Chemistry

(Chapter – 12) (Organic Chemistry – Some Basic Principles and Techniques)

(Class – XI)

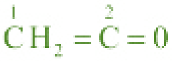
Exercises

Question 12.1:
What are hybridisation states of each carbon atom in the following compounds?

$CH_2{=}C{=}O$, $CH_3CH{=}CH_2$, $(CH_3)_2CO$, $CH_2{=}CHCN$, C_6H_6

Answer 12.1:

(i)



$\overset{1}{C}H_2=\overset{2}{C}=O$

C–1 is *sp*^{2} hybridised.

C–2 is *sp* hybridised.

(ii)

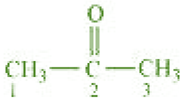
$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H_2$

C–1 is *sp*^{3} hybridised.

C–2 is *sp*^{2} hybridised.

C–3 is *sp*^{2} hybridised.

(iii)



$\underset{1}{CH_3}-\underset{2}{\overset{\overset{\displaystyle O}{\|}}{C}}-\underset{3}{CH_3}$

C–1 and C–3 are *sp*^{3} hybridised.

C–2 is *sp*^{2} hybridised.

(iv)

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}\equiv N$

C–1 is *sp*^{2} hybridised.

C–2 is *sp*^{2} hybridised.

C–3 is *sp* hybridised.

(v) C_6H_6
All the 6 carbon atoms in benzene are *sp*^{2} hybridised.

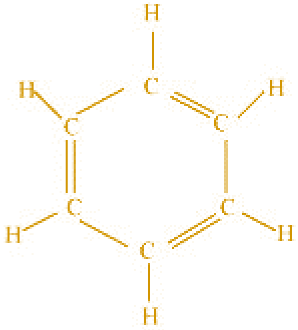
Question 12.2:

Indicate the σ and π bonds in the following molecules:

C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2 = C = CH_2$, CH_3NO_2, $HCONHCH_3$

Answer 12.2:

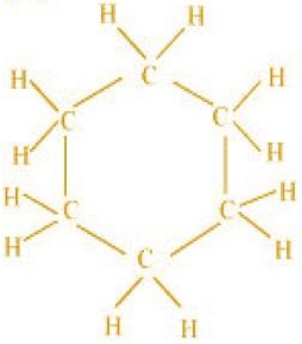
(i) C_6H_6



)

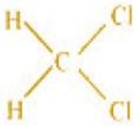
There are six C – C sigma (σ_{C-C}) bonds, six C–H sigma (σ_{C-H}) bonds, and three C=C pi (π_{C-C}) resonating bonds in the given compound.

(ii) C_6H_{12}



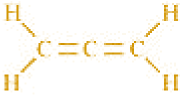
There are six C – C sigma (σ_{C-C}) bonds and twelve C–H sigma (σ_{C-H}) bonds in the given compound.

(iii) CH_2Cl_2



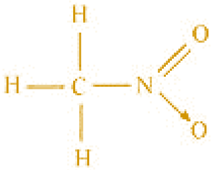
There two C–H sigma (σ_{C-H}) bonds and two C–Cl sigma (σ_{C-Cl}) bonds in the given compound.

(iv) $CH_2 = C = CH_2$



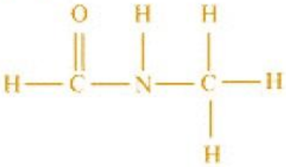
There are two C–C sigma (σ_{C-C}) bonds, four C–H sigma (σ_{C-H}) bonds, and two C=C pi (π_{C-C}) bonds in the given compound.

(v) CH_3NO_2



There are three C–H sigma (σ_{C-H}) bonds, one C–N sigma (σ_{C-N}) bond, one N–O sigma (σ_{N-O}) bond, and one N=O pi (π_{N-O}) bond in the given compound.

(vi) $HCONHCH_3$



There are two C–N sigma (σ_{C-N}) bonds, four C–H sigma (σ_{C-H}) bonds, one N–H sigma (σ_{N-H}) bond, and one C=O pi (π_{C-O}) bond in the given compound.

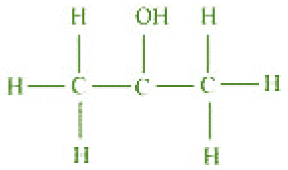
Question 12.3:

Write bond line formulas for: Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

Answer 12.3:

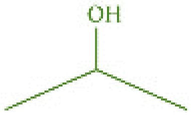
The bond line formulae of the given compounds are:

(a) Isopropyl alcohol

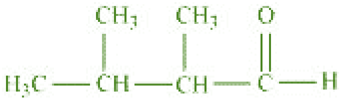


$$H-\overset{H}{\underset{H}{C}}-\overset{OH}{C}-\overset{H}{\underset{H}{C}}-H$$

⇒

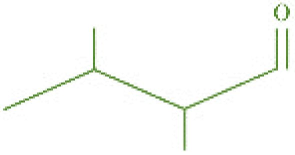


(b) 2, 3–dimethyl butanal

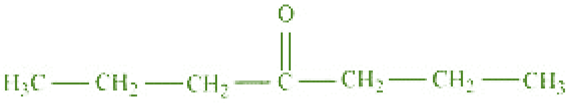


$$H_3C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-H$$

⇒

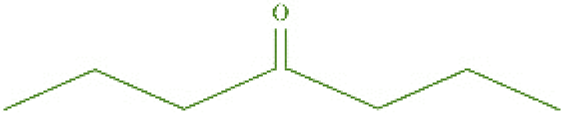


(c) Heptan–4–one



$$H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$$

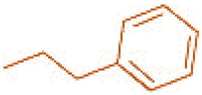
⇒



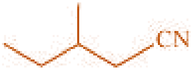
Question 12.4:

