to 9 units of monosaccharides is called oligosaccharides. They are further classified as di, tri and tetraccharides

Disaccharides: Carbohydrates which on hydrolysis produce two molecules of monosaccharides of same or different types. Examples: sucrose, maltose, lactose etc.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

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

Trisaccharide: Carbohydrates which on hydrolysis produce three molecules of monosaccharide of same or different types. Example: raffinose

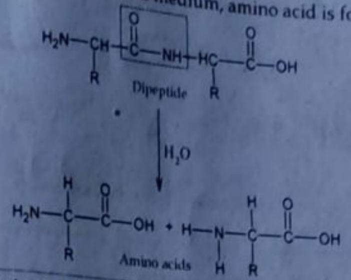
$$\underset{\text{Raffinose}}{C_{18}H_{32}O_{16}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glactose}}{C_6H_{12}O_6}$$

c. **Polysaccharides:** The carbohydrate which are polymeric molecules and which on hydrolysis give large number of monosaccharides molecule. The general formula $(C_6H_{10}O_5)_n$ where n = 100 - 3000. Examples: starch, glycogen, cellulose etc.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

75. 2052 Q.No. 14 **Give a chemical reaction for hydrolysis of dipeptide.** [2]

When a dipeptide is hydrolyzed in acid medium, amino acid is formed.



76. 2052 Q.No. 15 **Name four types of base residues present in DNA.** [2]

The four bases present in DNA are Adenine, Guanine, Cytocine and Thymine.

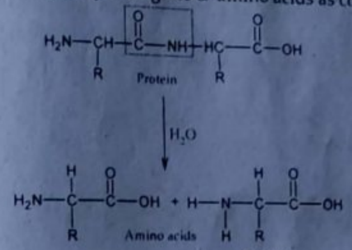
77. 2052 Q.No. 16 **What is saponification?** [2]

Please refer to 2072 Set D Q.No. 17

78. 2052 Q.No. 17 **What happens when protein is (a) Heated (b) Hydrolysed?** [2]

a. When protein is heated, it gets precipitated known as denatured protein.

b. When protein on hydrolysis, it gives α-amino acids as constituents.



❑❑❑

Unit

17

Chemistry in Service to Mankind

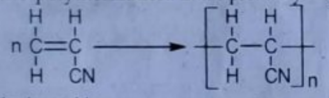
VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2076 Set B Q.No. 18 **Mention an important function of each of the following:** [0.5×4=2]
   i. DDT
   ii. Nitrogen fertilizer
   iii. Broad spectrum antibiotics
   iv. Tranquilizers

i. **DDT:** It is used to kill or control the insects.
ii. **Nitrogen fertilizer:** It is used to supply nitrogen nutrient to the plant.
iii. **Broad spectrum antibiotics:** It is used as antibiotics.
iv. **Tranquilizers:** It is used as antidepressant.

2. 2076 Set B Q.No. 19 **What is meant by homo-polymerization? Write an example of such polymer.** [1+1]

The polymerization of a single type of monomer to form a homopolymer is called homo-polymerization. Example: Polyvinyl cyanide


Vinyl cyanide
Polyvinyl cyanide (Orlon)

3. 2076 Set C Q.No. 18 **Mention an important function of each of the following:** [0.5×4=2]
   i. DDT
   ii. Nitrogen fertilizer
   iii. Tranquilizers
   iv. Broad spectrum antibiotics

Please refer to 2076 Set B Q.No.18

4. 2076 Set C Q.No. 19 **Name the monomers of bakelite and state the polymerization process of it.** [1+1]

The monomers of Bakelite are phenol and formaldehyde. Bakelite is condensation polymer and condensation polymerization process takes place.

Statement: The polymerization reaction in which the polymer is formed by the reaction between two different monomer units with the loss of some small molecules is called condensation polymerization reaction.

5. 2075 GIE Q.No. 16 **Name the monomers which on polymerization yields polyamide. What type of polymerization is this?** [1+1]

The monomers are hexamethylenediamine and adipic acid which undergo condensation polymerization yield polyamide i.e. Nylon-6,6. This is condensation polymerization.

$n\,NH_2(CH_2)_6NH_2$ (Hexamethylenediamine (Monomer)) $+$ $n\,HOOC(CH_2)_4COOH$ (Adipic acid (Monomer))

$$\downarrow \text{Condensation polymerization}$$

$$-NH[CO(CH_2)_4CONH(CH_2)_6NH]CO- + 2nH_2O$$

Nylon-6,6
(Polyamide)

6. 2075 GIE Q.No. 17 **Mention an example of each of:** [0.5 × 4=2]
   i. Antipyretic
   ii. Pesticides
   iii. Analgesics
   iv. Phosphatic fertilizer

Examples of

i. **Antipyretic drug:** Paracetamol
ii. **Pesticides:** BHC
iii. **Analgesics:** Aspirin
iv. **Phosphatic fertilizer:** Super phosphate of lime

7. 2075 Set A Q.No. 16 **Name the monomers which on polymerization yields bakalite. What type of polymerization is this?** [1+1]

The monomers of Bakelite are formaldehyde and phenol. It is condensation polymerization.

8. 2075 Set A Q.No. 17 **Give an important use of each of the followings:** [0.5×4=2]
   i. Weedicides
   ii. Antibiotics
   iii. Analgesics
   iv. Nitrogen fertilizer

i. **Weedicides:** It is used to kill or control the unwanted growth of weeds. Example: 2,4-D
ii. **Antibiotics:** It is used to destroy or control the growth or metabolism of some other micro-organism. Example: Penicillin
iii. **Analgesics:** It is used as pain killer. Example: Aspirin
iv. **Nitrogen fertilizer:** It is used to supply nitrogen nutrient to plant.Example: Urea

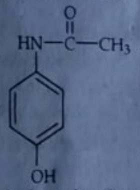
9. 2075 Set B Q.No. 18 **Distinguish between homopolymer and co-polymer with an example of each.** [1+1]

Homopolymer: The polymer which is formed from only one kind of monomer unit is called homopolymer. Example: PVC

Co-polymer: The polymer which is formed from more than one kind of monomer unit is called co-polymer. Example: Bakelite, Nylon-6, 6

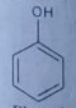
10. 2075 Set B Q.No. 19 **What are antipyretic drugs? Give the name and structure of an antipyretic drug.** [1+1]

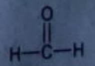
Antipyretic drug: The drug which are used to reduce body temperature in high fever is called antipyretic drug. Example: Paracetamol


N-(4-hydroxyphenyl)acetamide
Paracetamol or p-acetamidophenol

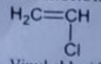
11. 2074 Supp. Q.No. 18 **Name with the structures the monomers of** [1+1]
   i. Bakelite
   ii. PVC

i. The monomers of Bakelite are Phenol and formaldehyde.


Phenol


Formaldehyde

ii. The monomer of PVC is polyvinyl chloride.



$H_2C{=}CH-Cl$

Vinyl chloride

12. 2074 Supp. Q.No. 19 **Mention an important use of each of the following.** [0.5 × 4 = 2]
    - i. **Antipyretic drug**
    - ii. **BHC**
    - iii. **Herbicides**
    - iv. **NPK fertilizers**

i. **Antipyretic drug:** It is used to lower the body temperature.

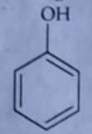
ii. **BHC:** It is used for insecticides.

iii. **Herbicides:** It is used to kill or control the growth of herbs.

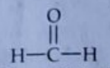
iv. **NPK fertilizers:** It is used in soil to improve the growth of plants.

13. 2074 Set A Q.No. 18 **Write an example of each of condensation polymer and an addition polymer. What are their monomers?** [1+1]

Condensation polymer is Bakelite. The monomers of Bakelite are phenol and formaldehyde. The structures are given below:



Phenol



Formaldehyde

Addition polymer is Polyethene. The monomer of polyethene is ethene. The structure is given below:

$H_2C{=}CH_2$

Ethene

14. 2074 Set A Q.No. 19 **Mention an important use of each of the following [0.5 × 4]**
    - i. **Analgesic drug**
    - ii. **Herbicides**
    - iii. **BHC**
    - iv. **Nitrogen fertilizer**

Following are the use of;

i. **Analgesic drug:** It is used to relief pain.

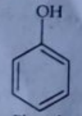
ii. **Herbicides:** It is used to kill or control the herbs or weeds.

iii. **BHC:** It is used to control or kill the insects.

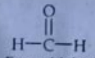
iv. **Nitrogen fertilizer:** It is used to supply the Nitrogen element to soil.

15. 2074 Set B Q.No. 18 **Name a condensation polymer and an addition polymer. What are the structures of their monomers?** [1+1]

Condensation polymer is Bakelite. The monomers of Bakelite are phenol and formaldehyde. The structures are given below:



Phenol



Formaldehyde

Addition polymer is Polyethene. The monomer of polyethene is ethene. The structure is given below:

$H_2C{=}CH_2$

Ethene

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16. 2074 Set B Q.No. 19 **Mention an important use of each of the following** [0.5 × 4]
    - i. **Antipyretics drug**
    - ii. **BHC**
    - iii. **Herbicides**
    - iv. **NPK fertilizers**

Important use of:

i. **Antipyretics drug:** It is used to reduce the body temperature to normal in high fever.

ii. **BHC:** It is used to control or kill the insects.

iii. **Herbicides:** It is used to kill and control herbs or weeds.

iv. **NPK fertilizers:** It is used to supply the Nitrogen, Phosphorous and Potassium elements to soil.

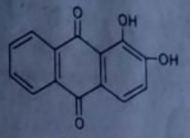
17. 2073 Supp Q.No. 16 **Distinguish between addition polymer and condensation polymer with an example of each.** [1+1]

Following are the difference between addition polymer and condensation polymer:

Addition polymer	Condensation polymer
It is formed from the monomer having carbon carbon double or triple bond.	It is formed by the condensation of two types of monomers with the elimination of molecules such as HCl, H_2O etc.
Example: Polyethene, PVC, Teflon etc.	Example: Bakelite, Nylon-6,6 etc.

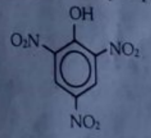
18. 2073 Supp Q.No. 17 **What is meant by synthetic dye? Write a structure of it.** [1+1]

Natural dyes: The dyes that are obtained from plants or animals are called natural dyes. It is mostly extracted from the coloured flowers. Example: alizarin (red dyes from madder root)



Alizarin

Synthetic dyes: The dyes that are prepared or synthesized by man in the laboratory are called synthetic dyes or man made dyes. Example- picric acid



Picric acid (bright yellow colour)

19. 2073 Supp Q.No. 18 **Name the nitrogen bases present in nucleic acid.** [2]

Nitrogen bases present in nucleic acid are adenine, guanine, cytosine, thymine and uracil.

20. 2073 Set C Q.No. 16 **Distinguish between synthetic polymer and natural polymer with an example of each.** [1+1]

Synthetic polymer: The polymers which are obtained artificially in the laboratory are called synthetic polymer. Example: Polyethene.

Natural polymer: The polymers which are obtained from living sources from the body parts of plants or animals are called natural polymers. Example: Protein.

21. 2073 Set C Q.No. 17 **What is meant by antipyretic drug? Write a structure of it.** [1+1]

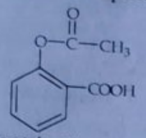
Please refer to 2075 Set B Q.No. 19

22. 2073 Set D Q.No. 16 **Distinguish between homopolymer and co-polymer with an example of each.** [1+1]

Please refer to 2075 Set B Q.No. 18

23. 2073 Set D Q.No. 17 **Write down the structure of** [1+1]
   - i. aspirin
   - ii. Paracetamole and mention their one use of each.

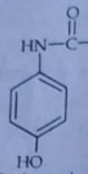
i. **Structure of aspirin:**



2-(acetyloxy)benzoic acid or Aspirin

Use: Aspirin is used to reduce fever as well as relief pain.

ii. **Structure of paracetamol:**



N-(4-hydroxyphenyl)acetamide or Paracetamol

Use: Paracetamol is used reduce body temperature in high fever.

24. 2072 Supp. Q.No. 18 **Give suitable example of each of the following:** [2]
   - i. Homopolymer
   - ii. Co-polymer
   - iii. Pesticides
   - iv. Synthetic dye

Example of:

i. **Homopolymer:** Polyethene is the polymer of ethene.

ii. **Co-polymer:** Bakelite is the polymer of phenol and formaldehyde.

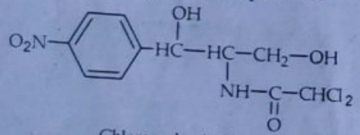
iii. **Pesticides:** DDT(Dichlorodiphenyl trichloroethane)

iv. **Synthetic dye:** p-hydroxyazobenzene(orange yellow dye)

25. 2072 Supp. Q.No. 19 **Give structural formula of each of the following:** [2]
   - i. antibiotic drug
   - ii. antipyretic drug

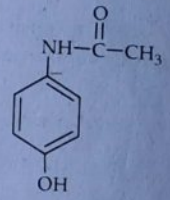
Structural formula of:

i. **Antibiotic drug: Chloramphenicol**



Chloramphenicol

ii. **Antipyretic drug: Paracetamol**

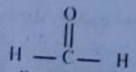


p-acetamidophenol(Paracetamol)

26. 2072 Set C Q.No. 18 **Write down the molecular formula of monomers of** [1+1]
   - i. Bakelite
   - ii. Nylon-6,6

The molecular formula of monomer of

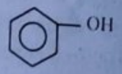
i. Bakelite =



$H-\overset{O}{\overset{\|}{C}}-H$

Formaldehyde

and



Phenol

ii. Nylon - 6,6 = $NH_2-(CH_2)_6-NH_2$ (Hexamethylene diamine) and $HOOC-(CH_2)_4-COOH$ (Adipic acid)

27. 2072 Set C Q.No. 19 **Mention an important use of each of the followings:** [0.5×4=2]
   - i. Antiseptics
   - ii. Antibiotics
   - iii. Germicides
   - iv. Herbicides

Important use of

i. **Antiseptics:** It is used to kill or prevent the growth of micro-organism in injured tissues without harming the living cells. Example: Dettol.

ii. **Antibiotics:** It is used to destroy or control the growth or metabolism of some other micro-organism. Example: Penicillin.

iii. **Germicides:** It is used to kill or control the growth of germs i.e. bacteria and virus.

iv. **Herbicides:** It is used to kill unwanted herbs. Example: 2, 4-D

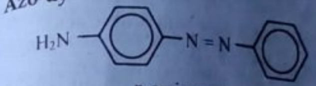
28. 2072 Set D Q.No. 18 **Write down the molecular formula of monomers of:** [1+1]
   - i. Bakelite
   - ii. Nylon – 6,6

Please refer to 2072 Set C Q.No. 18

29. 2072 Set D Q.No. 19 **Write down the structural formula of each of the following:** [0.5×4=2]
   - i. azo-dye
   - ii. analgesic drug
   - iii. pesticides
   - iv. nitrogen fertilizer

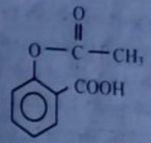
The structure formula of the following are:

i. Azo-dye



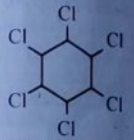
p-aminoazobenzene

ii. **Analgesic drug**



Acetyl Salicylic acid (Aspirin)

iii. Pesticides



BHC (Benzenehexachloride)

iv. **Nitrogen fertilizer**

$NH_2-\overset{O}{\overset{\|}{C}}-NH_2$

Urea

30. 2072 Set E Q.No. 18 **What type of polymer is bakelite? Mention its monomers.** [1+1]

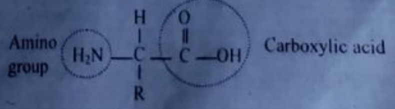
Bakelite is the condensation polymer. It is formed by the condensation of phenol and formaldehyde with the elimination of water. The monomers of Bakelite are phenol and formaldehyde.

31. 2072 Set E Q.No. 19 **Name any two fertilizers which supply potassium and nitrogen to the plants.** [1+1]

The fertilizer which supply potassium to the plant is saltpeter (KNO_3) and fertilizer which supply nitrogen to the plant is urea ($NH_2-CO-NH_2$).

32. 2071 Supp. Q.No. 17 **Why are amino acids amphoteric?** [2]

Amino acids contain both acidic carboxylic acid functional group and basic amino functional group. Due to the presence of both acidic and basic functional group in the same molecule, amino acid is amphoteric in nature.



Amino acid

33. **2071 Supp. Q.No. 18** **Distinguish between addition and condensation polymers with an example of each.** **[1+1]**

Following are the difference between addition and condensation polymers:

Condensation Polymer	Addition Polymer
1. The polymer which is formed by the condensation of two types of monomer with the elimination of H_2O, HCl, NH_3 etc. as by product is known as condensation polymer.	1. The polymer which is formed by the addition of two monomers is called addition polymer.
2. Example: Bakelite is formed by the condensation of phenol and formaldehyde.	2. Example: PVC is formed by the addition of vinyl chloride.

34. **2071 Supp. Q.No. 19** **What is meant by analgesics? Write an example of it.** **[1+1]**

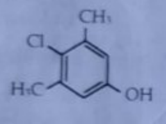
Analgesics: The drug which is used to relieve pain is called analgesics drug. It is also called pain killer. Example: Aspirin

35. **2071 Set C Q.No. 18** **What is meant by Co-polymer? Name a Co-polymer and monomers associated with it.** **[2]**

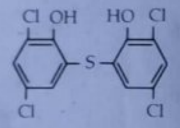
Co-polymer: The polymer which is formed by more than one kind of monomers units is called co-polymers. Examples: Polystyrene, Nylon-6,6 etc. The monomer of polystyrene is styrene and monomer of Nylon-6,6 is hexamethylene diamine and adipic acid.