Give the IUPAC names of the following compounds:

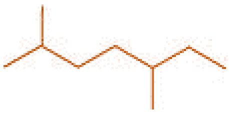
(a)



(b)

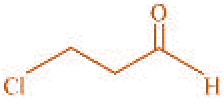


(c)



(d)

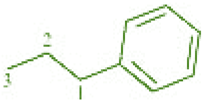
(e)



(f) Cl_2CHCH_2OH

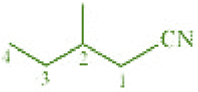
Answer 12.4:

(a)



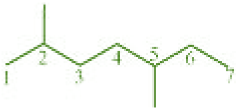
3–phenyl propane

(b)



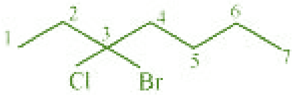
2–methyl–1–cyanobutane

(c)



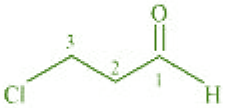
2, 5–dimethyl heptane

(d)



3–bromo–3–chloroheptane

(e)



3–chloropropanal

(f) Cl_2CHCH_2OH

1, 1–dichloro–2–ethanol

Question 12.5:

Which of the following represents the correct IUPAC name for the compounds concerned?

(a) 2,2-Dimethylpentane or 2-Dimethylpentane

(b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

(c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane

(d) But-3-yn-1-ol or But-4-ol-1-yne

Answer 12.5:

(a) The prefix *di* in the IUPAC name indicates that two identical substituent groups are present in the parent chain. Since two methyl groups are present in the C–2 of the parent chain of the given compound, the correct IPUAC name of the given compound is 2, 2–dimethylpentane.

(b) Locant number 2, 4, 7 is lower than 2, 5, 7. Hence, the IUPAC name of the given compound is 2, 4, 7–trimethyloctane.

(c) If the substituents are present in the equivalent position of the parent chain, then the lower number is given to the one that comes first in the name according to the alphabetical order. Hence, the correct IUPAC name of the given compound is 2–chloro– 4–methylpentane.

(d) Two functional groups – alcoholic and alkyne – are present in the given compound. The principal functional group is the alcoholic group. Hence, the parent chain will be suffixed with *ol*. The alkyne group is present in the C–3 of the parent chain. Hence, the correct IUPAC name of the given compound is But–3–yn–1–ol.

Question 12.6:

Draw formulas for the first five members of each homologous series beginning with the following compounds.

(a) H–COOH

(b) CH_3COCH_3

(c) H–CH=CH_2

Answer 12.6:

The first five members of each homologous series beginning with the given compounds are shown as follows:

(a)

H–COOH : Methanoic acid

CH_3–COOH : Ethanoic acid

CH_3–CH_2–COOH : Propanoic acid

CH_3–CH_2–CH_2–COOH : Butanoic acid

CH_3–CH_2–CH_2–CH_2–COOH : Pentanoic acid

(b)

CH_3COCH_3 : Propanone $CH_3COCH_2CH_3$

: Butanone

$CH_3COCH_2CH_2CH_3$: Pentan-2-one

$CH_3COCH_2CH_2CH_2CH_3$: Hexan-2-one

$CH_3COCH_2CH_2CH_2CH_2CH_3$: Heptan-2-one

(c)

H–CH=CH_2 : Ethene

CH_3–CH=CH_2 : Propene

CH_3–CH_2–CH=CH_2 : 1-Butene

CH_3–CH_2–CH_2–CH=CH_2 : 1-Pentene

CH_3–CH_2–CH_2–CH_2–CH=CH_2 : 1-Hexene

Question 12.7:

Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for:

(a) 2,2,4-Trimethylpentane

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

(c) Hexanedial

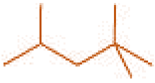
Answer 12.7:

(a) 2, 2, 4–trimethylpentane

Condensed formula

$(CH_3)_2CHCH_2C\ (CH_3)_3$

Bond line formula



(b) 2–hydroxy–1, 2, 3–propanetricarboxylic acid

Condensed Formula

$(COOH)CH_2C(OH)\ (COOH)CH_2(COOH)$

Bond line formula:

The functional groups present in the given compound are carboxylic acid (–COOH) and alcoholic (–OH) groups.

(c) Hexanedial

Condensed Formula

$(CHO)\ (CH_2)_4\ (CHO)$

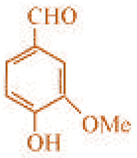
Bond line Formula

The functional group present in the given compound is aldehyde (–CHO).

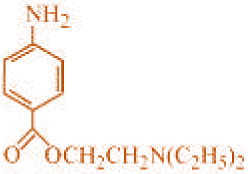
Question 12.8:

Identify the functional groups in the following compounds

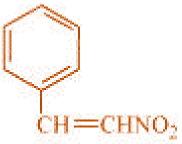
(a)



(b)



(c)

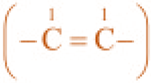


Answer 12.8:

The functional groups present in the given compounds are:

(a) Aldehyde (–CHO), Hydroxyl (–OH),

Methoxy (–OMe),

C=C double bond  $\left(-\overset{|}{C}=\overset{|}{C}-\right)$

(b) Amino ($-NH_2$),

Ketone (C = O),

Diethylamine ($N(C_2H_5)_2$)

(c) Nitro ($-NO_2$),

C=C double bond $\left(-C=C-\right)$

Question 12.9:

Which of the two: $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?

Answer 12.9:

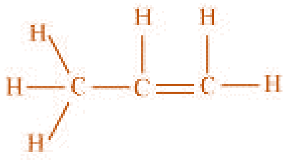
NO_2 group is an electron-withdrawing group. Hence, it shows –I effect. By withdrawing the electrons toward it, the NO_2 group decreases the negative charge on the compound, thereby stabilising it. On the other hand, ethyl group is an electron-releasing group. Hence, the ethyl group shows +I effect. This increases the negative charge on the compound, thereby destabilising it. Hence, $O_2NCH_2CH_2O^-$ is expected to be more stable than $CH_3CH_2O^-$.

Question 12.10:

Explain why alkyl groups act as electron donors when attached to a π system.

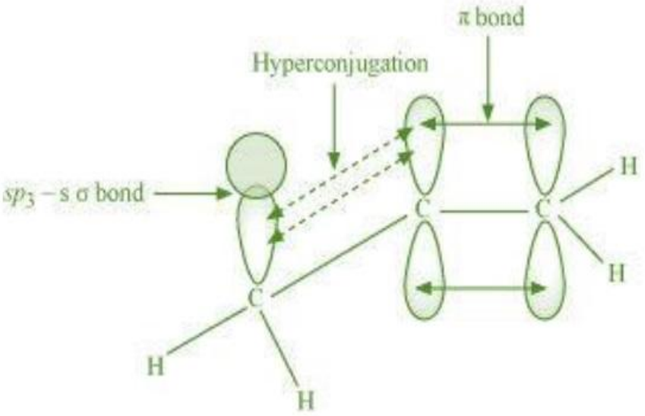
Answer 12.10:

When an alkyl group is attached to a π system, it acts as an electron-donor group by the process of hyperconjugation. To understand this concept better, let us take the example of propene.

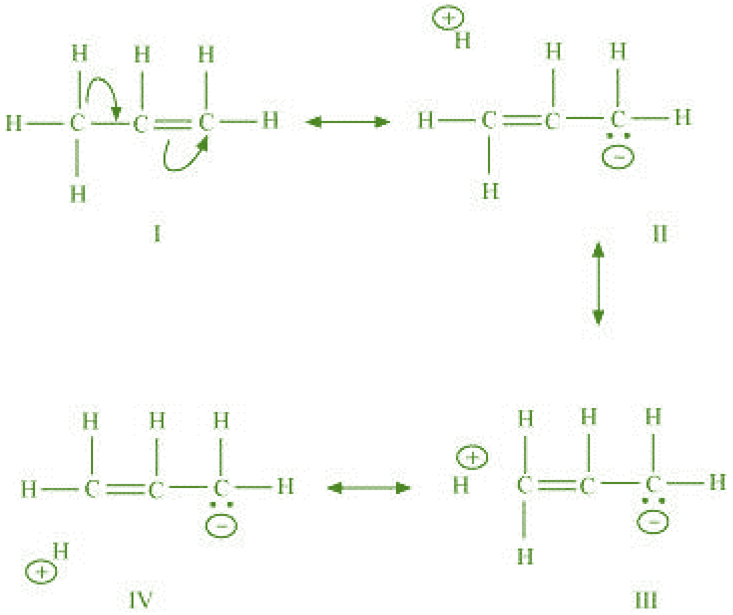


In hyperconjugation, the sigma electrons of the C–H bond of an alkyl group are delocalised. This group is directly attached to an atom of an unsaturated system. The delocalisation occurs because of a partial overlap of a sp^3 –s sigma bond orbital with an empty p orbital of the π bond of an adjacent carbon atom.

The process of hyperconjugation in propene is shown as follows:



This type of overlap leads to a delocalisation (also known as no-bond resonance) of the π electrons, making the molecule more stable.



Question 12.11:

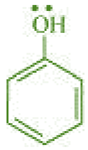
Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) C_6H_5OH **(b)** $C_6H_5NO_2$ **(c)** $CH_3CH = CH - CHO$

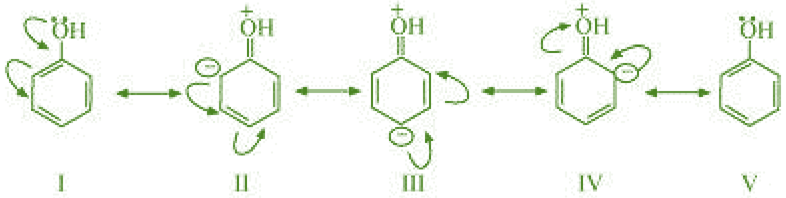
(d) C_6H_5CHO **(e)** $C_6H_5 - \overset{+}{C}H_2$ **(f)** $CH_3CH = CH\overset{+}{C}H_2$