36. **2071 Set C Q.No. 19** **Define antiseptics giving a suitable example.** **[2]**

The compound which kill or prevent the growth of micro-organism without being toxic and irritating to the living beings are called antiseptics. Examples: Dettol C (chloro xylenol), Bithional etc.



Chloroxylenol



Bithional

37. **2071 Set D Q.No. 18** **Write the monomers of:** **[2]**

a. Nylon – 66 **b. Bakelite**

a. **Nylon-6,6:** Monomers are hexamethylene diamine and adipic acid.
b. **Bakelite:** Mononers are formaldehyde and phenol.

38. **2071 Set D Q.No. 19** **Mention suitable use of each of:** **[2]**

a. antipyretics **b. pesticides**

a. **Antipyretics:** They are the drugs which are used to reduce fever. Example: aspirin, paracetamol etc.

b. **Pesticides:** Insecticides, fungicides, herbicides or weedicides which are used for the control of insects, weeds, rodants etc. are examples of pesticides.

39. **2070 Supp. Q.No. 17** **Distinguish between addition polymer and condensation polymers with an example of each.** **[2]**

Distinction between addition polymer and condensation polymer:

Addition polymer	Condensation polymer
It is formed from the monomer having carbon carbon double or triple covalent bond.	It is formed by the condensation of two types of monomer with the elimination of molecules such as H_2O,HCl etc.
Example: polyethene, PVC	Example: Nylon-6,6 , terylene

2070 Supp. Q.No. 19 **Mention a suitable example of each:** **[2]**

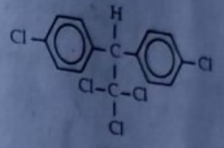
i. antibiotics **ii. phosphatic fertilizer**
iii. herbicides **iv. Insecticides**

Example:

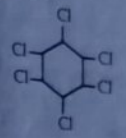
i. Antibiotics: Penicillin
ii. **Phosphatic fertilizer:** Super phosphate of lime $Ca(H_2PO_4)_2.2CaSO_4.2H_2O$
iii. Herbicides: 2,4-dichlorophenoxy acetic acid
iv. Insecticides: DDT

41. **2070 Set C Q.No. 18** **What are insecticides? Give an example.** **[2]**

Incecticides: The chemical used for killing insects are called insecticides. Examples: DDT, BHC



DDT



BHC

42. **2070 Set C Q.No. 19** **Name any one condensation polymer and addition polymer. What are their monomers?** **[2]**

Condensation polymers are formed by the condensation of two types of monomers with the elimination of molecules such as H_2O, HCl etc. example: Nylon-6,6. The monomer of Nylon-6,6 are hexamethylene diamine and adipic acid.

Addition polymers are formed from the monomer having carbon carbon double bond or triple bond. Example: polyethene. The monomer of polyethene is ethene.

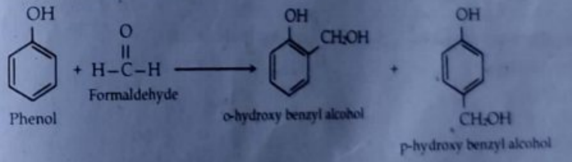
43. **2070 Set D Q.No. 18** **What are chemical fertilizers? Give two examples.** **[2]**

Chemical fertilizer: The fertilizers that are manufacture in factories to overcome the limitations of the organic fertilizers are called chemical fertilizers. Examles: Urea $H_2N-CO-NH_2$, Super phosphate $CaH_4(PO_4)_2$.

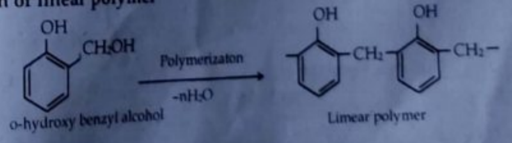
44. **2070 Set D Q.No. 19** **Write a method of preparation of each of the following polymers:** **[2]**

i. Bakelite **ii. PVC**

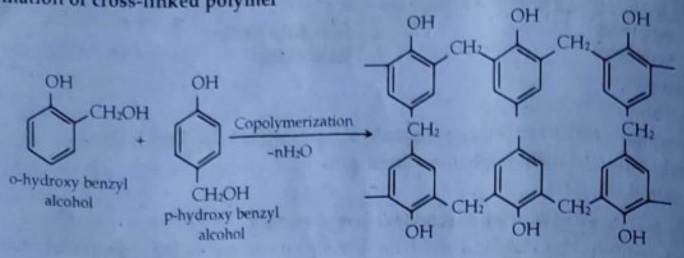
i. **Bakelite (phenol formaldehyde resins):** It is prepared by heating phenol and formaldehyde in basic medium.



Formation of linear polymer



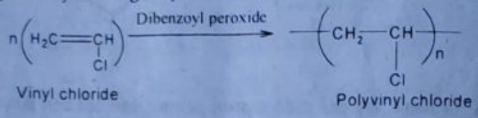
Formation of cross-linked polymer



Bakellite

Uses: It is used as glue, varnishes, lacquers, combs, electrical goods, gramophone records etc.

ii. **PVC:** It is prepared by heating vinyl chloride in an inert solvent dibenzoyl peroxide.



$$n\left(H_2C{=}\underset{Cl}{\underset{|}{CH}}\right)\xrightarrow{\text{Dibenzoyl peroxide}}-\!\!\left(CH_2-\underset{Cl}{\underset{|}{CH}}\right)_n\!\!-$$

Uses - It is used for making rain coats, hand bags, toys, housepipes, gramophone records, electrical insulations and floor covering.

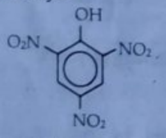
45. **2069 Supp. Set B Q.No. 16 Name of the monomers of baketile and what type of polymer is Bakelite.** [2]

Please refer to 2076 Set C Q.No. 19

46. **2069 Supp. Set B Q.No. 17 Write an examr le of each of the followings.** [2]

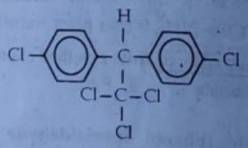
i. Synthetic dye
ii. Insecticides
iii. Phosphatic fertilizer
iv. Antipyretic drug

i. Synthetic dye:



Picric acid (bright yellow colour)

ii. Insecticide



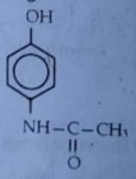
DDT

iii. **Phosphorous Fertilizer:**

Super phosphate

$CaH_4(PO_4)_2$

iv. **Antipyretic drug**



p-acetamidophenol

47. **2069 Set A Q.No. 18 Name the monomers of** [2]

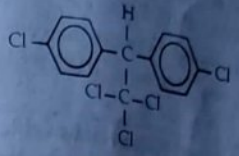
i. Bakelite
ii. Nylon-6,6

i. **Bakelite:** Mononers are formaldehyde and phenol.

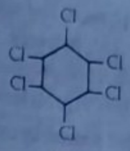
ii. **Nylon-6,6:** Monomers are hexamethylene diamine and adipic acid.

48. **2069 Set A Q.No. 19 Give the name of any two insecticides with their chemical formulae.** [2]

Incecticides: The chemical used for killing insects are called insecticides. Examples: DDT, BHC



DDT



BHC

49. **2069 (Set B) Q.No. 16 What are the starting materials for preparing the followings:** [2]

i. Polyvinyl chloride
ii. Bakelite

The starting material for preparation of polyvinyl chloride is vinyl chloride and the starting materials for the preparation of Bakelite are formaldehyde and phenol.

50. **2069 (Set B) Q.No. 17 Distinguish between antipyretics and analgesics with an example of each.** [2]

Antipyretics drug reduce fever whereas analgesics drug relief pain. Example: Aspirin

51. **2068 Q.No. 10 Give the names of one natural and one synthetic polymer. What are the monomers present in them?** [2]

The monomers present in natural and synthetic polymers are

Name	Polymer	Monomer
Natural	$-\!\left(CH_2-CH{=}\underset{CH_3}{\underset{\mid}{C}}-CH_2\right)_n\!-$ Rubber	$CH_2{=}CH-\underset{CH_3}{\underset{\mid}{C}}{=}CH_2$ Isoprene
Synthetic	$-\!\left(CH_2-CH_2-CH_2-CH_2\right)_n\!-$ Polyethene	$CH_2{=}CH_2$ Ethene

52. **2068 Q.No. 11 What are antibiotics? Give an example of broad spectrum antibiotic.** [2]

Antibiotics: Many micro-organisms produce certain chemicals which are capable of destroying or controlling the growth or metabolism of some other micro-organism. Such chemical compounds are known as antibiotic. Example of broad spectrum antibiotic is ampicillin.

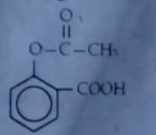
53. **2066 Q. No. 9 Mention one examples of each of the followings:** [2]

i. Mixed Fertilizer
ii. Analgesic Drug
iii. Antiseptic
iv. Azo-dye

i. **Mixed Fertilizer**

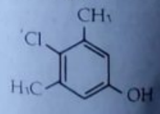
NPK fertilizer

ii. **Analgesic Drug**



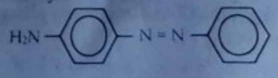
Acetyl salicylic acid (aspirin)

iii. **Antiseptic**



Chloroxylenol

iv. **Azodye**



p-minoazobeCH2OH'

54. 2066 Q. No. 10 **Classify polymers on the basis of monomer unit.** [2]

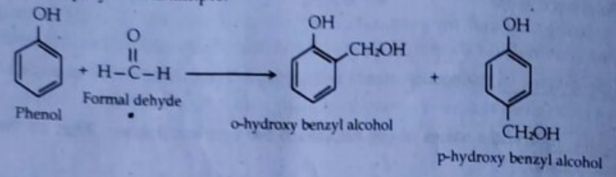
On the basis of monomer unit, there are two polymers

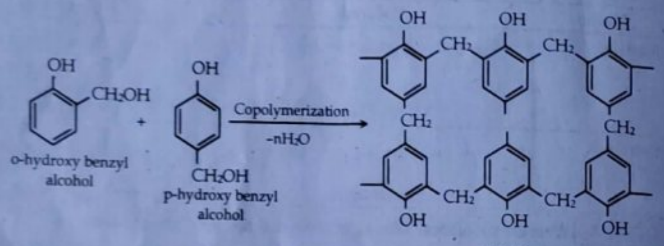
Homopolymers: The polymer which is formed from only one kind of monomers is called homopolymers. Examples: Polyethene, PVC, Teflon etc.

Co-polymers: The polymers which are formed by more than one kind of monomers units are called co-polymers. Examples: Styrene ($C_6H_5CH{=}CH_2$), Buna-S rubber ($CH_2{=}CH-CH{=}CH_2$), Nylon-6,6 etc.

55. 2065 Q.No. 9 **What is meant by condensation polymer? Write an example of it.** [2]

The polymer which is formed by the condensation or combination of two types of monomer with the elimination of H_2O, HCl, NH_3, etc. as by product is known as condensation polymer. Example:



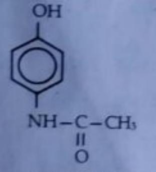


Bakellite

56. 2065 Q.No. 10 **Give an example of each of the following:** [2]

- i. **Antipyretic drug**
- ii. **Phosphorus fertilizer**
- iii. **Disaccharide**
- iv. **Insecticide**

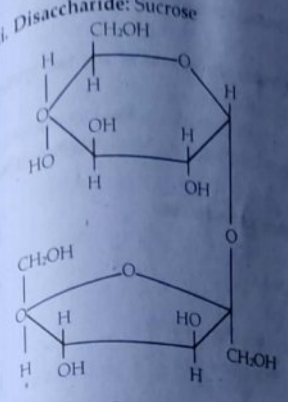
i. **Antipyretic drug**



p-acetamidophenol

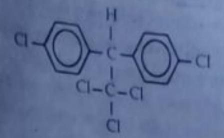
ii. **Phosphorous Fertilizer:** Super phosphate
$CaH_4(PO_4)_2$

iii. **Disaccharide:** Sucrose



Sucrose

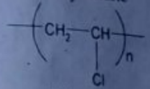
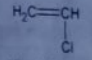
iv. **Insecticide**



DDT

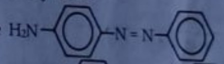
57. 2064 Q.No. 11 **Name any two synthetic polymers specifying the monomers of each.** [2]

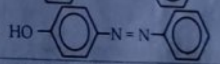
The monomers of two synthetic polymers are

Name of synthetic polymer	Monomer
$-(CH_2-CH_2-CH_2-CH_2)_n-$ Polyethene	$CH_2{=}CH_2$ Ethene
 Polyvinyl chloride	 Vinyl chloride

58. 2064 Q.No. 12 **Write any two examples of azo-dyes with their formulae.** [2]

The two examples of azodyes are:

P-aminoazobenzene 

P-hydroxyazobenzene 

59. 2063 Q.No. 9 **What are natural and synthetic dyes? Give one example of each.** [2]

Please refer to 2073 Supp Q No. 17

60. 2063 Q.No. 10 **Write an example of each of the following with their formula.** [2]
(i) A synthetic fertilizer (ii) An insecticide

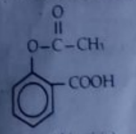
i. **A synthetic fertilizer:** Ammonium sulphate $(NH_4)_2SO_4$
ii. **An insecticide:** BHC i.e. Benzene hexachloride

61. 2062 Q.No. 9 **What are insecticides? Write any two example of insecticides.** [2]

Please refer to 2069 Set A Q No. 19

62. 2062 Q.No. 10 **What is an antipyretic drug? Write an example with its structure.** [2]

They are the drugs which are used to reduce fever. Example: aspirin



Acetyl salicylic acid (aspirin)

63. 2061 Q.No. 11 **What is insecticide? Write the name of any two insecticides.** [2]

➢ Please refer to 2069 Set A Q.No. 19

64. 2061 Q.No. 12 **What is meant by a synthetic fertilizer? Write the formula of any two synthetic fertilizers.** [2]

➢ The fertilizer which is prepared or synthesized on large scale in the laboratories or industries is known as synthetic fertilizers. Two examples are: Ammonium sulphate $(NH_4)_2SO_4$, Urea $H_2N-CO-NH_2$

65. 2060 Q.No. 9 **What are insecticides? Write any two examples of insecticides.** [2]

➢ Please refer to 2069 Set A Q.No. 19

66. 2060 Q.No. 11 **Specify the monomers of Bakelite and Nylon-6,6.** [2]

➢ The monomer of Bakelite is phenol and formaldehyde

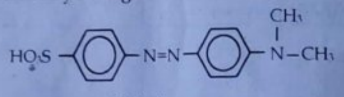
The monomers of Nylon are adipic acid and hexamethylenediamine

67. 2059 Q.No. 11 **Give an example each from analgesic and antipyretic drugs.** [2]

➢ **Analgesic:** Aspirin, **Antipyretic:** Paracetamol.

68. 2059 Q.No. 12 **What is an azo dye? Give one example with structure.** [2]

➢ **Azo dyes:** The dyes contain one or more azo groups (-N=N-) as the primary chromophore. Example: Methyl orange.



Methyl orange

69. 2058 Q.No. 11 **Give an example of azodye and write its structure.** [2]

➢ Please refer to 2059 Q.No. 12

70. 2058 Q.No. 12 **Define polymerization and write an example.** [2]

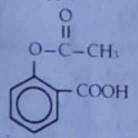
➢ The combination of many small molecules to form large molecules is called polymerization. Example:

$$n\ (H_2C{=}CH_2) \xrightarrow[\text{High pressure}]{\text{High temperature}} -\!\left[CH_2-CH_2\right]_n\!-$$

Ethene Polyethene

71. 2057 Q.No. 11 **Give the name and structure of an antipyretic drug.** [2]

➢ Aspirin is antipyretic drug. Structure of antipyretic is



Acetyl salicylic acid (aspirin)

72. 2057 Q.No. 12 **Name the monomers of Bakelite and Nylon.** [2]

➢ **Bakelite:** Mononers are formaldehyde and phenol.

Nylon-6,6: Monomers are hexamethylenediamine and adipic acid.

73. 2056 Q.No. 10 **Give two characteristics of a Dye.** [2]

➢ Two characteristics of dye are:

i. It possesses color to the fabrics, food etc. for their beutification and distinction.

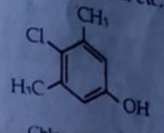
ii. It contains some functional group which is suitable for coloration.

74. 2055 Q.No. 18 **Name any two synthetic polymers.** [2]

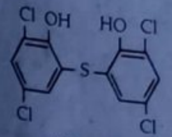
➢ **Synthetic polymers:** The polymers which are prepared in the laboratory are called synthetic polymers. Examples- Polyethene, PVC etc.

75. 2054 Q.No. 19 **What is the difference between an antiseptic and an antipyretic drug?** [2]

➢ **Antiseptic drug:** The compound which kill or prevent the growth of micro-organism without being toxic and irritating to the living beings are called antiseptics. Examples: Dettol-C (chloroxylenol), Bithional etc.

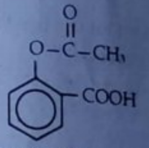


Chloroxylenol

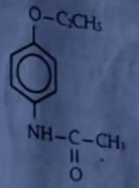


Bithional

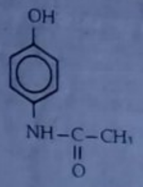
Antipyretic drug: They are the drugs which are used to reduce fever. Example: aspirin, phenacetin, paracetamol etc.