Answer 12.11:

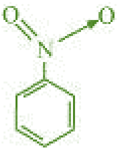
(a) The structure of C_6H_5OH is:



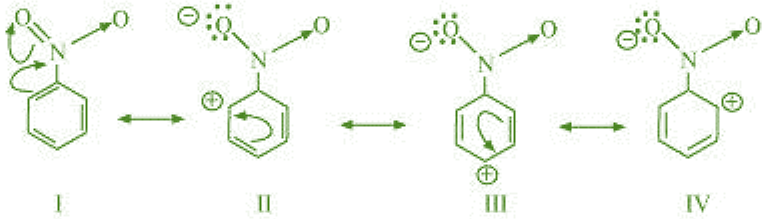
The resonating structures of phenol are represented as:



(b) The structure of $C_6H_5NO_2$ is:

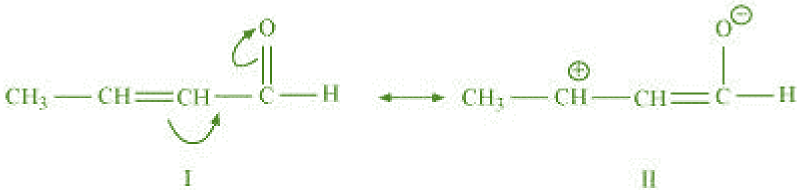


The resonating structures of nitro benzene are represented as:

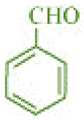


(c) $CH_3CH = CH - CHO$

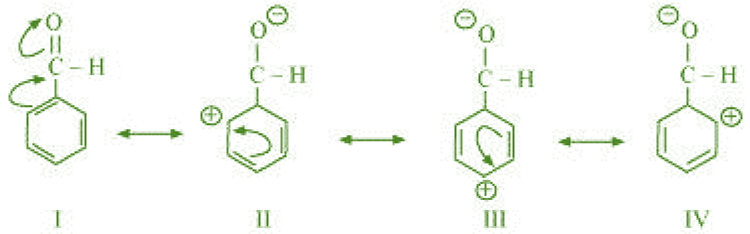
The resonating structures of the given compound are represented as:



(d) The structure of C_6H_5CHO is:

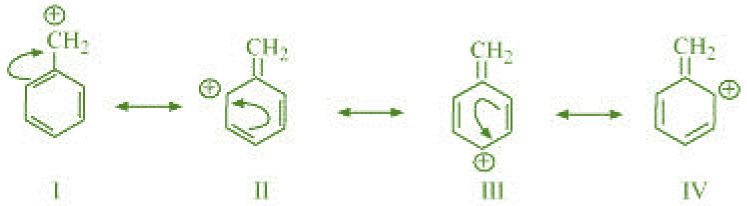


The resonating structures of benzaldehyde are represented as:



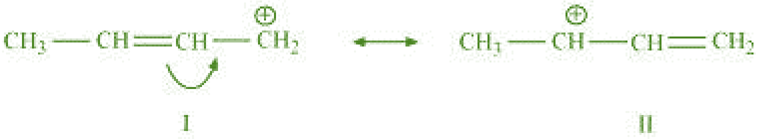
(e) $C_6H_5CH_2^{\oplus}$

The resonating structures of the given compound are:



(f) $CH_3\ CH = CH\ CH_2^{\oplus}$

The resonating structures of the given compound are:



Question 12.12:

What are electrophiles and nucleophiles? Explain with examples.

Answer 12.12:

An electrophile is a reagent that takes away an electron pair. In other words, an electron-seeking reagent is called an electrophile (E^+). Electrophiles are electrondeficient and can receive an electron pair.

Carbocations $\left(CH_3CH_2^+\right)$ and neutral molecules having functional groups such as carbonyl group ($>C=O$) are examples of electrophiles.

A nulceophile is a reagent that brings an electron pair. In other words, a nucleus-seeking reagent is called a nulceophile (Nu:).

For example: OH^-, NC^-, carbanions (R_3C^-), etc.

Neutral molecules such as $H_2\ddot{O}$ and ammonia also act as nulceophiles because of the presence of a lone pair.

Question 12.13:

Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

(b) $CH_3COCH_3 + \mathbf{\overset{-}{C}N} \longrightarrow (CH_3)_2C(CN) + (OH)$

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Answer 12.13:

Electrophiles are electron-deficient species and can receive an electron pair. On the other hand, nucleophiles are electron-rich species and can donate their electrons.

(a) $CH_3COOH + \mathbf{HO^-} \longrightarrow CH_3COO^- + H_2O$

Here, HO^- acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleusseeking species.

(b) $CH_3COCH_3 + \mathbf{\overset{-}{C}N} \longrightarrow (CH_3)_2C(CN) + (OH)$

Here, ^-CN acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleusseeking species.

(c) $C_6H_5 + \mathbf{CH_3\overset{+}{C}O} \longrightarrow C_6H_5COCH_3$

Here, $CH_3\overset{+}{C}O$ acts as an electrophile as it is an electron-deficient species.

Question 12.14:

Classify the following reactions in one of the reaction type studied in this unit.

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

(b) $(CH_3)_2\,C = CH_2 + HCl \rightarrow (CH_3)_2\,ClC{-}CH_3$

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$

(d) $(CH_3)_3\,C - CH_2\,OH + HBr \rightarrow (CH_3)_2\,CBrCH_2CH_3 + H_2O$

Answer 12.14:

(a) It is an example of substitution reaction as in this reaction the bromine group in bromoethane is substituted by the –SH group.

(b) It is an example of addition reaction as in this reaction two reactant molecules combine to form a single product.

(c) It is an example of elimination reaction as in this reaction hydrogen and bromine are removed from bromoethane to give ethene.

(d) In this reaction, substitution takes place, followed by a rearrangement of atoms and groups of atoms.

Question 12.15:

What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?

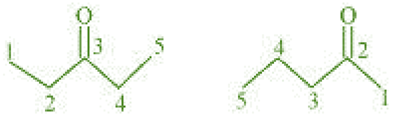
(a)

(b)

(c)

Answer 12.15:

(a) Compounds having the same molecular formula but with different structures are called structural isomers. The given compounds have the same molecular formula but they differ in the position of the functional group (ketone group).



In structure I, ketone group is at the C-3 of the parent chain (hexane chain) and in structure II, ketone group is at the C-2 of the parent chain (hexane chain). Hence, the given pair represents structural isomers.

(b) Compounds having the same molecular formula, the same constitution, and the sequence of covalent bonds, but with different relative position of their atoms in space are called geometrical isomers.

In structures I and II, the relative position of Deuterium (D) and hydrogen (H) in space are different. Hence, the given pairs represent geometrical isomers.

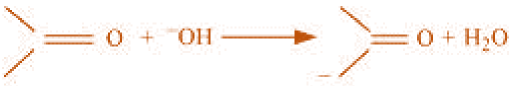
(c) The given structures are canonical structures or contributing structures. They are hypothetical and individually do not represent any real molecule. Hence, the given pair represents resonance structures, called resonance isomers.

Question 12.16:
For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

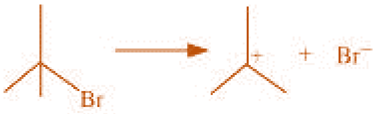
(a)

$$CH_3O-OCH_3 \longrightarrow CH_3\dot{O} + \dot{O}CH_3$$

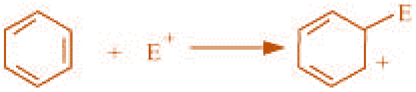
(b)



(c)

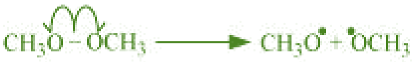


(d)



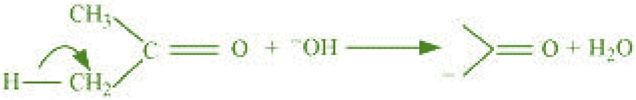
Answer 12.16:

(a) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



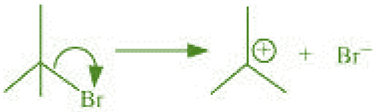
It is an example of homolytic cleavage as one of the shared pair in a covalent bond goes with the bonded atom. The reaction intermediate formed is a free radical.

(b) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



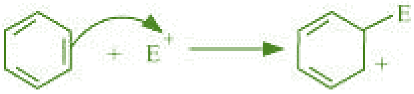
It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the carbon of propanone. The reaction intermediate formed is carbanion.

(c) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the bromine ion. The reaction intermediate formed is a carbocation.

(d) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is a heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments. The intermediate formed is a carbocation.

Question 12.17:

Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

Answer 12.17:

Inductive effect

The permanent displacement of sigma (σ) electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present, is called inductive effect. Inductive effect could be + I effect or – I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess – I effect.
For example,

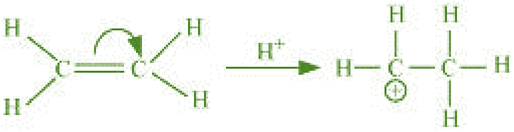
$$F \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_3$$

When an atom or group attracts electrons towards itself less strongly than hydrogen, it is said to possess + I effect.
For example,

$$CH_3 \rightarrow CH_2 \rightarrow Cl$$

Electrometric effect

It involves the complete transfer of the shared pair of π electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent. For example,



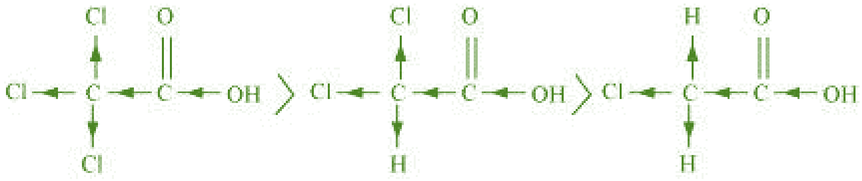
Electrometric effect could be + E effect or – E effect.