Acetyl salicylic acid (aspirin)



Phenacetin



P-acetamidophenol

76. 2053 Q.No. 10 **What is an azo dye?** [2]

➢ Please refer to 2059 Q.No. 12

❑❑❑

INORGANIC CHEMISTRY (SECTION C)

Unit 18

Heavy Metals

18.1 Copper

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2074 Supp. Q.No. 20 2074 Set A Q.No. 20 Give the balanced chemical reaction for the preparation of black oxide from blue vitriol. How is black oxide converted into red oxide?** **[1+1]**

Preparation of black oxide from blue vitriol: When blue vitriol is treated with NaOH, cupric hydroxide is obtained which on heating gives black oxide of copper.

$$\underset{\text{Blue vitriol}}{CuSO_4} + 2\,NaOH \longrightarrow \underset{\text{Cupric hydroxide}}{Cu(OH)_2} + Na_2SO_4$$

$$Cu(OH)_2 \xrightarrow[\Delta]{} \underset{\substack{\text{Cupric oxide}\\ \text{Black oxide}}}{CuO} + H_2O$$

When black oxide is heated with copper, red oxide of copper is obtained.

$$\underset{\text{Black oxide}}{CuO + Cu} \xrightarrow[\Delta]{} \underset{\text{Red oxide}}{Cu_2O}$$

2. **2074 Set B Q.No. 20 Give the balanced chemical reaction for the preparation of copper sulphate from copper. What happens when blue vitriol is heated at 100°C?** **[1+1]**

The balanced chemical reaction for the preparation of copper sulphate from copper is given below:

$$Cu + \text{Conc. } 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2$$

When blue vitriol is heated at 100°C, Copper sulphate monohydrate is obtained.

$$\underset{\text{Blue vitriol}}{CuSO_4.5\,H_2O} \xrightarrow[\Delta]{100\,^\circ C} \underset{\text{Copper sulphate monohydrate}}{CuSO_4.H_2O} + 4\,H_2O$$

3. **2073 Supp Q.No. 20 What happens when copper sulphate solution is treated with ammonia solution?** **[2]**

When copper sulphate solution is treated with ammonia solution, bluish white ppt of copper hydroxide is obtained. If excess of ammonia solution is added, deep blue solution of tetra-ammino cupric hydroxide complex is obtained.

$$CuSO_4 + 2\,NH_4OH \longrightarrow \underset{\text{Bluish white ppt}}{Cu(OH)_2} + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 4\,NH_4OH \xrightarrow{\text{Excess}} [Cu(NH_3)_4](OH)_2 + 4\,H_2O$$

Deep blue solution

Tetra-ammino cupric hydroxide complex

4. **2073 Set C Q.No. 20 Starting from copper how would you obtain blue vitriol?** **[2]**

Copper is heated with conc. H_2SO_4, copper sulphate is obtained which on crystallization gives blue vitriol.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$CuSO_4 \text{ solution} \xrightarrow{\text{Crystallization}} \underset{\text{Blue vitriol}}{CuSO_4.5\,H_2O}$$

5. **2073 Set D Q.No. 20 Write the action of heat on blue vitriol.** **[2]**

When copper sulphate penta-hydrate is kept in open air the two molecules of water is lost and pale blue coloured copper sulphate is formed. When heated upto 100°C then again two molecules is lost and bluish copper sulphate is formed which on further heating upto 250°C then colourless copper sulphate is formed.

$$CuSO_4.5\,H_2O \underset{-2\,H_2O}{\overset{\text{Exposed on open air}}{\rightleftharpoons}} \underset{\text{Pale blue}}{CuSO_4.3\,H_2O} \underset{-2\,H_2O}{\overset{100^\circ C}{\rightleftharpoons}} \underset{\text{Bluish white}}{CuSO_4.H_2O} \underset{-\,H_2O}{\overset{250^\circ C}{\rightleftharpoons}} \underset{\text{Colourless}}{CuSO_4}$$

6. **2072 Supp. Q.No. 21 Write down the molecular formula of:** **[2]**

   i. **Copper pyrite** ii. **Calamine**
   iii. **Calomel** iv. **Cinnabar**

Molecular formula of:

i. Copper pyrite: $CuFeS_2$
ii. Calamine: $ZnCO_3$
iii. Calomel:Hg_2Cl_2
iv. Cinnabar: HgS

7. **2072 Set C Q.No. 21ii Give reason: Mettalic copper turns black when exposed to moist air?** **[1]**

When copper metal is exposed in moist air for a long time, black basic copper carbonate is obtained.

$$2Cu + CO_2 + H_2O + O_2 \longrightarrow CuCO_3.Cu(OH)_2$$

8. **2071 Supp. Q.No. 21i Write an important use of red oxide** **[0.5]**

Red oxide: It is used as red antitrust pigment.

9. **2071 Supp. Q.No. 21iii Write an important use of blue vitriol** **[0.5]**

Blue vitriol: It is used as modrant in dyeing.

10. **2071 Set C Q. No. 21 What is meant by copper matte?** **[2]**

Copper sulphide contains some amount of iron sulphide as impurtues which is called copper matte.

11. **2071 Set D Q. No. 21 Write an important use of each of the followings:** **[2]**

   a. **red oxide** b. **blue vitriol**

Use of

a. Red oxide: It is used as a red antirust pigment.
b. Blue vitriol: It is used as laboratory reagent.

12. **2070 Set C Q. No. 22 Write a reaction for the preparation of each of the following:** **[2]**

   i. **CuO** ii. **Cu_2O.**

i. CuO: It is prepared by heating copper in the presence of air below 1000°C.

$$2Cu + O_2 \xrightarrow{<1000^\circ C} 2\,CuO$$

ii. Cu_2O: It is prepared by heating copper in the presence of air above 1000°C.

$$4Cu + O_2 \xrightarrow{> 1000^\circ C} 2Cu_2O$$

13. **2060 Q. No. 18 A light blue colored precipitate 'A' obtained by the addition of caustic soda in the solution of cupric sulphate is converted to a black precipitate 'B' on heating. What are 'A' and 'B'? [2]**

The blue coloured ppt. 'A' is obtained by the addition of NaOH with $CuSO_4$ solution. So, the compound 'A' must be $Cu(OH)_2$ which on further heating gives a black ppt of CuO. Thus, the compound 'B' is CuO.

$$\underset{\text{Cupric sulphate}}{CuSO_4} + 2NaOH \longrightarrow \underset{\text{Cupric hydroxide(A)}}{Cu(OH)_2} + Na_2SO_4$$

$$Cu(OH)_2 \xrightarrow[\Delta]{} \underset{\substack{\text{Cupric oxide}\\ \text{Black ppt}}}{CuO} + H_2O$$

14. **2059 Q. No. 16 Write a compound of Cu (II) which is insoluble in water but soluble in dilute acid without effervescence. [2]**

The compound black oxide of copper i.e. cupric oxide (CuO) which is insoluble in water but soluble in dilute acid without effervescence.

$CuO + 2HCl(dil.) \longrightarrow CuCl_2 + H_2O$

15. **2058 Q. No. 14 What happens when NH_3 is passed over red-hot CuO? [2]**

When HN_3 is passed over red – hot CuO, CuO is reduced to Cu and forming N_2 gas.

$2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$

16. **2057 Q. No. 18 Name two important ores of copper with formulae. [2]**

The two important ores are Copper pyrites ($CuFeS_2$) and Copper glance (Cu_2S)

17. **2056 Q. No. 18 Group B Give any one method of conversion of cupric sulphate into cuprous oxide with chemical equations. [2]**

When cupric sulphate is reduced with glucose in the presence of alkali, red ppt of cuprous oxide is formed.

$$2CuSO_4 + 4NaOH \xrightarrow[2[H]]{\text{Glucose}} 2Na_2SO_4 + 2H_2O + \underset{\text{Red ppt}}{Cu_2O\downarrow}$$

18. **2053Q. No.7B(c) Copper turning is treated with conc. HNO_3. [2]**

When copper turning is treated with conc. HNO_3 in a test tube, NO_2 gas is evolved with the formation of copper nitrate.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + \underset{\text{Brown gas}}{2NO_2} + 2H_2O$$

19. **2053 Q. No. 2 Group A When copper wire is put into a solution of silver nitrate beautiful crystals are deposited on the surface of the copper. What are these crystals chemically? Write the reaction involved. [2]**

When copper wire is put into a solution of silver nitrate solution, beautiful crystals of silver are deposited.

$$Cu + 2AgNO_3 \longrightarrow \underset{\text{Crystals}}{2Ag} + Cu(NO_3)_2$$

20. **2053 Q. No. 18 Group A What is the effect of heat on copper sulphate penta-hydrate? [2]**

Please refer to 2073 Set D Q.No. 20

21. **2051 Q. No. 7(c) A copper coin is dropped into concentrated nitric acid in a test tube. [2]**

When copper coin is dropped into conc. HNO_3 acid in test tube, nitrogen peroxide is formed which is brown gas.

$$4HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + \underset{\text{Nitrogen peroxide}}{2NO_2} + 2H_2O$$

SHORT QUESTIONS ANSWERS [5 MARKS]

22. **2076 Set B Q.No. 26 2074 Set B Q.No. 26 2072 Set C Q.No. 26 2072 Set D Q.No. 26 2072 Supp. Q.No. 26 2069 Supp. Set B Q. No. 29 How is blister copper extracted from copper pyrites? [5]**

Extraction of copper:

Principle: Copper is extracted mainly from copper pyrites ore by means of self reduction process. This process consists of the following steps:

a. Concentration: The ore is concentrated by Froth floatation process.

b. Roasting: It is then roasted in a Reverberatory furnace in a current of air. The volatile impurities such as free sulphur, arsenic and antimony are removed as their volatile oxides and the ore is partially oxidized.

$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 3SO_2 + 2FeO$

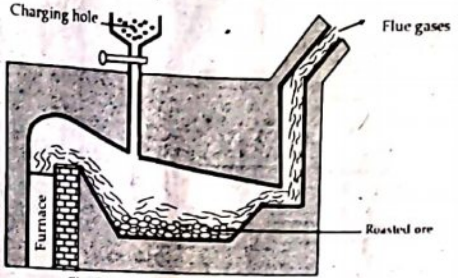


Fig: Reverberatory furnace

c. Smelting in a blast furnace: Cu_2S does not oxidize till all the FeS is oxidized to FeO. Hence, the roasted ore is heated in a blast furnace lined inside with silica in a blast of hot air. Here, most of FeS is osidized to FeO and forms fusible ferrous silicate slag.

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_3(slag)$

Thus two layers get separated in the hearth of the furnace. The lower layer is a molten mixture of Cu_2S and little FeS called MATTE and the upper is of molten slag. The slag is separated out through the slag hole and the matte is transferred to a Bessemer converter for Bessemerization.

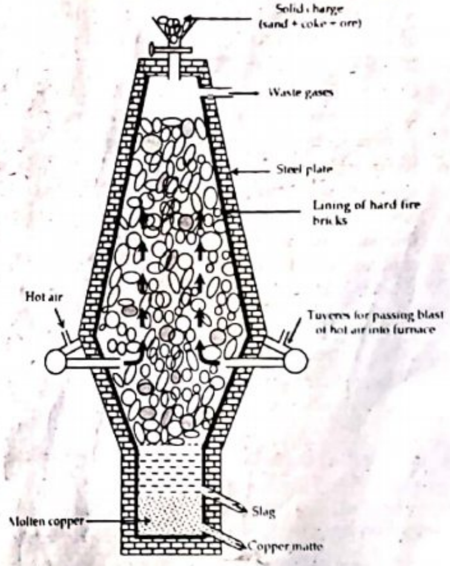


Figure: Blast furnace

d. Bessemerization: The matte is heated in a Bessemer converter in a current of air when the remaining portion of FeS is oxidised to FeO which combines with (SiO_2) lining of Bessemer converter to form ferrous silicate slag.

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_3(slag)$

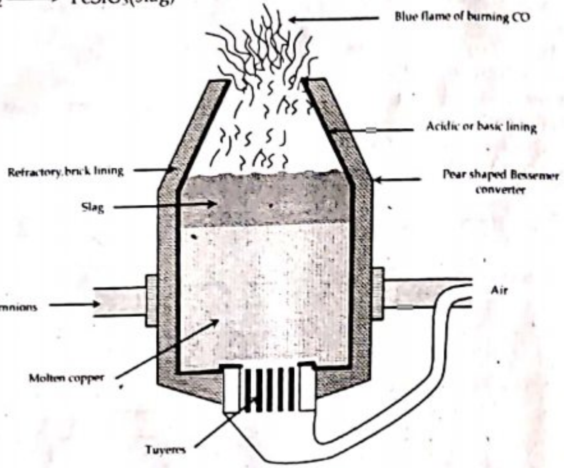


Fig: Bessemer Converter

When all FeS is converted to $FeSiO_3$ slag which is removed, cuprous sulphide beigns to be oxidised. When about two-thirds of the Cu_2S is oxidized to Cu_2O,the latter is reduced by means of Cu_2S to metallic copper.

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

Copper obtained in this way is impure and is called BLISTER COPPER because there are blisters on its surface due to the escape of SO_2 gas.

e. Refining: Crude copper is purified by the process of electrolysis using of $CuSO_4.5H_2O$ acidified with dilute H_2SO_4 as the electrolyte. Thick slabs of impure copper are used as anodes and thin sheets of pure copper as cathodes. On electrolysis, anodes dissolve and thin slabs of Cu-cathodes become converted to thick slabs of pure Cu. Thus, pure copper is obtained at the cathodes.

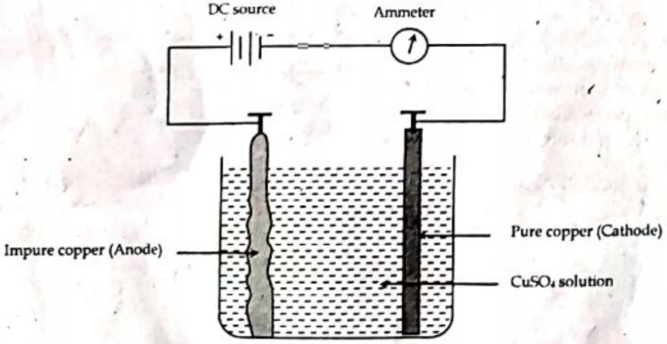


Fig: Electro-refining

$CuSO_4 \xrightarrow{\text{Electrolysis}} Cu^{++} + SO_4^{2-}$

Reaction:

At the cathode: $Cu^{++} + 2e^- \longrightarrow Cu$ (pure)

At the anode: $Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$

23. **2072 Set E Q.No. 29 How is blister copper extracted from its copper pyrite ore?** **[5]**

Please refer to 2076 Set B Q.No. 26

24. **2070 Supp. Q. No. 29 Starting from copper pyrites, how can you obtain blister copper?** **[5]**

Please refer to 2076 Set B Q.No. 26

25. **2070 Set D Q. No. 29 Write the preparations, properties and uses of Blue vitriol.** **[5]**

Preparation:

i. By dissolving CuO,$Cu(OH)_2$ and $CuCO_3$ in dilute H_2SO_4, filtering and crystallizing the filtrate.

$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$

$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$

ii. By heating Cu with conc. H_2SO_4.

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$

iii. By heating $CuCl_2.2H_2O$ or $Cu(NO_3)_2.3H_2O$ with conc.H_2SO_4.

$CuCl_2 + H_2SO_4 \longrightarrow CuSO_4 + 2HCl$

$2Cu(NO_3)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 2H_2O + 4NO_2 + O_2$

$$\underset{}{CuSO_4 \text{ solution}} \xrightarrow{\text{Crystallization}} \underset{\text{Blue vitriol}}{CuSO_4.5H_2O}$$

Physical properties:

i. It is a blue crystalline solid.

ii. It is soluble in water.

Chemical properties:

i. **Action of heat:** On heating, it becomes white and anhydrous at 250°C. The anhydrous $CuSO_4$ turns blue when treated with water.

$$\underset{\text{Blue}}{CuSO_4.5H_2O} \xrightarrow[\Delta]{100^\circ C} CuSO_4.H_2O \xrightarrow[\Delta]{250^\circ C} \underset{\text{white}}{CuSO_4} \xrightarrow[\Delta]{640^\circ C} CuO + SO_2$$

$$\underset{\text{white}}{CuSO_4} \xrightarrow{5H_2O} \underset{\text{Blue}}{CuSO_4.H_2O}$$

ii. **Action of hot NaOH:** When NaOH solution is added to a solution of cupric sulphate, a greenish blue ppt. of $Cu(OH)_2$ is obtained which turns black on heating.

$$CuSO_4 + 2NaOH \longrightarrow \underset{\text{Greenish blue ppt}}{Cu(OH)_2} + Na_2SO_4$$

$$Cu(OH)_2 \longrightarrow \underset{\text{Black ppt.}}{CuO + H_2O}$$

iii. **Action of NH_4OH solution:** When NH_4OH solution is added to a solution of $CuSO_4.5H_2O$ in water, a blue ppt of $Cu(OH)_2$ is formed which dissolves in excess of NH_4OH solution, to give a deep blue solution of tetra-ammino cupric hydroxide complex.

$$CuSO_4 + 2\,NH_4OH \longrightarrow \underset{\text{Greenish blue ppt}}{Cu(OH)_2\downarrow} + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 4NH_4OH \longrightarrow \underset{\text{Deep blue solution}}{[Cu(NH_3)_4](OH)_2} + 4H_2O.$$

iv. **Action of KI solution:** When KI solution is added to a solution of $CuSO_4.5H_2O$, potassium iodide is oxidized to iodine.

$$2CuSO_4 + 4KI \longrightarrow \underset{\text{White ppt}}{Cu_2I_2\downarrow} + 2K_2SO_4 + \underset{\text{Brown ppt}}{I_2\downarrow}$$

v. **Action of KCN:** When KCN solution is added to a solution of $CuSO_4$, a white ppt. of cuprous cyanide is first formed which dissolves in excess of KCN solution to form colourless potassium cuprocyanide solution.

$$2CuSO_4 + 4KCN \longrightarrow \underset{\text{White ppt}}{Cu_2(CN)_2\downarrow} + 2K_2SO_4 + C_2N_2$$

$$Cu_2(CN)_2 + 6KCN \longrightarrow \underset{\text{Colourless solution}}{2K_3[Cu(CN)_4]}.$$

Uses:

i. It is used as a germicide.
ii. It is used in electroplating.
iii. It is used in electric cells.
iv. It is used in refining of crude copper.
v. It is also used to prepare green dyes.