+ E effect: When the electrons are transferred towards the attacking reagent

– E effect: When the electrons are transferred away from the attacking reagent

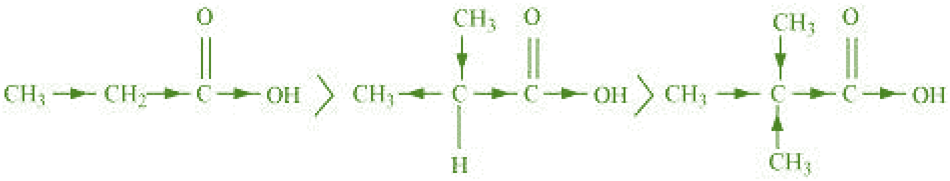
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

The order of acidity can be explained on the basis of Inductive effect (– I effect). As the number of chlorine atoms increases, the – I effect increases. With the increase in – I effect, the acid strength also increases accordingly.



(b) $CH_3CH_2COOH > (CH_3)_2\ CHCOOH > (CH_3)_3\ C.COOH$

The order of acidity can be explained on the basis of inductive effect (+ I effect). As the number of alkyl groups increases, the + I effect also increases. With the increase in + I effect, the acid strength also increases accordingly.



Question 12.18:

Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation

(b) Distillation

(c) Chromatography

Answer 12.18:

(a) Crystallisation

Crystallisation is one of the most commonly used techniques for the purification of solid organic compounds.

Principle: It is based on the difference in the solubilites of the compound and the impurities in a given solvent. The impure compound gets dissolved in the solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher temperature. The solution is concentrated to obtain a nearly saturated solution. On cooling the solution, the pure compound crystallises out and is removed by filtration.

For example, pure aspirin is obtained by recrystallising crude aspirin. Approximately 2 – 4 g of crude aspirin is dissolved in about 20 mL of ethyl alcohol. The solution is heated (if necessary) to ensure complete dissolution. The solution is then left undisturbed until some crystals start to separate out. The crystals are then filtered and dried.

(b) Distillation

This method is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have a sufficient difference in their boiling points.

Principle: It is based on the fact that liquids having different boiling points vapourise at different temperatures. The vapours are then cooled and the liquids so formed are collected separately.

For example, a mixture of chloroform (b.p = 334 K) and aniline (b.p = 457 K) can be separated by the method of distillation. The mixture is taken in a round bottom flask fitted with a condenser. It is then heated. Chloroform, being more volatile, vaporizes first and passes into the condenser. In the condenser, the vapours condense and chloroform trickles down. In the round bottom flask, aniline is left behind.

(c) Chromatography

It is one of the most useful methods for the separation and purification of organic compounds.

Principle: It is based on the difference in movement of individual components of a mixture through the stationary phase under the influence of mobile phase.

For example, a mixture of red and blue ink can be separated by chromatography. A drop of the mixture is placed on the chromatogram. The component of the ink, which is less adsorbed on the chromatogram, moves with the mobile phase while the less adsorbed component remains almost stationary.

Question 12.19:
Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Answer 12.19:
Fractional crystallisation is the method used for separating two compounds with different solubilities in a solvent S. The process of fractional crystallisation is carried out in four steps.

(a) **Preparation of the solution:** The powdered mixture is taken in a flask and the solvent is added to it slowly and stirred simultaneously. The solvent is added till the solute is just dissolved in the solvent. This saturated solution is then heated.

(b) **Filtration of the solution:** The hot saturated solution is then filtered through a filter paper in a China dish.

(c) **Fractional crystallisation:** The solution in the China dish is now allowed to cool. The less soluble compound crystallises first, while the more soluble compound remains in the solution. After separating these crystals from the mother liquor, the latter is concentrated once again. The hot solution is allowed to cool and consequently, the crystals of the more soluble compound are obtained.

(d) **Isolation and drying:** These crystals are separated from the mother liquor by filtration. Finally, the crystals are dried.

Question 12.20:
What is the difference between distillation, distillation under reduced pressure and steam distillation ?

Answer 12.20:
The differences among distillation, distillation under reduced pressure, and steam distillation are given in the following table.

	Distillation	Distillation under reduced pressure	Steam distillation
1.	It is used for the purification of compounds that are associated with non-volatile impurities or those liquids, which do not decompose on boiling. In other words, distillation is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have sufficient difference in boiling points.	This method is used to purify a liquid that tends to decompose on boiling. Under the conditions of reduced pressure, the liquid will boil at a low temperature than its boiling point and will, therefore, not decompose.	It is used to purify an organic compound, which is steam volatile and immiscible in water. On passing steam, the compound gets heated up and the steam gets condensed to water. After some time, the mixture of water and liquid starts to boil and passes through the condenser. This condensed mixture of water and liquid is then separated by using a separating funnel.
2.	Mixture of petrol and kerosene is separated by this method.	Glycerol is purified by this method. It boils with decomposition at a temperature of 593 K. At a reduced pressure, it boils at 453 K without decomposition.	A mixture of water and aniline is separated by steam distillation.

Question 12.21:

Discuss the chemistry of Lassaigne's test.