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26. **2069 Set A Q. No. 23** **Write the chemistry of blue vitriol.** **[5]**

➢ Please refer to **2070 Set D Q. No. 29**

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27. **2069 Set B Q. No. 29** **Mention the preparations, properties and used of blue vitriol.** **[5]**

➢ Please refer to **2070 Set D Q. No. 29**

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28. **2067 Q. No. 29** **How would you convert copper into blue vitriol? Name any one alloy of each of:** **[5]**

i. Copper and Zinc. ii. Copper and tin.

➢ Copper is heated with conc. H_2SO_4, copper sulphate is obtained which on crystallization gives blue vitriol.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$CuSO_4\ \text{solution} \xrightarrow{\text{Crystallization}} \underset{\text{Blue vitriol}}{CuSO_4.5H_2O}$$

Alloys of

i. copper and zinc = brass
ii. copper and tin = bronze

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29. **2065 Q. No. 28** **Write the chemistry of blue vitriol?** **[5]**

➢ Please refer to **2070 Set D Q. No. 29**

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30. **2063 Q. No. 31** **How is metal copper extracted from its pyrite ore? How is it refined? Write the action of it upon:**

i. Moist air and ii. Conc. H_2SO_4 **[5]**

➢ Extraction of copper from pyrite ore: Please refer to **2076 Set B Q.No. 26**

Reaction of copper metal

i. **Action with moist air:** After long exposer to moist air, a green layer of its basic carbonate is formed over it.

$$2Cu + H_2O + CO_2 + O_2 \longrightarrow \underset{\text{Basic copper corbonate}}{CuCO_3.Cu(OH)_2}$$

ii. **Action of conc.H_2SO_4:** When heated with conc. H_2SO_4, sulphur dioxide gas is formed.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

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31. **2062 Q. No. 28a** **Copper sulphate crystal turns white powder on heating.** **[5]**

➢ Copper sulphate crystal when heated with slowly to 100°C loses four molecules of water giving bluish white salt. The last molecule of water escapes out at 250°C and white anhydrous copper sulphate is formed.

$$CuSO_4.5H_2O \xrightleftharpoons[\text{-2}H_2O]{\text{Exposed on open air}} \underset{\text{Pale blue}}{CuSO_4.3H_2O} \xrightleftharpoons[\text{-2}H_2O]{100°C} \underset{\text{Bluish white}}{CuSO_4.H_2O} \xrightleftharpoons[\text{-}H_2O]{250°C} \underset{\text{Colourless}}{CuSO_4}$$

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32. **2062 Q. No. 28c** **A brown gas is obtained when copper is treated with conc. nitric acid.** **[5]**

➢ When copper turning is treated with conc. HNO_3, a brown gas NO_2 is evolved with the formation of copper nitrate.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + \underset{\text{Brown gas}}{2NO_2\uparrow} + 2H_2O$$

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33. **2062 Q. No. 28 (d)** **Copper becomes green when exposed to air for long time.** **[5]**

➢ Copper on exposure to air in presence of carbon dioxide, it is slowly converted to green basic copper carbonate.

$$2Cu + CO_2 + H_2O + O_2 \longrightarrow \underset{\text{Green basic carbonate}}{CuCO_3.Cu(OH)_2}$$

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34. **2055 Q. No. 31(c)2057 Q. No. 33(b)** **Write short notes on: Chemistry of Blue Vitriol.** **[5]**

➢ Please refer to **2070 Set D Q. No. 29**

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35. **2054Q. No. 27(b)** **Ammonium hydroxide is added to a solution of copper sulphate.** **[5]**

➢ When ammonium hydroxide is added to a solution of copper sulphate solution, a bluish white ppt. of copper hydroxide is formed which on further combination of excess of ammonium hydroxide then deep blue solution of tetramine copper sulphate is obtained.

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Tetramine copper(II) sulphate}}{[Cu(NH_3)_4]SO_4} + 4H_2O$$

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36. **2053 Q. No. 2 Group B** **Point out the important processes involved in the extraction of copper from its sulphide ore.** **[5]**

➢ Please refer to **2076 Set B Q.No. 26**

LONG ANSWER QUESTIONS

37. **2066 Q. No. 32** **Starting from copper pyrite, how would you obtain pure copper? Explain the steps involved in the process with necessary diagram for it. Give the chemical reaction for the followings:**

i. Copper is exposed to moist air.
ii. Conversion of copper into blue vitriol. **[7+1+2]**

➢ Extraction of copper: Please refer to **2076 Set B Q.No. 26**

i. Copper is exposed to moist air:

Reaction of copper metal

a. **Action with moist air:** After long exposer to moist air, a green layer of its basic carbonate is formed over it.

$$2Cu + H_2O + CO_2 + O_2 \longrightarrow CuCO_3.Cu(OH)_2$$

b. **Action of conc.H_2SO_4:** When heated with conc. H_2SO_4, sulphur dioxide gas is formed.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

c. **Reaction with conc.HNO_3:** When heated with conc.HNO_3, brown fumes of NO_2 gas is evolved.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Uses of copper:

a. It is used for making alloys.
b. It is used for making electrical utensils.

ii. Conversion of copper into blue vitriol: Please refer to **2067 Q. No. 29**

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38. **2064 Q. No. 32** **How is blister copper extracted from copper pyrite? How does the metal react with: (a) moist air (b) conc. H_2SO_4 (c) conc. HNO_3? Mention the important uses of the metal.** **[6+3+1]**

➢ Extraction of copper: Please refer to **2076 Set B Q. No. 26**

Reaction of copper metal: Please refer to 2066 Q. No. 32

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39. **2060 Q. No. 30 How is pure copper extracted from copper pyrite? Discuss its metallurgical operations with necessary chemical reactions and diagrams.** [10]

↘ Please refer to 2076 Set B Q No. 26

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40. **2059 Q. No. 28 Write a method of preparation of blue vitriol. Describe its action with** [1+2+2]
    i. **ammonia solution till excess**
    ii. **aqueous potassium iodide**

↘ **Preparation of blue vitriol:** Please refer to 2070 Set D Q. No. 29

Action of Copper sulphate with:

i. Copper sulphate solution is treated with ammonia, a buish white ppt. of copper hydroxide is formed. On addition of excess of ammonia, the ppt. dissolves and blue solution of tetramine copper sulphate is obtained.

$$CuSO_4 + 2NH_4OH \longrightarrow \underset{\text{Bluish white ppt.}}{Cu(OH)_2} + (NH_4)_2SO_4$$

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Blue (tetramine copper sulphate)}}{Cu(NH_3)_4SO_4} + 4H_2O$$

ii. When KI solution is added to a solution of $CuSO_4.5H_2O$, potassium iodide is oxidized to iodine.

$$2CuSO_4 + 4KI \longrightarrow \underset{\text{White ppt}}{Cu_2I_2\downarrow} + 2K_2SO_4 + \underset{\text{Brown ppt}}{I_2\downarrow}$$

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41. **2057 Q. No. 32 How is metal copper extracted from its sulphide ore? How is it refined?** [7+3]

↘ Please refer to 2076 Set B Q No. 26

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42. **2056 Q. No. 31 How is blister copper extracted starting from concentrated copper pyrites one? How is it refined electrolytically?** [8+2]

↘ Please refer to 2076 Set B Q No. 26

WRITE SHORT NOTES ON [5MARKS]

43. **2076 Set C Q.No. 33ii 2075 GIE Q.No. 33iv 2075 Set B Q.No. 33i 2074 Set A Q.No. 33b 2073 Supp Q.No. 33i 2073 Set C Q.No. 33i 2073 Set D Q.No. 33i Extraction of blister copper from copper pyrites** [5]

↘ Please refer to 2076 Set B Q No. 26

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44. **2075 Set A Q.No. 33iii 2070 Set C Q. No. 33 a Chemistry of Blue Vitriol.** [5]

↘ Please refer to 2070 Set D Q No. 29

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45. **2074 Supp. Q.No. 33(i) 2071 Supp. Q.No. 33d 2071 Set C Q. No. 33 d Extraction of blister of copper** [5]

↘ Please refer to 2076 Set B Q No. 26

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46. **2071 Set D Q. No. 33 d Chemistry of black oxide of copper** [5]

↘ Chemistry of black oxide of copper (CuO)

Preparation:

i. It can be prepared by heating copper in presence of air below 1373K.

$$2Cu + O_2 \xrightarrow{< 1373\text{ K}} 2Cu_2O$$

ii. It can be prepared by heating copper hydroxide, carbonate or nitrate.

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$
$$CuCO_3 \longrightarrow CuO + CO_2$$
$$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

Properties:

i. It is black powder.
ii. It is insoluble in water.
iii. It reacts with acids to give corresponding salts.

$$CuO + 2HCl \xrightarrow[\Delta]{} CuCl_2 + H_2O$$
$$CuO + H_2SO_4 \xrightarrow[\Delta]{} CuSO_4 + H_2O$$
$$CuO + 2HNO_3 \xrightarrow[\Delta]{} Cu(NO_3)_2 + H_2O$$

iv. It is reduced to metallic copper with H_2, CO, NH_3 etc.

$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$CuO + CO \longrightarrow Cu + CO_2$$
$$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$$

Uses:

i. It is used for the manufacture of coloured glass.
ii. It gives green blue glaze to glass.

18.2 Zinc

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 20 How is lithopone prepared? Write its an important application.** [1+1]

↘ When zinc sulphate is treated with barium sulphide, double salt lithopone is obtained which is used as white pigment.

$$ZnSO_4 + BaS \longrightarrow \underset{\text{Lithopone (Double salt)}}{ZnS.BaSO_4}$$

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2. **2076 Set C Q.No. 20 How is granulated zinc obtained? Write its an important application.** [1+1]

↘ Granulated zinc is obtained by pouring of molten zinc into water which having irregular shape. It is used in chemistry as a source of hydrogen when acted upon by hydrochloric or sulphuric acids.

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3. **2075 Set B Q.No. 22 Give balanced chemical equations for the followings.** [1+1]
    i. **Zinc white is heated with cobalt nitrate**
    ii. **Zinc is exposed to moist air**

↘

i. When zinc white (ZnO) is heated with cobalt nitrate ($Co(NO_3)_2$), a green mass cobalt zincate is obtained which is called Rinmann's green.

$$2\,Co(NO_3)_2 \longrightarrow 2\,CoO + 2\,NO_2 + O_2$$
$$ZnO + CoO \longrightarrow \underset{\text{Cobalt zincate}}{CoZnO_2}$$

ii. When zinc is exposed to moist air, basic zinc carbonate is obtained.

$$2\,Zn + CO_2 + H_2O + O_2 \longrightarrow \underset{\text{Basic zinc carbonate}}{ZnCO_3.Zn(OH)_2}$$

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4. **2074 Supp. Q.No. 22 2074 Set A Q.No. 22 2074 Set B Q.No. 22 What product would you expect when zinc white is heated with cobalt nitrate? Write an application of the product.** [1+1]

↘ Zinc oxide is heated with cobalt nitrate, a green mass cobalt zincate is formed which is called **Rinmann's green.** It is used to detect basic radicals like Zn^{++}, Mg^{++}, Al^{+++}, etc.

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$$
$$ZnO + CoO \longrightarrow \underset{\text{Cobalt zincate (Rinmann's green)}}{CoZnO_2}$$

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5. **2073 Supp Q.No. 21 Give reactions for the extraction of metallic zinc from zinc blende.** [2]

↘ The reaction for the extraction of zinc from zinc blende are:

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$
$$ZnO + C \longrightarrow Zn + CO$$

6. **2073 Set C Q.No. 21 What happens when Zinc white is** **[1+1]**

   i. **heated** ii. **treated with caustic alkali.**

i. When zinc white (ZnO) is heated, it becomes yellow colour.

$$ZnO \xrightarrow[\Delta]{} \text{Yellow colour}$$

ii. When zinc white (ZnO) is treated with caustic alkali (NaOH), Sodium zincate is obtained.

$$ZnO + 2NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2O$$

7. **2073 Set D Q.No. 21 Give the reactions for the extraction of metallic zinc from zinc blende.** **[2]**

Please refer to **2073 Supp Q.No. 21**

8. **2072 Set E Q.No. 20i What happens when Zinc is exposed to moist air.** **[1]**

Due to the formation of a protective layer of basic $ZnCO_3$ over zinc surface, zinc becomes dull in moist air.

$$Zn + CO_2 + H_2O \longrightarrow \underset{\text{Basic zinc carbonate}}{ZnCO_3.Zn(OH)_2} + H_2O$$

9. **2072 Set E Q.No. 20ii What happens when White vitriol is strongly heated.** **[1]**

When white vitriol is heated upto 100°C then zinc sulphate monohydrate is obtained which on further heating at 300°C, only zinc sulphate is formed and again on heating above 800°C then zinc sulphate is decomposed to form zinc oxide.

$$ZnSO_4.7H_2O \xrightarrow{100°C} \underset{\substack{\text{zinc sulphate}\\ \text{Monohydrate}}}{ZnSO_2 + H_2O} \xrightarrow{300°C} \underset{\text{zinc sulphate}}{ZnSO_4} \xrightarrow{>800°C} \underset{\text{zinc oxide}}{ZnO} + SO_2 + O_2$$

10. **2072 Supp. Q.No. 22 Starting from metalic Zinc, how would you prepare white vitriol?** **[2]**

When zinc is treated with dilute H_2SO_4, aqueous solution of zinc sulphate ($ZnSO_4$) is obtained which on crystallization gives white vitriol.

$$Zn + \text{dil. } H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

$$ZnSO_4(aq.) \xrightarrow{\text{Crystallization}} \underset{\text{White vitriol}}{ZnSO_4.7H_2O}$$

11. **2072 Set C Q.No. 22 What is Rinman's green? Write its important uses.** **[1+1]**

Please refer to **2074 Supp. Q No. 22**

12. **2071 Supp. Q.No. 22 How is Rinmann's green prepared? Write its one important use.** **[1+1]**

Please refer to **2074 Supp. Q No. 22**

13. **2071 Set C Q. No. 22 Give a correct balanced chemical reaction for the preparation of** **[2]**

    a. **White vitriol**
    b. **Philosopher's wool**

Preparation of

a. **White vitriol:** It is prepared by reacting zinc oxide with dil. H_2SO_4.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

b. **Philosopher's wool:** It is prepared by heating zinc carbonate.

$$ZnCO_3 \xrightarrow[\Delta]{} ZnO + CO_2$$

14. **2071 Set D Q. No. 22 What happens when zinc white is:** **[2]**

    a. **heated with cobaltnitrate**
    b. **dissolved with caustic alkali**

a. Please refer to **2074 Supp. Q.No. 22**

b. When zinc white is dissolved with caustic alkali, sodium zincate is obtained.

$$ZnO + 2NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2O$$

15. **2070 Supp. Q. No. 22 How is Rinmann's green prepared? Give its one important use.** **[2]**

Please refer to **2074 Supp. Q No. 22**

16. **2070 Set C Q. No. 22 Or Write action of heat on white vitriol.** **[2]**

When white vitriol is heated upto 100°C then zinc sulphate monohydrate is obtained which on further heating at 300°C, only zinc sulphate is formed and again on heating above 800°C then zinc sulphate is decomposed to form zinc oxide.

$$ZnSO_4.7H_2O \xrightarrow{100°C} \underset{\substack{\text{zinc sulphate}\\ \text{Monohydrate}}}{ZnSO_2 + H_2O} \xrightarrow{300°C} \underset{\text{zinc sulphate}}{ZnSO_4} \xrightarrow{>800°C} \underset{\text{zinc oxide}}{ZnO} + SO_2 + O_2$$

17. **2070 Set D Q. No. 21 What happens when:** **[2]**

    i. **Zinc white is heated with cobalt nitrate.**
    ii. **Metallic zinc is dissolved in hot conc. NaOH.**

i. **Zinc white is heated with cobalt nitrate.**

It is heated with cobalt nitrate to form a green mass called **Rinmann's green.**

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$$

$$ZnO + CoO \longrightarrow CoZnO_2$$

ii. **Metallic zinc is dissolved in hot conc. NaOH.**

When zinc is dissolved in hot and conc. NaOH then sodium zincate is obtained with the evolution of hydrogen gas.

$$Zn + 2NaOH \xrightarrow[\Delta]{} \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2$$

18. **2069 (Set A) Q. No. 20 What happens when zinc white is heated?** **[2]**

When zinc white is heated, it becomes yellow colour.

$$ZnO \longrightarrow \text{Yellow colour}$$

19. **2069 (Set B) Q. No. 20 i, ii, iv Write the molecular formula of:** **[2]**

    i. **Philosopher's wool**
    ii. **Rimman's green**
    iii. **Calamine**

i. Philosopher's of wool (ZnO)

ii. Rinman's green ($CoZnO_2$)

iii. Calamine ($ZnCO_3$)

20. **2069 Supp. Set B Q. No. 20 How would you obtain white vitriol from zinc?** **[2]**

Zinc metal is treated with dil. H_2SO_4, zinc sulphate is obtained.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

The solution of $ZnSO_4$ on evaporation and crystallization below (312K) gives white crystal of $ZnSO_4.7H_2O$

$$ZnSO_4(aq.) \xrightarrow[\text{at crystallization point}]{\text{Evaporation}} \underset{\text{White vitriol}}{ZnSO_4.7H_2O}$$

21. **2068 Q. No. 18 Give the molecular formula of:** **[2]**

    i. **Philosopher's wool**
    ii. **Calamine**

➣
i. Philosopher's of wool (ZnO)
ii. Calamine ($ZnCO_3$)

22. 2068 Q. No. 20 **What is the action of heat on white vitriol?** [2]

➣ Please refer to 2072 Set E Q.No. 20ii

23. 2067 Q. No. 19 **Why do zinc become dull in contract of moist air?**

➣ Please refer to 2072 Set E Q.No. 20i

24. 2066 Q. No. 18i **Name one important use of each of the followings: Zinc** [2]

➣ It is used for galvanizing iron.

25. 2065 Q. No. 20 i **Give the balanced chemical equation:** [2]
Zinc is dissolved in hot and conc. NaOH solution.

➣ Zinc is dissolved in hot and conc. NaOH solution.

$$Zn + 2NaOH \xrightarrow[\Delta]{} \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2$$

26. 2064 Q. No. 19 **Write an important use of each of following substances:** [2]
    i. **Calomel**
    ii. **Green vitriol**
    iii. **Zinc white**

➣
i. **Calomel:** It is used for making calomel electrodes.
ii. **Green Vitriol:** It is used in medicine
iii. **Zinc white:** It is used as white pigment.

27. 2063 Q. No. 19b **What happens when: Zinc oxide is heated with cobalt nitrate.** [2]

➣ Zinc oxide is heated with cobalt nitrate, a green mass cobalt zincate is formed which is called Rinmann's green.

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$$
$$ZnO + CoO \longrightarrow \underset{\text{Cobalt zincate}}{CoZnO_2}$$

28. 2063 Q. No. 20 **Write the formulae of the following ores of metals:** [2]
    i. **Magnetite**
    ii. **Calamine**

➣ Formulae of
i. Magnetite: Fe_3O_4
ii. Calamine: $ZnCO_3$

29. 2062 Q. No. 20 iii **Write an important use of each of the following substances: White vitriol** [2]

➣ **White vitriol:** It is used for the preparation of lithopone a popular white paint.

30. 2061 Q. No. 18 **Write the name of two ores of Zinc with their molecular formulae.** [2]

➣ The two ores of Zn are:
Zinc blende (ZnS), Calamine ($ZnCO_3$)

31. 2059 Q. No. 20 **What action takes place when aqueous sodium hydroxide is added to zinc sulphate solution drop by drop till excess?** [2]

➣ When sodium hydroxide is added to the solution of zinc sulphate a white ppt. of zinc hydroxide appears which dissolves in excess NaOH forming sod.zincate.

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + 2H_2O$$

32. 2058 Q. No. 19 **Name two ores of zinc with their formulae.** [2]

➣ Please refer to 2061 Q. No. 18

33. 2056 Q. No. 6 **Why zinc displace copper from copper sulphate solution?** [2]

➣ Zn is more electropositive metal than Cu and the standard reduction potential of Zn is -0.76V while that of Cu is +0.34V. So, Zn displaces less electropositive metal Cu from $CuSO_4$ solution.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

34. 2056 Q. No. 12 **Why is zinc not considered as a transition element?** [2]

➣ Zinc is not considered as a transition element due to the following properties:
i. It has completely filled d-orbital. $3d^{10}4s^2$
ii. Its compounds are colourless.
iii. It shows only one oxidation state +2.

35. 2052 Q. No. 6 b **Write action of cobalt nitrate heat on zinc oxide** [2]

➣
i. **Heat on ZnO:** When zinc white is heated, it becomes yellow colour.
ZnO ⟶ Yellow colour
ii. **Cobalt nitrate on ZnO:** It is heated with cobalt nitrate to form a green mass called **Rinmann's green.**

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$$
$$ZnO + CoO \longrightarrow \underset{\text{Rinmann's green}}{CoZnO_2}$$

36. 2052 Q. No. 7 **How will you obtain crystals of white vitriol? Give a chemical reaction.** [2]

➣ It is prepared by heating Zinc,Zinc oxide,Zinc carbonate or Zinc hydroxide with dilute sulphuric acid.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$
$$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + CO_2 + H_2O$$
$$Zn(OH)_2 + H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O$$

The solution of $ZnSO_4$ on evaporation and crystallization below (312K) gives white crystal of $ZnSO_4.7H_2O$

$$ZnSO_4\,(aq.) \xrightarrow[\text{at crystallization point}]{\text{Evaporation}} ZnSO_4.7H_2O$$

SHORT ANSWER QUESTIONS [5 MARKS]

37. 2071 Supp. Q.No. 26 **How is zinc extracted from zinc blende?** [5]

➣ Most of zinc is extracted from zinc blende ore by carbon-reduction process.
Principle involved in the extraction of Zn: Zinc is extracted from zinc blende ore by means of carbon reduction process. This process consists of the following steps:

i. **Concentration of the ore:** The ore is concentrated by the froth floatation process.
ii. **Roasting of the ore in a multiple heath furnace:** The concentration ore is roasted in a hot air in a multiple hearth furnace when it is oxidized to its oxide.

$$2\,ZnS + 3O_2 \longrightarrow 2\,ZnO + 2SO_2\uparrow$$

iii. **Reduction of ZnO with coke in a vertical retort furnace:**

$$ZnO + C \longrightarrow Zn + CO\uparrow$$

The vapour of Zn and CO come out from an outlet present below the top of the furnace which are then bubbled under water .Zinc vapours condense under water to form solid zinc which is called **spelter** and CO gas escapes out.

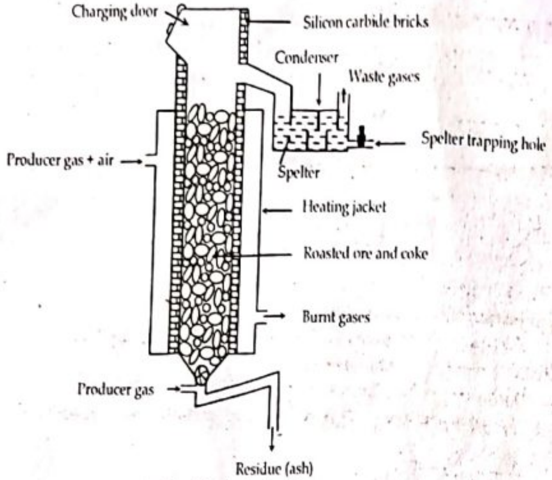

Fig: Vertical retort furnace

iv. **Purification:** The spelter (impure zinc) is purified by electrolysis using $ZnSO_4$ solution acidified with dil. H_2SO_4 as an electrolyte. The thick slabs of spelter zinc is suspended in the electrolyte and are connected to the positive terminal of a battery and thin sheets of pure zinc suspended between the anode act as cathode as they are connected to the positive terminal. On passing current, anode of impure zinc dissolve and pure zinc gets deposited on the cathode. Thus, thick slabs of pure zinc are formed at the cathode.

At anode: $Zn \longrightarrow Zn^{++} + 2e^-$

At cathode: $Zn^{++} + 2e^- \longrightarrow Zn$

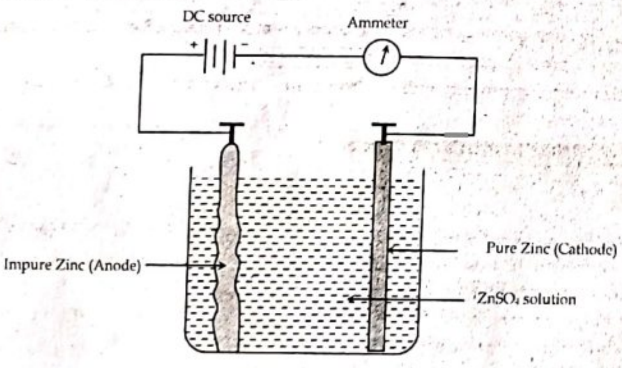

Fig: Electro-refining

38. 2069 Set B Q. No. 29 OR **Give the chemistry of Zinc white.** **[5]**

Preparation:

i. It is prepared by the combustion of zinc in excess of air by calcinations of zinc carbonate, zinc nitrate or zinc hydroxide.

$$Zn + O_2 \xrightarrow[\Delta]{} 2ZnO$$

$$ZnCO_3 \xrightarrow[\Delta]{} ZnO + CO_2$$

$$2Zn(NO_3)_2 \xrightarrow[\Delta]{} 2ZnO + 4NO_2 + O_2$$

$$Zn(OH)_2 \xrightarrow[\Delta]{} ZnO + H_2O$$

Physical properties:

i. It is white powder.

ii. It is very light.

iii. is insoluble in water.

Chemical properties:

i. **Amphoteric nature:** It dissolves both is acid as well as strong base.

$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

ii. **Heated with reducing agent:** It is reduced to metallic zinc when heated with reducing agent.

$ZnO + C \longrightarrow Zn + CO$

$ZnO + CO \longrightarrow Zn + CO_2$

$ZnO + H_2 \longrightarrow Zn + H_2O$

iii. **With cobalt nitrate:** It is heated with cobalt nitrate to form a green mass called **Rinmann's green.**

$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$

$ZnO + CoO \longrightarrow CoZnO_2$

Uses:

i. It is used as white paint.

ii. It is used as medicine and surgical dressing.

iii. It is used to prepare **Rinmann's green.**

39. 2067 Q. No. 27 **Starting from zinc blend, how would you obtain pure zinc? What is galvanization?** **[5]**

Extraction of zinc: Please refer to 2071 Supp. Q No. 26

Galvanization: The process of depositing a thin layer of zinc over the surface of iron is known as galvanization.

40. 2066 Q. No. 27 **Write the chemistry of white vitriol.**

Chemistry of white vitriol $ZnSO_4.7H_2O$

Preparation

i. It is prepared by heating Zinc, Zinc oxide, Zinc carbonate or Zinc hydroxide with dilute sulphuric acid.

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + CO_2 + H_2O$

$Zn(OH)_2 + H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O$

The solution of $ZnSO_4$ on evaporation and crystallization below (312K) gives white crystal of $ZnSO_4.7H_2O$

$$ZnSO_4\,(aq.) \xrightarrow[\text{at crystallization point}]{\text{Evaporation}} ZnSO_4.7H_2O$$

ii. It is also prepared by roasting zinc blende (ZnS) at high temperature i.e. 903K

$$ZnS + 2O_2 \xrightarrow{\text{at 903 K}} ZnSO_4$$

Physical properties:

i. It is colourless, efflorescent crystalline solid.

ii. It is highly soluble in water.

Chemical properties:

i. **Action of heat:** When white vitriol is heated upto 100°C then zinc sulphate monohydrate is obtained which on further heating at 300°C, only zinc sulphate is formed and again on heating above 800°C then zinc sulphate is decomposed to form zinc oxide.

$$ZnSO_4.7H_2O \xrightarrow{100°C} \underset{\text{zinc sulphate Monohydrate}}{ZnSO_2 + H_2O} \xrightarrow{300°C} \underset{\text{zinc sulphate}}{ZnSO_4} \xrightarrow{>800°C} \underset{\text{zinc oxide}}{ZnO + SO_2 + O_2}$$

ii. **Action of NaOH:** When sodium hydroxide is added to the solution of zinc sulphate a white ppt. of zinc hydroxide appears which dissolves in excess NaOH forming sod.zincate.

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$

iii. **With barium sulphide:** Zinc sulphate reacts with barium sulphide to give lithopone.

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

iv. **With sodium carbonate:** When sodium carbonate is added to the solution of zinc sulphate, a white ppt. of basic zinc carbonate is formed.

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\text{Basic Zinc carbonate}}{ZnCO_3.\,3\,Zn(OH)_2} + 4Na_2SO_4 + 3CO_2$$

Uses

i. It is used as eye lotion.

ii. It is used for preparation of lithopone.

iii. It is used for zinc plating.

iv. It is used as mordant dye.

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41. **2065 Q. No. 27 Explain the principle and process sketching a well-labelled diagram for the extraction of zinc from its ore. What happens when zinc is exposed to moist air?** [5]

Please refer to 2071 Supp. Q No. 26

Zinc is exposed to moist air: Please refer to 2072 Set E Q.No. 20

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42. **2064 Q. No. 31(iv) Write short notes on Chemistry of White Vitriol.** [5]

Please refer to 2066 Q. No 27

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43. **2062 Q. No. 27 Write two chemical reactions for the preparation of Zinc white, and justify its amphoteric nature by giving suitable chemical reactions. Write its one important use.** [5]

Preparation of zinc white:

i. It is prepared by heating zinc with oxygen.

$$Zn + O_2 \xrightarrow[\Delta]{} 2\,ZnO$$

ii. It is prepared by heating zinc nitrate.

$$2\,Zn(NO_3)_2 \xrightarrow[\Delta]{} 2\,ZnO + 4\,NO_2 + O_2$$

Amphoteric nature of zinc white i.e. ZnO: It dissolves both is acid as well as strong base.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

Uses of zinc white: It is used as medicine and surgical dressing.

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44. **2061 Q. No. 24 How is Zinc extracted from its ore?** [5]

Please refer to 2071 Supp. Q No. 26

45. **2058 Q. No. 27 Write the preparation, properties and uses of white vitriol.** [5]

Please refer to 2066 Q. No 27

46. **2054 Q. No. 26 Describe the different steps involved in extraction of zinc from zinc blende.** [5]

Please refer to 2071 Supp. Q.No. 26

LONG ANSWER QUESTIONS [10 MARKS]

47. **2056 Q. No. 29 Name the important ores of zinc. Describe the extraction of pure zinc from its sulphide ore. Give the chemistry of white vitriol.** [10]

Important ores of zinc: Please refer to 2061 Q. No 18

Extraction of zinc: Please refer to 2071 Supp. Q.No. 26

Chemistry of white zinc: Please refer to 2069 Set B Q. No. 29

WRITE SHORT NOTES ON

48. **2075 GIE Q.No. 33iii 2075 Set B Q.No. 33iii 2072 Set C Q.No. 33b 2070 Supp. Q. No. 33 c 2070 Set D Q. No. 33 a 2069 Supp. Set B Q. No. 33 b 2063 Q. No. 31(iii) 2057 Q. No. 31(c) Chemistry of white vitriol.** [5]

Please refer to 2066 Q. No. 27

49. **2075 Set A Q.No. 33iv 2074 Set B Q.No. 33d 2070 Set C Q. No. 33 b 2069 (Set A) Q. No. 33 v 2068 Q. No. 31i Extraction of zinc from zinc blende.** [5]

Please refer to 2071 Supp. Q.No. 26

50. **2072 Set D Q.No. 33c 2071 Set C Q. No. 33 c Chemistry of zinc white** [5]

Please refer to 2069 Set B Q. No. 29 OR

51. **2060 Q. No. 31(ii) Extraction of zinc.** [5]

Please refer to 2071 Supp. Q.No. 26

18.3 Mercury

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2075 GIE Q.No. 20 2075 Set A Q.No. 20 How is Nessler's reagent prepared from corrosive sublimate? Give a Laboratory use of Nessler's reagent.** [1+1]

When KI is added to mercuric chloride solution then a scarlet ppt. of mercuric iodide is formed which is dissolved in excess of KI to form a complex potassium mercuric iodide i.e. Nessler's reagent.

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\text{Scarlet ppt}}{HgI_2}$$

$$HgI_2 + \underset{\text{Excess}}{2KI} \longrightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

Use: It is used for the detection of ammonium salts in the laboratory.

2. **2075 Set B Q.No. 20 What happen when ammonia gas is passed through the aqueous solution of** [1+1]

   i. **Corrosive sublimate** ii. **Calomel**

i. When ammonia gas is passed through the aqueous solution of corrosive sublimate $(HgCl_2)$, a white ppt of ammonobasic mercuric chloride is obtained.

$$HgCl_2 + 2\,NH_3 \longrightarrow \underset{\substack{\text{Ammonobasic mercuric chloride}\\ \text{White ppt}}}{Hg(NH_2)Cl} + NH_4Cl$$

ii. When ammonia gas is passed through the aqueous solution of calomel(Hg_2Cl_2), black mercury and mercuric amido chloride is obtained.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow \underset{\text{Black [Mercury and mercuric amido chloride]}}{[Hg + Hg(NH_2)Cl] + NH_4Cl}$$

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3. **2072 Set E Q.No. 21 How would you convert calomel into corrosive sublimate and vice versa giving suitable chemical equations?** **[1+1]**

When corrosive sublimate is heated with mercury then calomel is obtained. Calomel on strong heating gives corrosive sublimate.

$$\underset{\text{Corrosive sublimate}}{HgCl_2} + Hg \longrightarrow \underset{\text{Calomel}}{Hg_2Cl_2}$$

$$\underset{\text{Calomel}}{Hg_2Cl_2} \xrightarrow{\text{Strongly heat}} \underset{\text{Corrosive sublimate}}{HgCl_2 + Hg}$$

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4. **2072 Set C Q.No. 20 Write down a balanced chemical equation for the preparation of calomel. What happens when calomel is treated with ammonia solution?** **[1+1]**

Preparation of Calomel (Hg_2Cl_2):

It is prepared by treating a solution of mercurous nitrate with HCl or NaCl.