Answer 121.21:

Lassaigne's test

This test is employed to detect the presence of nitrogen, sulphur, halogens, and phosphorous in an organic compound. These elements are present in the covalent form in an organic compound. These are converted into the ionic form by fusing the compound with sodium metal.

$$\mathrm{Na + C + N \xrightarrow{\Delta} NaCN}$$

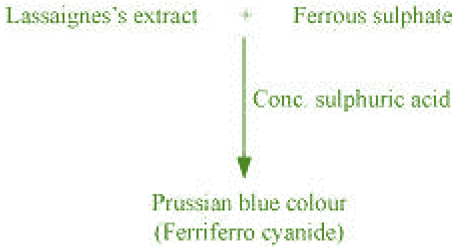
$$\mathrm{2Na + S \xrightarrow{\Delta} Na_2S}$$

$$\mathrm{Na + X \xrightarrow{\Delta} NaX}$$

$$\mathrm{(X = Cl, Br, I)}$$

The cyanide, sulphide, and halide of sodium formed are extracted from the fused mass by boiling it in distilled water. The extract so obtained is called Lassaigne’s extract. This Lassaigne’s extract is then tested for the presence of nitrogen, sulphur, halogens, and phosphorous.

(a) Test for nitrogen



Chemistry of the test

In the Lassaigne’s test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$$\mathrm{6CN^- + Fe^{2+} \longrightarrow \left[Fe(CN)_6\right]^{4-}}$$

$$\mathrm{3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue colour}}{Fe_4\left[Fe(CN)_6\right]_3 . xH_2O}}$$

(b) Test for sulphur

$$\text{(i) Lassaigne's extract} + \text{Lead acetate} \xrightarrow{\text{acetic acid}} \text{Black precipitate}$$

Chemistry of the test

In the Lassaigne’s test for sulphur in an organic compound, the sodium fusion extract is acidified with acetic acid and then lead acetate is added to it. The precipitation of lead sulphide, which is black in colour, indicates the presence of sulphur in the compound.

$$\mathrm{S^{2-} + Pb^{2+} \longrightarrow \underset{(Black)}{PbS}}$$

(ii) Lassaigne's extract + Sodium nitroprusside $\longrightarrow$ Violet colour

Chemistry of the test

The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour also indicates the presence of sulphur in the compound.

$$S^{2-} + \left[Fe(CN)_5 NO\right]^{2-} \longrightarrow \underset{(Violet)}{\left[Fe(CN)_5 NOS\right]^{-4}}$$

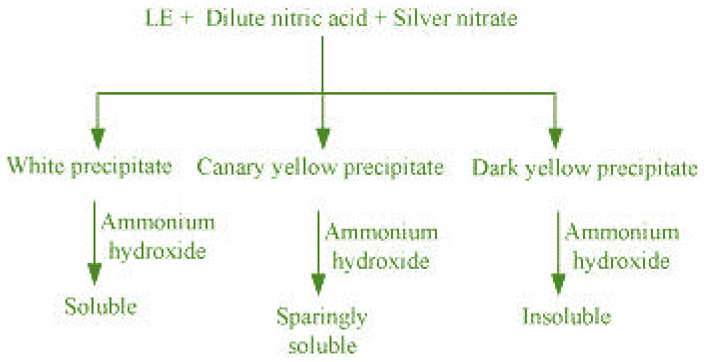
If in an organic compound, both nitrogen and sulphur are present, then instead of NaCN, formation of NaSCN takes place.

$Na + C + N + S \rightarrow NaSCN$

This NaSCN (sodium thiocyanate) gives a blood red colour. Prussian colour is not formed due to the absence of free cyanide ions.

$$Fe^{3+} + SCN^{-} \longrightarrow \underset{(Blood\ red)}{\left[Fe(SCN)\right]^{2+}}$$

(c) Test for halogens



Chemistry of the test

In the Lassaigne's test for halogens in an organic compound, the sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$$X^{-} + Ag^{+} \longrightarrow AgX$$
$$(X = Cl, Br, I)$$

If nitrogen and sulphur both are present in the organic compound, then the Lassaigne's extract is boiled to expel nitrogen and sulphur, which would otherwise interfere in the test for halogens.

Question 12.22:
Differentiate between the principle of estimation of nitrogen in an organic compound by **(i)** Dumas method and **(ii)** Kjeldahl's method.

Answer 12.22:
In Dumas method, a known quantity of nitrogen containing organic compound is heated strongly with excess of copper oxide in an atmosphere of carbon dioxide to produce free nitrogen in addition to carbon dioxide and water. The chemical equation involved in the process can be represented as

$$CxHyNz + (2x + y/2)\,CuO \longrightarrow xCO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)Cu$$

The traces of nitrogen oxides can also be produced in the reaction, which can be reduced to dinitrogen by passing the gaseous mixture over a heated copper gauge. The dinitrogen produced is collected over an aqueous solution of potassium hydroxide. The volume of nitrogen produced is then measured at room temperature and atmospheric pressure.

On the other hand, in Kjeldahl's method, a known quantity of nitrogen containing organic compound is heated with concentrated sulphuric acid. The nitrogen present in the compound is quantitatively converted into ammonium sulphate. It is then distilled with excess of sodium hydroxide. The ammonia evolved during this process is passed into a known volume of H_2SO_4. The chemical equations involved in the process are

$$\text{Organic compound} \xrightarrow{\text{Conc.}\,H_2SO_4} (NH_4)_2\,SO_4$$

$$(NH_4)_2\,SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$

The acid that is left unused is estimated by volumetric analysis (titrating it against a standard alkali) and the amount of ammonia produced can be determined. Thus, the percentage of nitrogen in the compound can be estimated. This method cannot be applied to the compounds, in which nitrogen is present in a ring structure, and also not applicable to compounds containing nitro and azo groups.