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$

$$Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$$

When calomel is treated with ammonia solution, black metallic mercury and mercuric amido chloride is obtained.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow \underset{\text{Black}}{[Hg + Hg(NH_2)Cl]} + NH_4Cl$$

---

5. **2072 Set D Q.No. 20 What happens when Corrosive sublimate is:** **[1+1]**
   i. **treated with excess KI solution?**
   ii. **heated with excess $SnCl_2$ solution.**

i. When corrosive sublimate is treated with excess KI solution, a complex potassium mercuric iodide is obtained which is called Nessler's reagent.

$$HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$$

$$HgI_2 + 2KI \xrightarrow{\text{Excess}} \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

ii. When corrosive sublimate is heated with excess $SnCl_2$ solution, metallic mercury is obtained

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \xrightarrow{\text{Excess}} \underset{\text{Metallic mercury}}{2Hg} + SnCl_4$$

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6. **2071 Supp. Q.No. 21ii Write an important use of corrosive sublimate** **[0.5]**

It is used in agriculture for fungicide.

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7. **2071 Supp. Q.No. 21iv Write an important use of calomel** **[0.5]**

It is used for making calomel electrode.

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8. **2071 Set D Q. No. 21 Write an important use of each of the followings:**
   b. **corrosive sublimate**
   d. **calomel** **[2]**

Use of:

a. Corrosive sublimate ($HgCl_2$): It is used to prepare Nessler's reagent.

b. Calomel (Hg_2Cl_2): It is used as fungicides.

9. **2070 Supp. Q. No. 21 Given a balanced chemical equation for the preparation of corrosive sublimate. What is its action on KI solution?** **[2]**

Calomel on strong heating gives corrosive sublimate.

$$\underset{\text{Calomel}}{Hg_2Cl_2} \xrightarrow{\text{Strongly heat}} \underset{\text{Corrosive sublimate}}{HgCl_2 + Hg}$$

Action of corrosive sublimate with KI solution: When KI is added to mercuric chloride solution then a scarlet ppt of mercuric iodide is formed which is dissolved in excess of KI to form a complex potassium mercuric iodide i.e. Nessler's reagent.

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\text{Scarlet ppt}}{HgI_2}$$

$$HgI_2 + \underset{\text{Excess}}{2KI} \longrightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

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10. **2070 Set C Q. No. 21 2070 Set D Q. No. 20 What is Nessler's reagent? How it is prepared?** **[2]**

Please refer to 2075 GIE Q.No. 20

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11. **2069 Supp. Set B Q. No. 21 What is meant by mercury poisoning?** **[2]**

Mercury poisoning (also known as hydrargyria or mercurialism) is type of metal poisoning and a medical condition caused by exposure to mercury or its compounds. Mercury is a heavy metal occurring in several forms, all of which can produce toxic effects in high enough doses.

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12. **2069 (Set A) Q. No. 21 How is corrosive sublimate converted into calomel and vice-versa?** **[2]**

Please refer to 2072 Set E Q.No. 21

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13. **2069 Set B Q. No. 21 How is Nessler's reagent prepared? Give its one use.** **[2]**

Please refer to 2075 GIE Q.No. 20

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14. **2068 Q. No. 18iii Give the molecular formula of: Nessler's reagent** **[1]**

The molecular formula of Nessler's reagent is K_2HgI_4 (potassium mercuric iodide).

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15. **2065 Q. No. 18 iv Write any one use of each of the following: Calomel** **[1]**

Calomel: It is used for making medicine.

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16. **2065 Q. No. 20 ii Give the balanced chemical equation: Corrosive Sublimate reacts with excess KI solution.** **[2]**

When KI is added to mercuric chloride solution then a scarlet ppt of mercuric iodide is formed which is dissolved in excess of KI to form a complex potassium mercuric iodide i.e. Nessler's reagent.

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\text{Scarlet ppt}}{HgI_2}$$

$$HgI_2 + \underset{\text{excess}}{2KI} \longrightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

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17. **2064 Q. No. 20i Write the action of Mercury with aqua regia.** **[1]**

Mercury reacts with aqua regia i.e. 3:1 ratio of HCl and HNO_3, mercuric chloride i.e. corrosive sublimate is formed.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + \underset{\text{Nitrosyl chloride}}{NOCl} + 2[Cl]$$

$$Hg + 2[Cl] \longrightarrow \underset{\text{Mercuric chloride}}{HgCl_2}$$

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18. **2062 Q. No. 20 ii Write an important use of each of the following substances:** **[1]**
    Corrosive sublimate

Corrosive sublimate: It is used for preparing Nessler's reagent.

19. **2061 Q. No. 20** **What happens when $HgCl_2$ is allowed to react with $SnCl_2$?** **[2]**

Mercuric chloride is reduced to mercury by stannous chloride.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

20. **2058 Q. No. 20** **What happens when mercuric chloride reacts with excess of KI solution?** **[2]**

Please refer to 2065 Q. No. 20 i

SHORT ANSWER QUESTIONS [5 MARKS]

21. **2076 Set C Q.No. 26** **Write the chemistry of corrosive sublimate.** **[5]**

Chemistry of corrosive sublimate:

Preparation:

1. It is prepared by heating mercury with chlorine.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

2. It is also prepared by treating mercury with aqua regia (1:3 vol. of HNO_3 and HCl)

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl$$

$$Hg + 2Cl \longrightarrow Hg\,Cl_2$$

3. It is also prepared by treating mercuric sulphate with sodium chloride

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

Physical properties

1. It is colourless crystalline solid.
2. It is slightly soluble in water.
3. It is extremely poisonous.

Chemical properties

1. **Action with $SnCl_2$:**

It reacts with $SnCl_2$ to give $SnCl_4$

$$\underset{\text{Mercuric chloride}}{2HgCl_2} + SnCl_2 \longrightarrow \underset{\text{Mercurous chloride}}{Hg_2Cl_2} + SnCl_4$$

2. **Action with KI solution:**

It reacts with KI solution to give scarlet ppt of mercuric iodide. When excess of KI solution is added, ppt dissolves due to the formation of complex potassium mercuric iodide

$$HgCl_2 + 2\,KI \longrightarrow \underset{\text{Scarlet ppt}}{HgI_2\downarrow} + 2\,KCl$$

$$HgI_2 + 2KI \longrightarrow \underset{\substack{\text{Potassium mercuric iodide}\\ \text{(Nessler's reagent)}}}{K_2HgI_4}$$

3. **Action with NaOH:**

It reacts with NaOH to give yellow ppt of mercuric oxide.

$$HgCl_2 + 2NaOH \longrightarrow \underset{\text{(Yellow ppt)}}{HgO} + 2NaCl + H_2O$$

4. **Action with ammonia:**

It reacts with ammonia to give white ppt of ammonobasic mercuric chloride

$$HgCl_2 + 2NH_3 \longrightarrow \underset{\substack{\text{Ammonobasic mercuric chloride}\\ \text{(White ppt)}}}{Hg(NH_2)Cl} + NH_4Cl$$

Uses:

i. It is used in agriculture for fungicide.
ii. It is used in button cells.
iii. It is used in prepare Nessler's reagent.

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22. **2074 Supp. Q.No. 26** **2074 Set A Q.No. 26** **Explain the process of extraction of mercury from cinnabar. Why is mercury called quick silver?** **[4+1]**

Extraction of mercury:

The most important ore of Hg is cinnabar (HgS).

Extraction: Hg is extracted from cinnabar ore by carbon reduction process. This process consists of the following steps:

a. **Concentration of cinnabar by froth floatation process:** Cinnabar is a sulphide ore and hence it is concentrated by froth floatation process.

b. **Roasting of the concentrated ore:** The concentrated ore is roasted in air when it gets oxidized to HgO and portion decomposes to Hg and O_2

$$2HgS + 3O_2 \xrightarrow[\Delta]{} 2HgO + 2SO_2\uparrow$$

$$2HgO \xrightarrow[\Delta]{} 2Hg + O_2\uparrow$$

c. **Smelting in a shaft furnace:** The roasted ore is mixed with coke and the mixture is heated in a shaft furnace to about 1000°C. Under this condition, HgO gets reduced to Hg.

$$HgO + C \longrightarrow Hg + O_2\uparrow$$

The vapours of Hg and CO are led into a tank containing water where mercury vapours condenses to form liquid mercury.

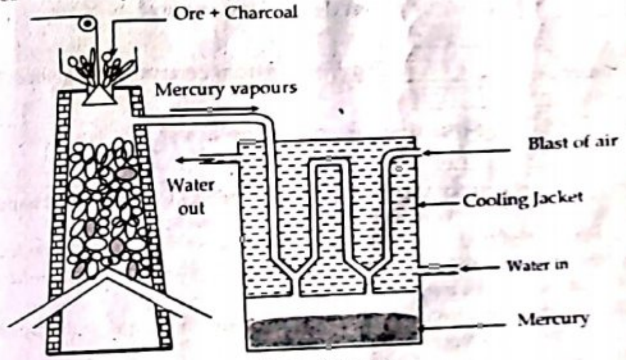

Fig: Shaft furnace

d. **Purification:** Mercury contains some solid as well as soluble base-metals impurities. It is purified in following steps:

i. **Filtration through chamois leather:** Impure mercury is filtered through a chamois leather bag when mercury filters out and solid impurities remain in the bag.

ii. **Treatment with 5% HNO_3:** The filtered Hg is treated with 5% HNO_3 when most of the base metals impurities dissolve in HNO_3 but Hg does not dissolve. This Hg is separated, washed with water and dried.

iii. **Distillation in vacuum:** The dry mercury is distilled in vacuum when very pure Hg is obtained.

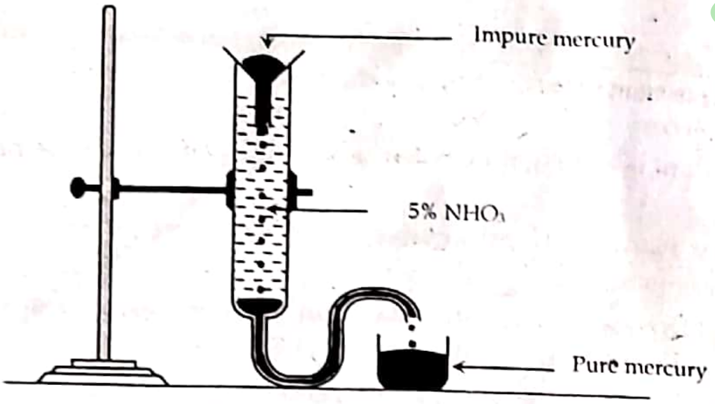

Fig: Purification of mercury

Mercury is called quick silver:

Mercury has long been known as quick silver, because it is a silver liquid. The chemical symbol also reflects this property. The symbol, Hg, comes from the Latin term hydrargyrum, meaning "watery silver."

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23. 2073 Supp Q.No. 25 2073 Set C Q.No. 25 **Write down the chemistry of corrosive sublimate.** **[5]**

✍ Please refer to 2073 Supp Q.No. 25

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24. 2070 Set D Q. No. 29 Or **How is mercury extracted from its ore and refined?** **[5]**

✍ Please refer to 2074 Supp. Q No. 26

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25. 2070 Supp. Q. No. 29 OR **Explain the process of extraction of mercury from its ore.** **[5]**

✍ Please refer to 2074 Supp. Q.No. 26

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26. 2070 Set C Q. No. 26 2069 (Set A) Q. No. 23 OR **How is mercury extracted from Cinnabar?** **[5]**

✍ Please refer to 2074 Supp. Q.No. 26

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27. 2069 Supp. Set B Q. No. 29 Or **How is mercury extracted from its ore?** **[5]**

✍ Please refer to 2074 Supp. Q.No. 26

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28. 2068 Q. No. 27 **Write one method of preparation of $HgCl_2$ and Hg_2Cl_2 of each. What happens when an aqueous solution of $HgCl_2$ is treated with:** **[5]**
   - i. **an aqueous solution of KI**
   - ii. **an aqueous solution of $SnCl_2$**

   What peculiar behaviour does mercury have?

✍ **Preparation of $HgCl_2$:** Mercuric chloride is prepared in large scale by heating the mercury in a current of chlorine.

$$Hg + Cl_2 \xrightarrow[\Delta]{} HgCl_2$$

Preparation of Hg_2Cl_2: Mercurous chloride is prepared by treating a solution of mercurous nitrate with HCl or NaCl.

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$

$$Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$$

i. When KI is added to mercuric chloride solution then a scarlet ppt of mercuric iodide is formed which is dissolved in excess of KI to form a complex potassium mercuric iodide i.e. **Nessler's reagent**.

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\text{Scarlet ppt}}{HgI_2}$$

$$HgI_2 + \underset{\text{excess}}{2KI} \longrightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

ii. Mercuric chloride is reduced to mercury by stannous chloride.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

Peculier behavior of Mercury: It can form alloy and called amalgam.

29. 2067 Q. No. 31 i **Write short notes on chemistry of calomel**

Preparation:

i. Mercurous chloride is prepared by treating a solution of mercurous nitrate with HCl or NaCl.

$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$

$Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$

ii. Mercurous chloride is prepared by heating a mixture of mercuric sulphate, mercury and common salt.

$HgSO_4 + 2NaCl + Hg \longrightarrow Hg_2Cl_2 + Na_2SO_4$

iii. Mercurous chloride is prepared by passing sulphur dioxide through the solution of mercuric chloride.

$2HgCl_2 + 2H_2O + SO_2 \longrightarrow Hg_2Cl_2 + H_2SO_4 + 2HCl$

Physical properties:

i. It is an amorphous and colourless white powder.

ii. It is non poisonous.

iii. It is springly soluble in water.

Chemical properties:

i. **With conc. HNO_3:** It dissolves in hot and conc. HNO_3 to give mercuric chloride.

$3Hg_2Cl_2 + 8HNO_3 \longrightarrow 3HgCl_2 + 3Hg(NO_3)_2 + 4H_2O + 2NO$

ii. **With aquaregia:** It dissolves in aquaregia to form mercuric chloride.

$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl$

$Hg_2Cl_2 + 2Cl \longrightarrow HgCl_2$

iii. **With ammonia:** When ammonia gas is passed through calomel then black metallic mercury and mercuric amido chloride is formed.

$Hg_2Cl_2 + 2NH_3 \longrightarrow [Hg + Hg(NH_2)Cl] + NH_4Cl$

Black [Mercury and mercuric amido chloride]

iv. **Action of heat:** It decomposes on heating into mercuric chloride.

$Hg_2Cl_2 \xrightarrow[\Delta]{} 2\,Hg + HgCl_2$

v. **With $SnCl_2$:** It is reduced to mercury with $SnCl_2$.

$SnCl_2 + Hg_2Cl_2 \longrightarrow 2Hg + SnCl_4$

Uses:

i. It is used for making medicine.

ii. It is used for making calomel electrode.

30. 2065 Q. No. 31 ii **Describe chemistry of calomel**

Please refer to 2067 Q. No. 31 i

[5]

31. 2064 Q. No. 31(iii) **Write short notes on Extraction of Hg**

Please refer to 2074 Supp. Q.No. 26

[5]

32. 2057 Q. No. 27 **Write two methods of preparation of corrosive sublimate. Give its action upon. (a) excess of KI and (b) NH_3.** [5]

Two method of Preparation of corrosive sublimate:

i. Mercuric chloride is prepared in large scale by heating the mercury in a current of chlorine.

$Hg + Cl_2 \xrightarrow[\Delta]{} HgCl_2$

ii. Mercuric chloride is prepared by heating a mixture of mercuric sulphate with common salt.

$$HgSO_4 + 2NaCl \xrightarrow[\Delta]{} HgCl_2 + Na_2SO_4$$

Action of corrosive sublimate upon:

a. **Excess of KI:** When KI is added to mercuric chloride solution then a scarlet ppt of mercuric iodide is formed which is dissolved in excess of KI to form a complex potassium mercuric iodide i.e. **Nessler's reagent.**

$$HgCl_2 + 2KI \longrightarrow 2KCl + \underset{\text{Scarlet ppt}}{HgI_2}$$

$$HgI_2 + \underset{\text{excess}}{2KI} \longrightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$$

b. **NH_3:** When ammonia gas is passed through mercuric chloride, white ppt of mercuric amido chloride is formed.

$$HgCl_2 + 2NH_3 \longrightarrow \underset{\text{White ppt}}{[Hg(NH_2)Cl]} + NH_4Cl$$

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33. 2055 Q. No. 24 **How is mercury extracted from its ore?**

➣ Please refer to 2074 Supp. Q.No. 26 [5]

34. 2053 Q. No. 20 **How is calomel prepared? Give its important properties & uses.**

➣ Please refer to 2067 Q. No. 31 i [5]

35. 2052 Q. No. 20 **Briefly describe the metallurgy of mercury.**

➣ Please refer to 2074 Supp. Q.No. 26 [5]

WRITE SHORT NOTES ON

36. 2076 Set B Q.No. 33ii 2071 Set D Q. No. 33 c 2069 (Set B) Q. No. 33b **Extraction of mercury from cinnabar**

➣ Please refer to 2074 Supp. Q.No. 26 [5]

37. 2072 Supp. Q.No. iv 2066 Q. No. 31 ii 2063 Q. No. 31(ii) 2059 Q. No. 31(d) 2062 Q. No. 31(b) 2058 Q. No. 31(b) **Extraction of mercury.**

➣ Please refer to 2074 Supp. Q.No. 26 [5]

38. 2072 Set E Q.No. 33ii 2061 Q. No. 31(i) 2056 Q. No. 31(b) **Chemistry of calomel.**

➣ Please refer to 2067 Q. No. 31 i [5]

39. 2071 Supp. Q.No. 33c **Chemistry of corrosive sublimate**

➣ Please refer to 2076 Set C Q.No. 26 [5]

40. 2054 Q. No. 30(a) **Purification of mercury**

➣ Please refer to 2074 Supp. Q.No. 26 [5]

18.4 Iron

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. 2076 Set B Q.No. 22 2076 Set C Q.No. 22 **What is meant by (i) quenching of steel. (ii) annealing of steel?** [1+1]

➣

i. **Quenching or hardening:** The process of heating steel to redness and then cooling it suddenly by plunging it in water or oil is called quenching. This makes steel extremely hard and brittle.

ii. **Annealing of steel:** The process of heating steel to bright redness followed by slow cooling is called annealing.

2. 2075 GIE Q.No. 22 **Give the composition and uses of wrought iron.** [1+1]

➣ The compositions of wrought iron are 99.99 % Fe and 0.05 - 0.25% C.It is used to make nuts and bolts.

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3. 2075 Set A Q.No. 22 **Give the compositions and important use of cast iron.** [1+1]

➣ The cast iron consists of 2.5 - 4.5 % carbon along with little quantity of Si, P, S, Mn etc as impurities. It is used for making pipes, heavier parts of machinery.

4. 2074 Supp. Q.No. 21 **Distinguish between quenching and tempering of steel.** [1+1]

➣ Following are the difference between quenching and tempering of steel.

Quenching of steel	Tempering of steel
It is the process of heating steel beyond critical temperature and cooling suddenly either plunging in oil or in water.	It is the process of heating steel below redness and then cooled slowly.
It makes steel very hard and used to make nail, chain, rail, beam, spring etc.	It makes steel neither too hard not too brittle.

5. 2074 Set A Q.No. 21 **What is the composition of stainless steel? Give an important use of such steel.** [1+1]

➣ **Composition of stainless steel:** Stainless steel contains about 12% Cr and 1 - 8% Ni and 0.2 to 0.3% carbon. It is used in the manufacture of household and hospital utensils.

Use of steel: It is used to make machinery parts.

6. 2074 Set B Q.No. 21 **Distinguish between quenching and tempering of steel.** [1+1]

➣ Please refer to 2074 Supp. Q.No. 21

7. 2073 Supp Q.No. 22 2073 Set C Q.No. 22 **Name any two important ores of iron. Which parts of Nepal are these ores mainly found?** [1+1]

➣ The two important ores of iron are Haematite (Fe_2O_3) and Magnetite (Fe_3O_4). In Nepal, iron ores are found mostly in the areas of Phulchoki of Lalitpur district (Bagmati), Tanhu of Gandaki Zone, Ramechhap of Janakpur zone and also in Piuthan, Bandipur.

8. 2073 Set D Q.No. 22 **Write down chemical reactions that occur in zone of reduction of blast furnace during extraction of iron.** [2]

➣ **Zone of reduction:** Temperature in the upper part of the blast furnace is 400-800°C. In this region of the furnace Fe_2O_3 is reduced to Fe by means of CO.

$$Fe_2O_3 + C \longrightarrow 2FeO + CO$$

$$FeO + CO \longrightarrow Fe + CO_2$$

9. 2072 Supp. Q.No. 20 **What is meant by Thomas Slag? Write its one use.** [1+1]

➣ **Thomas Slag:** The finely powdered basic slag obtained in the Thomas Gilchrist process. It consists of phosphates and is used as a fertilizer.

10. 2072 Set D Q.No. 22 **Write chemical reactions involved in zone of reduction of blast furnace during extraction of iron.** [2]

➣ Please refer to 2073 Set D Q.No. 22

11. 2072 Set E Q.No. 22 **What is the composition of stainless steel? Write its uses.** [1+1]

➣ Stainless steel contains about 12% Cr and 1 - 8% Ni and 0.2 to 0.3% carbon. It is used in the manufacture of household and hospital utensils.

12. 2071 Supp. Q.No. 20 **What is the composition of stainless steel? Write its one use.** [1+1]

➣ Please refer to 2072 Set E Q.No. 22

13. 2071 Set C Q. No. 20 **What is the composition of spiegeleisen? Write its one use.** [2]

➣ Spiegeleisen is an alloy of Fe, Mn and C. It is used for the manufacture of steel by Bessemer's process.

14. 2071 Set D Q. No. 20 **What is meant by quenching of steel?** [2]

➣ **Quenching or hardening:** The process of heating steel to redness and then cooling it suddenly by plunging it in water or oil is called quenching. This makes steel extremely hard and brittle.

15. **2070 Supp. Q. No. 20 What is the composition of steel? Write its one use.** [2]

➣ It contains 0.25 to 2 % of carbon along with small amount of other impurities such as Mn,Cr,Ni etc. It is used for making parts of machine.

16. **2070 Set C Q. No. 20 Differentiate between cast iron and wrought iron.** [2]

➣ Following are the difference between cast iron and wrought iron:

Cast iron	Wrought iron
i. It contains 2-5 % of carbon.	i. It contains 0.12 – 0.25 % carbon.
ii. It is difficult to weld and magnetize.	ii. It can easily weld and magnetize.

17. **2070 Set D Q. No. 22 Why is open-hearth process more advantageous than Bessemer process of manufacture of steel?** [2]

➣ The open hearth process is more advantageous than Bessemer converter process for the manufacture of steel due to following reasons:

i. Better quality of steel can be manufactured.
ii. Large quantity of steel can be manufactured in once operation.
iii. Low quality of iron ore or cast iron can be directly used.
iv. The temperature can be controlled.

18. **2069 (Set A) Q. No. 22 Write the molecular formula of:** [2]

i. Mohr's salt **ii. Green vitriol**

➣

i. Mohr's salt: $FeSO_4.(NH_4)_2SO_4.6H_2O$
ii. Green vitriol: $FeSO_4.7H_2O$

19. **2069 (Set B) Q. No. 20 iii Write the molecular formula of:** [1]

Mohr's salt

➣ Mohr's salt: $FeSO_4.(NH_4)_2SO_4.6H_2O$

20. **2069 Set B Q. No. 22 Write chemical reaction occurring in zone of reduction in the extraction of iron.** [2]

➣ Please refer to 2073 Set D Q.No. 22

21. **2068 Q. No. 19 What is meant by tempering of steel? Mention one important use of tempered steel.** [2]

➣ The process of heating the quenched steel to a temperature much below redness and then cooling it slowly is called tempering. Such steel is neither so hard nor so brittle.

Use: It is used for making automobile parts.

22. **2067 Q. No. 20 What reaction occurs in the combustion zone in the blast furnace during extraction of iron?** [2]

➣ In the combustion zone during the extraction of iron, carbon burns with air to form carbon dioxide and high heat energy.

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$

23. **2066 Q. No. 18 ii Name one important ore of each of the followings: Iron** [2]

➣ Iron is a reactive metal and hence it does not occur in the form of metal in nature. Its important ores are the following:

a. Rede Haemetite Fe_2O_3
b. Brown Haemetite $2Fe_2O_3.3H_2O$
c. Magnetite Fe_3O_4

24. **2066 Q. No. 20 Mention the function of Spiegeleisen in the manufacture of Steel.** [2]

➣ Spiegeleisen is an alloy of Fe, Mn and C. It is used for the manufacture of steel by Bessemer's process. During the process cast iron is heated in a Bessemer's converter by a hot blast of air. The disappearance of blue flame indicates the complete oxidation of carbon. At this stage, the spiegeleisen is added to give the fixed concentration of carbon in iron. The major function of spiegeleisen in the manufacture of steel is to convert the iron into steel.

25. **2065 Q. No. 19 Define Rusting of iron.** [2]

➣ When iron is exposed on moist air for a long time, a reddish brown layer is coated on the outer surface of iron. The reddish brown coating is called rust. The formation of rust on the surface of iron is called rusting of iron. The hydrated ferric oxide is called rust i.e. $Fe_2O_3.x\,H_2O$.

26. **2063 Q. No. 19a What happens when: Few drops of potassium ferrocyanide is added to aqueous solution of FeCl₃.** [2]

➣ When few drops of $K_4[Fe(CN)_6]_3$ is added to aq. Solution of $FeCl_3$ then Prussian blue ppt of ferroso ferricyanide is obtained.

$$\underset{\text{Ferric chloride}}{4FeCl_3} + \underset{\text{Pot.ferrocyanide}}{3K_4[Fe(CN)_6]} \longrightarrow \underset{\substack{\text{Prussian blue ppt}\\\text{Ferroso ferricyanide}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

27. **2062 Q. No. 20 iv Write an important use of each of the following substances: Wrought iron** [2]

➣ Wrought iron: It is used in making electromagnets.

28. **2061 Q. No. 19 Write two methods by which rusting of iron can be prevented.** [2]

➣ Prevention from rusting

a. By galvanizing iron with Zn or Sn.
b. By covering iron surface with paint, coal tar, liquor etc.

29. **2060 Q. No. 19 What is tempering of steel?** [2]

➣ The process of heating the quenched steel to a temperature much below redness and then cooling it slowly. Such steel is neither so hard nor so brittle.

30. **2059 Q. No. 19 What is stainless steel?** [2]

➣ The alloy of steel which contains about 11 - 12 % Cr, 8% Ni and 0.08 - 10% C. It is not corroded by atmospheric moisture, acids and bases. It is used to make house-hold utensils, watch, automobiles parts etc.

31. **2057 Q. No. 19 Write two methods of prevention of corrosion.** [2]

➣ Please refer to 2061 Q. No. 19

32. **2056 Q. No. 13 What is the function of limestone in the smelting of iron?** [2]

➣ The function of lime stone in smelting of iron is to remove acidic impurities present.

$$\underset{\text{Lime stone}}{CaCO_3} \xrightarrow{1000^\circ C} CaO + CO_2$$

$$\underset{\text{Flux}}{CaO} + \underset{\text{Impurities}}{SiO_2} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

33. **2055 Q. No. 10 Give two ways to prevent corrosion.** [2]

➣ Please refer to 2061 Q. No. 19

34. **2054 Q. No. 9 What is a transition element? Mention two of its important characteristics.** [2]

➣ The elements having partially i.e. incompletely filled d-orbital is called transition element. They are commonly known as d-block elements.

Two important characteristics:

a. The outer most electronic configuration of transition element is $(n-1)d^{1-10}, n^{1-2}$
b. They are generally used as catalyst during chemical reaction.

35. **2053 Q. No. 18 Write the principle involved in manufacture of steel by Open Hearth process.** [2]

➣ Following are the basic principle involved in the manufacture of steel by open hearth process:

i. The hearth of furnace is lined with magnesite in basic process and with silica in acid process.
ii. The charge consists of 70-80% cast iron, 20-30% scrap iron and little haematite.
iii. The charge is heated by producer gas.

36. **2053 Q. No. 17 Give two methods for preventing rusting of iron.** [2]

➣ Please refer to 2061 Q. No. 19

SHORT ANSWER QUESTIONS [5 MARKS]

37. 2075 GIE Q.No. 26 **How is Steel manufactured by Open-Hearth process?** [5]

Open- Hearth process:

In this process, a mixture of cast iron, steel, iron ore and lime is charged in a open hearth furnace. The furnace is lined with dolomite or silica depending upon the nature of impurities present in cast iron. The mixture and air is passed through the furnace at 1500°C. The impurities are oxidized by iron ore and removed as slag or gases.

$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$

$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$

$10Fe_2O_3 + 6P \longrightarrow 20Fe + 6P_2O_5$

$2P_2O_5 + 6CaO \longrightarrow 2Ca_3(PO_4)_2$

$2P_2O_5 + 6MgO \longrightarrow 2Mg_3(PO_4)_2$

$2Fe_2O_3 + 3Si \longrightarrow 4Fe + 3SiO_2$

$SiO_2 + CaO \longrightarrow CaSiO_3$

$Fe_2O_3 + 3Mn \longrightarrow 2Fe + 3MnO$

$MnO + SiO_2 \longrightarrow MnSiO_3$

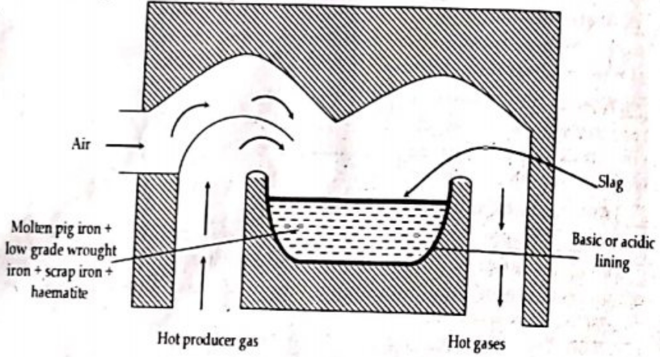

Fig: Open hearth process

38. 2075 Set A Q.No. 26 **How is steel manufactured by Open Hearth process?** [5]

Please refer to 2075 GIE Q No. 26

39. 2075 Set B Q.No. 26 **How is steel manufactured by Open Hearth process? Write the composition of stainless steel.** [4+1]

Manufacture of steel by Open-Hearth process: Please refer to 2075 GIE Q.No. 26

Composition of stainless steel: 12 % Cr + 1 - 8 % Ni + 0.2 - 0.3 % C.

40. 2071 Set C Q. No. 28 **How is cast iron extracted from Iron pyrites?** [5]

Occurrence: Iron is a reactive metal and hence it does not occur in the form of metal in nature. Its important ores are the following:

1. Red Haemetite Fe_2O_3
2. Brown Haemetite $2Fe_2O_3.3H_2O$
3. Magnetite Fe_3O_4

Extraction: Most of iron is extracted from Fe_2O_3 ore by Carbon reduction process.

Carbon reduction process: It involves the following process.

1. **Washing the ore:** The ore is washed with stream of water to remove earthy and silicious gangue.
2. **Calcination:** The ore is heated in air to remove moisture and other volatile impurities from it. Sulphur burns away as SO_2 and arsenic away as As_2O_3 vapours.

$S + O_2 \longrightarrow SO_2$

$4As + 3O_2 \longrightarrow 2As_2O_3$

3. **Smelting:** The calcinated ore is mixed with coke and lime stone and the mixture is heated in a blast furnace in a blast of hot air. The following reactions occur in different zones of the blast furnace.

a. **Zone of combustion:** This region lies near the heart of furnace. Carbon burns in hot air to form CO and CO_2 and produces a lot of heat.

$2C + O_2 \xrightarrow[\Delta]{} 2CO + 58\ Kcal$

$C + O_2 \xrightarrow[\Delta]{} CO_2 + 97\ Kcal$

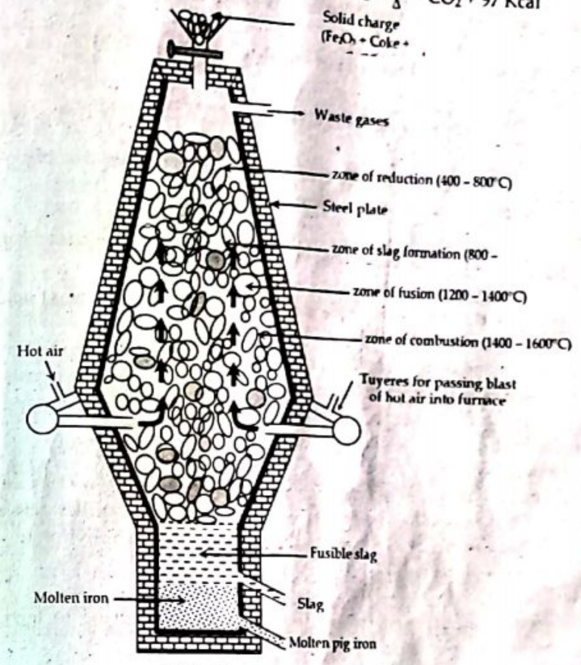

Fig: Blast Furnace

b. **Zone of reduction:** Temperature in the upper part of the blast furnace is 400-800° C. In this region of the furnace Fe_2O_3 is reduced to Fe by means of CO.

$Fe_2O_3 + C \longrightarrow 2FeO + CO$

$FeO + CO \longrightarrow Fe + CO_2$

c. **Zone of slag formation:** In this region of the furnace temperature is about 800-1200°C. At this temperature $CaCO_3$ flux decomposes to CaO and CO_2.

$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2$

The basic CaO then combines with the acidic gangue such as P_2O_5 and SiO_2 present in the ore to form $Ca_3(PO_4)_2$ and $CaSiO_3$ slag.

$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2$ Slag

$CaO + SiO_2 \longrightarrow CaSiO_3$ slag

d. **Zone of fusion:** In this region of the furnace temperature is 1200-1400°C. The iron melts in this zone and absorbs C. Si, P, S, Mn etc. In this way molten pig iron is obtained. This collects in the hearth lighter with slag. Thus, two layer of molten material collect in the hearth. The lower layer is that of molten pig iron and upper layer is that of molten slag. The slag is removed from upper slag hole and molten pig iron is obtained from the lower tapping hole present in the hearth.

$SiO_2 + 2C \longrightarrow Si + 2CO$

$MnO + C \longrightarrow Mn + CO$

$P_2O_5 + 5C \longrightarrow 2P + 5CO$

e. **Purification:** Iron is generally purified by hammering or polling process. In this process red hot pig iron is hammered with heavy steam hammers when most of the impurities are thrown out and white shining sheet of 90% pure iron is obtained which is called wrought iron.

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41. 2071 Set D Q. No. 26 How is cast iron extracted from Iron pyrites? **[5]**

✍ Please refer to 2071 Set C Q. No. 28

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42. 2067 Q. No. 31 iii Write short notes on manufacture of steel by Open Hearth process. **[5]**

✍ Please refer to 2075 GIE Q No. 26

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43. 2065 Q. No. 31 iii Describe the Manufacture of steel by Open Hearth Process **[5]**

✍ Please refer to 2075 GIE Q.No. 26

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44. 2064 Q. No. 27 Draw a neat labelled sketch of blast furnace for the extraction of pig iron and write down the chemical reactions involved at different zones.

✍ Please refer to 2071 Set C Q. No. 28

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45. 2063 Q. No. 27 How is steel manufactured by open hearth process? What is quenching of steel? **[5]**

✍ Please refer to 2075 GIE Q.No. 26

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46. 2059 Q. No. 27 What is rusting? Describe electrochemical theory of rusting of iron. List any two methods of prevention of rusting. **[5]**

✍ **Rusting of iron and its prevention:** When iron is exposed on moist air for a long time, a reddish brown layer is coated on the outer surface of iron is called rust. The reddish brown coating is called rust. The formation of rust on the surface of iron is called rusting of iron. The hydrated ferric oxide is called rust i.e. $Fe_2O_3.x\,H_2O$.

There are two theories

Electrochemical Theory: When impure iron comes in contact with water containing dissolved CO_2 then a voltaic cell is set up. The iron and impurities acts as electrodes while water has dissolved oxygen and carbon dioxide acts as an electrolyte.

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode: $H_2O + O + 2e^- \longrightarrow 2OH^-$

In the presence of dissolved oxygen, ferrous ions are oxidized to ferric ion which combines with hydroxyl ion to form ferric hydroxide.

$2Fe^{2+} + H_2O + O \longrightarrow 2Fe^{3+} + 2OH^-$

$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3$ or $3Fe_2O_3.3H_2O$ (Rust)

Chemical Theory: The presence of CO_2 and water forms carbonic acid which combines with iron to form ferrous bicarbonate.

$CO_2 + H_2O \longrightarrow H_2CO_3$

$Fe + H_2CO_3 \longrightarrow \underset{\text{Ferrous bicarbonate}}{Fe(HCO_3)_2} + H_2$

The ferrous bicarbonate is precipitated to ferric hydroxide in the presence of water and oxygen.

$4Fe(HCO_3)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3 + 8CO_2$

Prevention from rusting:

1. By galvanizing iron with Zn or Sn.
2. By covering iron surface with a paint,coal tar,liquor etc.
3. By electroplating iron surface with Ni,Cr,Cu etc.

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47. 2056 Q. No. 23 How is steel manufactured by Open hearth process? Mention its advantage over Bessemer process. **[5]**

✍ **Open- Hearth process:** Please refer to 2075 GIE Q.No. 26

Advantage of the open hearth process over Bessemer converter process:

a. Better quality of steel can be manufactured.
b. Large quantity of steel can be manufactured in once operation.
c. Low quality of iron ore or cast iron can be directly used.
d. The temperature can be controlled.

48. **2052 Q. No. 21 Explain any four methods for preventing rusting of iron.** **[5]**

Following are four methods for preventing rusting of iron:

a. **Galvanization:** Iron metal is coated with thin film of zinc metal for preventing rusting.

b. **Application of antirust solution:** Iron metal is treated with antirust solution like conc.HNO_3, H_3PO_4, $K_2Cr_2O_7$ for preventing rusting.

c. **Cathodic protection:** Iron metal is used as cathode and other more electropositive metal like Mg,Zn,Al etc. acts as anode and electropositive cell is established. More electropositive metal is coated on the surface of iron and prevent from rusting.

d. **Protective coating:** Iron metal can be prevented from rusting by coating the surface with non-coroding metal like Ni,Cr,Zn etc. or by coating with oil, grease, paints, varnishes, enamels etc. or deposition of thin layer of oxide film over the surface of iron like Fe_3O_4.

LONG ANSWER QUESTIONS [10 MARKS]

49. **2055 Q. No. 29 Describe the extraction of iron from its' principal ores, giving a neat sketch of the furnace used and the probable reactions occurring their in.** **[10]**

Please refer to 2071 Set C Q. No. 28

50. **2054 Q. No. 29 How is cast iron produced from iron ore? Discuss the reactions involved.** **[10]**

Please refer to 2071 Set C Q. No. 28

WRITE SHORT NOTES ON [5 MARKS]

51. **2076 Set B Q.No. 33i 2076 Set C Q.No. 33i Chemistry of rusting theory of iron** **[5]**

Please refer to 2059 Q. No. 27

52. **2074 Supp. Q.No. 33(iii) 2074 Set A Q.No. 33a 2074 Set B Q.No. 33a Theory of corrosion in iron** **[5]**

Please refer to 2059 Q. No. 27

53. **2073 Supp Q.No. 33ii 2069 (Set B) Q. No. 33c 2061 Q. No. 31(ii) Manufacture of steel by Bassemer's process.** **[5]**

Bessemer-Converter process: In this process the molten cast iron is poured into a large egg shaped Bessemer converter. It is made up of steel and outer surface is lined with fire bricks silica. When the impurities are Mn,Si,C etc. then Bessemer converter is lined with silica and the impurities are P,S,C etc. then the Bessemer converter is lined with dolomite and the corresponding process is called acidic and basic process respectively. The converter is mounted on horizontal axis. A blast of hot air under pressure is passed through the molten cast iron.

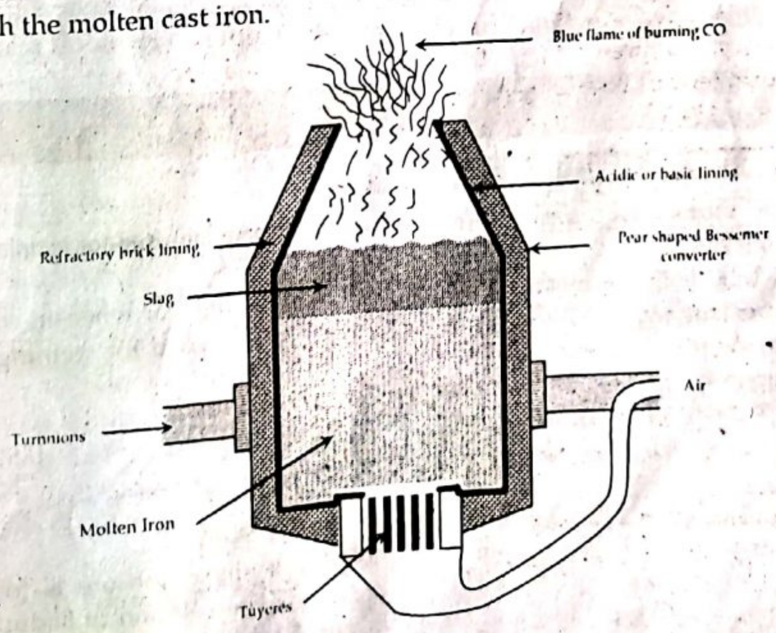

Fig: Bessemer Converter

Following reaction occurs.

Acidic Bessemerization process

$2C + O_2 \longrightarrow 2CO$

$2Mn + O_2 \longrightarrow 2MnO$

$Si + O_2 \longrightarrow SiO_2$

$MnO + SiO_2 \longrightarrow MnSiO_3$ (slag)

Basic Bessemetrization process

$2C + O_2 \longrightarrow 2CO$

$S + O_2 \longrightarrow SO_2$

$P_4 + 5O_2 \longrightarrow 2P_2O_5$

$6CaO + 2P_2O_5 \longrightarrow 2Ca_3(PO_4)_2$(slag)

$6MgO + 2P_2O_5 \longrightarrow 2Mg_3(PO_4)_2$ (slag)

54. **2073 Set C Q.No. 33ii 2072 Set E Q.No. 33i 2070 Supp. Q. No. 33 d 2069 Supp. Set B Q. No. 33 a Manufacture of steel by Open-hearth process.**

Please refer to 2075 GIE Q.No. 26

55. **2073 Set D Q.No. 33ii 2072 Set C Q.No. 33a 2072 Set D Q.No. 33b 2070 Set D Q. No. 33 b 2069 (Set A) Q. No. 33 a 2066 Q. No. 31 iii 2060 Q. No. 31(iii) 2058 Q. No. 31(c) Rusting of iron**

Please refer to 2059 Q. No. 27

56. **2072 Supp. Q.No. 33iii Chemistry of Open Hearth process for the manufacture of steel.** [5]

Please refer to 2075 GIE Q.No. 26

57. **2070 Set C Q. No. 33 a or Theory of corrosion.** [5]

Please refer to 2059 Q. No. 27

58. **2068 Q. No. 31ii Rusting of iron and its prevention.** [5]

Please refer to 2059 Q. No. 27

59. **2055 Q. No. 31(b) Definition and general properties of Transition elements.** [5]

Transition elements: Those elements which have partially filled d-orbitals in metallic state is called transition elements.

General properties:

a. Transition elements have high melting and boiling point.
b. Salts of transition elements are coloured in the solid state.
c. The compounds of transition elements show paramagnetic behavior.
d. Transition elements exhibit variable oxidation states.
e. Transition elements have ability to act as catalyst in different chemical reactions.

18.5 Silver

VERY SHORT ANSWER QUESTIONS [2 MARKS]

1. **2076 Set B Q.No. 21 2076 Set C Q.No. 21 Why is silver nitrate solution used for staining fingers of voters during election?** [2]

Silver nitrate is reduced to metallic silver on exposure to light or when in contact with organic matter. Due to this silver nitrate solution is widely used for staining fingers of voters during election.

$$2\,AgNO_3 \xrightarrow[\text{Light}]{\text{Organic matter}} \underset{\text{Black}}{2\,Ag\downarrow} + 2\,NO_2 + O_2$$

2. **2075 GIE Q.No. 21 2075 Set A Q.No. 21 What is meant by 'Spongy Silver'?** [2]

During the extraction of silver from Argentite ore of silver, the ore is treated with sodium cyanide, sodium argento cyanide is obtained. The solution of sodium argento cyanide combines with zinc dust and forms sodium tetra cyanozincate and precipitated silver. This precipitated silver is called spongy silver.

$$\underset{\text{Argentite}}{Ag_2S} + 4\,NaCN \rightleftharpoons \underset{\text{Sod. argento cyanide}}{2\,Na[Ag(CN)_2]} + Na_2S$$

$$\underset{\text{Sod. argento cyanide}}{2\,Na[Ag(CN)_2]} + Zn \longrightarrow \underset{\text{Sod. tetra cyanozincate}}{Na_2[Zn(CN)_4]} + \underset{\text{Spongy silver}}{2\,Ag\downarrow}$$

3. **2075 Set B Q.No. 21 Silver nitrate solution is widely used for staining fingers of voters durin electron. Give reason.** [2

Please refer to 2076 Set B Q.No. 21

4. **2072 Set C Q.No. 21 Give reason: Silver nitrate produces permanent black stain on the skin?** [1]

Silver nitrate is reduced to metallic silver on exposure to light or when in contact with organic matter. A black stain is, therefore, produced on skin when it comes into contact with clothes or skin in the presence of sunlight.

$$2AgNO_3 \xrightarrow[\text{Light}]{\text{Organic compound}} \underset{\text{black}}{2Ag\downarrow} + 2NO_2 + O_2$$

5. **2072 Set D Q.No. 21 Why does silver nitrate produces permanent black stain on the skin? Write an important use of silver nitrate.** [1+1]

Silver nitrate produces permanent black stain: Please refer to 2072 Set C Q.No. 21

Use of Silver nitrate:

i. Silver halides especially silver bromide prepared from $AgNO_3$ are used in photography.
ii $AgNO_3$ is used as laboratory reagent in the detection of halides ion in the salt sample.

6. **2064 Q. No. 18 Why does Silver nitrate solution produce black-stain on the skin in presence of sun light?** [2]

Please refer to 2072 Set C Q.No. 21

7. **2062 Q. No. 18 What is the action of heat on silver nitrate?** [2]

When silver nitrate is heated above its m.p. (212°C) it is decomposed to $AgNO_2$ and O_2.

$$2AgNO_3 \xrightarrow{212^\circ C} 2AgNO_2 + O_2$$

When it is heated further to redness at 450°C, it gives metal silver.

$$2\,AgNO_3 \xrightarrow[\Delta]{} 2\,Ag + 2\,NO_2 + O_2$$

8. **2061 Q. No. 9 (f) What do you mean by noble metals? Give any two examples.** [2]

The metals which are unreactive towards acids, bases and salts solution are called noble metals. They are Gold (Au), Platinum (Pt) and Palladium (Pd).

9. **2058 Q. No. 12 What happens when $AgNO_3$ is heated at 450°C.**

Please refer to 2062 Q. No. 18

10. **2055 Q. No.20 Give two uses of silver nitrate.** [2]

The two uses are

i. Silver halides especially silver bromide prepared from $AgNO_3$ are used in photography.
ii $AgNO_3$ is used as laboratory reagent in the detection of halides ion in the salt sample.

11. **2053 Q. No. 19 Group A How is presence of halide ions are tested with silver nitrate solution?** [2]

In order to test the halides ions present in the given solution, about 1 mL of given solution is taken is clean test tube and about 2-3 drops of silver nitrate solution is added. The colours of ppt formed indicates the presence of halides ion in the given solution.

Following are the reactions:

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + NO_3^-$$

$$AgNO_3 + Br^- \longrightarrow \underset{\text{Pale yellow ppt}}{AgBr\downarrow} + NO_3^-$$

$$AgNO_3 + I^- \longrightarrow \underset{\text{Yellow ppt}}{AgI\downarrow} + NO_3^-$$

12. **2053 Q. No. 22 Group A** **Why silver ores are leached with metal cyanides for the extraction of silver? [2]**

Silver metal can be extracted from sulphide ore Argentite or silver glance (Ag_2S). The argentite ore is treated with 0.4 to 0.7 % NaCN by blowing a current of air, sodium argento cyanide is obtained

$$Ag_2S + 4NaCN \longrightarrow \underset{\text{Sod. argentocyanide}}{2Na[Ag(CN)_2]} + NaCl$$

Sod. argentocyanide is treated with more electropistive metal zinc which displaces silver from solution.

$$2Na[Ag(CN)_2] + Zn \longrightarrow 2\,Ag + \underset{\text{Sod. zincocyanide}}{Na_2\,[Zn(CN)_4]}$$

13. **2053 Q. No. 25** **What do you mean by noble metals? Name at least three noble metals you know. [2]**

The metals which are unreactive towards acids, bases and salts solution are called noble metals. They are Gold (Au), Platinum (Pt) and Palladium (Pd).

LONG ANSWER QUESTIONS [5 MARKS]

14. **2054 Q. No. 25** **Give the various steps involved in the extraction of silver from silver glance. [5]**

Extraction principle of silver from silver glance:

Most of Ag is extracted from silver glance ore by **Mac Arthur cyanide process.** In this process following steps is used:

1. Concentration of argentite ore by froth floatation process.
2. Dissolution of the concentrated ore in 0.6% NaCN solution.

$$Ag_2S + 4NaCN \longrightarrow \underset{\substack{\text{Sodium argento}\\\text{Cyanide sol}^{n}}}{2Na[Ag(CN)_2]} + Na_2S$$

The solution is filtered and the filtrate is used for the recovery of silver.

3. **Precipitation of Ag by Zn:** The filtrate containing $Na[Ag(CN)_2]$ and Na_2S is treated with zinc when silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \longrightarrow \underset{\text{Sod.zincocyanide}}{Na_2[Zn\,(CN)_4]} + 2Ag\downarrow$$

The precipitated silver is filtered, dried and purified by electrolysis. The excess zinc dissolves in the alkaline medium.

$$Na_2S + 2H_2O \longrightarrow 2NaOH + H_2S\uparrow$$

$$Zn + 2\,NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2\uparrow$$

4. **Purification:** It is purified by electrolysis. $AgNO_3$ solution acidified with dilute HNO_3 is used as the electrolyte. Rods of impure Ag are made anodes and then sheets of pure Ag are made cathodes. On electrolysis impure Ag anodes dissolve and pure silver is deposited at the cathodes.

At cathode: $Ag^+ + e^- \longrightarrow Ag$

At anode: $Ag \longrightarrow Ag^+ + e^-$

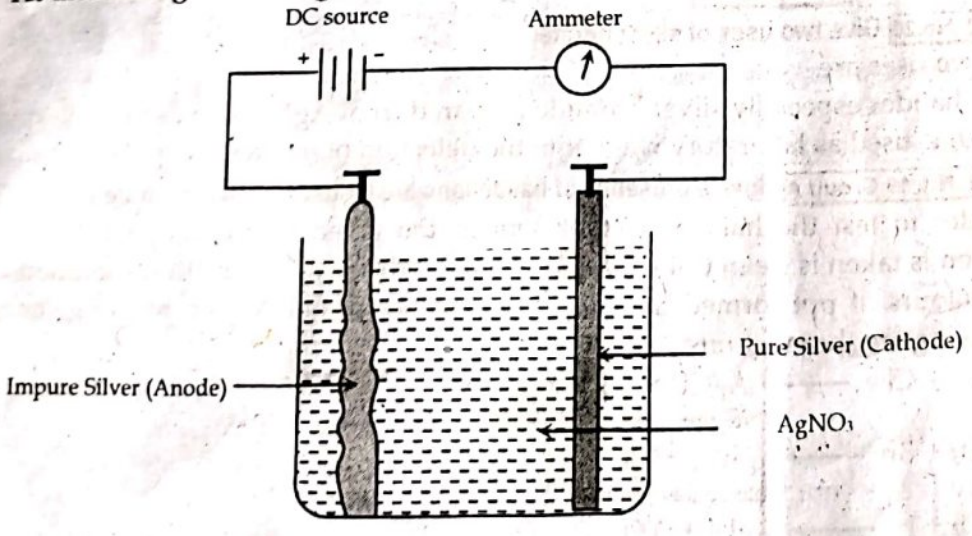

Fig: Electro-refining

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