Question 12.23:

Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Answer 12.23:

Estimation of halogens

Halogens are estimated by the Carius method. In this method, a known quantity of organic compound is heated with fuming nitric acid in the presence of silver nitrate, contained in a hard glass tube called the Carius tube, taken in a furnace. Carbon and hydrogen that are present in the compound are oxidized to form CO_2 and H_2O respectively and the halogen present in the compound is converted to the form of AgX.

This AgX is then filtered, washed, dried, and weighed.

Let the mass of organic compound be *m* g.

Mass of AgX formed = m_1 g

1 mol of Agx contains 1 mol of X.

Therefore,

Mass of halogen in m_1 g of AgX $= \dfrac{\text{Atomic mass of X} \times m_1 \text{ g}}{\text{Molecular mass of AgX}}$

Thus, % of halogen will be $= \dfrac{\text{Atomic mass of X} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}$

Estimation of Sulphur

In this method, a known quantity of organic compound is heated with either fuming nitric acid or sodium peroxide in a hard glass tube called the Carius tube. Sulphur, present in the compound, is oxidized to form sulphuric acid. On addition of excess of barium chloride to it, the precipitation of barium sulphate takes place. This precipitate is then filtered, washed, dried, and weighed.

Let the mass of organic compound be *m* g.

Mass of $BaSO_4$ formed = m_1 g

1 mol of $BaSO_4$ = 233 g $BaSO_4$ = 32 g of Sulphur

Therefore, m_1 g of $BaSO_4$ contains $\dfrac{32 \text{ x } m_1}{233}$ g of sulphur.

Thus, percentage of sulphur $= \dfrac{32 \text{ x } m_1 \text{ x } 100}{233 \times m}$

Estimation of phosphorus

In this method, a known quantity of organic compound is heated with fuming nitric acid. Phosphorus, present in the compound, is oxidized to form phosphoric acid. By adding ammonia and ammonium molybdate to the solution, phosphorus can be precipitated as ammonium phosphomolybdate.

Phosphorus can also be estimated by precipitating it as $MgNH_4PO_4$ by adding magnesia mixture, which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound be *m* g.

Mass of ammonium phosphomolybdate formed = m_1 g

Molar mass of ammonium phosphomolybdate = 1877 g

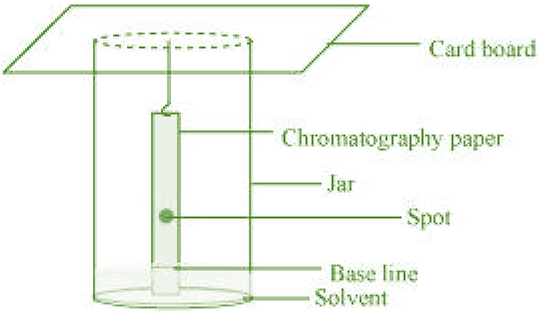
$$\text{Thus, percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m}\%$$

If P is estimated as $Mg_2P_2O_7$,

$$\text{Then, percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222 \times m}\%$$

Question 12.24:
Explain the principle of paper chromatography.

Answer 12.24:
In paper chromatography, chromatography paper is used. This paper contains water trapped in it, which acts as the stationary phase. On the base of this chromatography paper, the solution of the mixture is spotted. The paper strip is then suspended in a suitable solvent, which acts as the mobile phase. This solvent rises up the chromatography paper by capillary action and in the procedure, it flows over the spot. The components are selectively retained on the paper (according to their differing partition in these two phases). The spots of different components travel with the mobile phase to different heights. The paper so obtained (shown in the given figure) is known as a chromatogram.



Question 12.25:
Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

Answer 12.25:
While testing the Lassaigne's extract for the presence of halogens, it is first boiled with dilute nitric acid. This is done to decompose NaCN to HCN and Na_2S to H_2S and to expel these gases. That is, if any nitrogen and sulphur are present in the form of NaCN and Na_2S, then they are removed. The chemical equations involved in the reaction are represented as

$$\mathrm{NaCN + HNO_3 \longrightarrow NaNO_3 + HCN}$$
$$\mathrm{Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S}$$

Question 12.26:
Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Answer 12.26:
Nitrogen, sulphur, and halogens are covalently bonded in organic compounds. For their detection, they have to be first converted to ionic form. This is done by fusing the organic compound with sodium metal. This is called "Lassaigne's test". The chemical equations involved in the test are

$$\mathrm{Na + C + N \longrightarrow NaCN}$$
$$\mathrm{Na + S + C + N \longrightarrow NaSCN}$$
$$\mathrm{2Na + S \longrightarrow Na_2S}$$
$$\mathrm{Na + X \longrightarrow NaX}$$
$$\mathrm{(X = Cl, Br, I)}$$

Carbon, nitrogen, sulphur, and halogen come from organic compounds.

Question 12.27:
Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Answer 12.27:
The process of sublimation is used to separate a mixture of camphor and calcium sulphate. In this process, the sublimable compound changes from solid to vapour state without passing through the liquid state. Camphor is a sublimable compound and calcium sulphate is a non-sublimable solid. Hence, on heating, camphor will sublime while calcium sulphate will be left behind.

Question 12.28:
Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Answer 12.28:
In steam distillation, the organic liquid starts to boil when the sum of vapour pressure due to the organic liquid (p_1) and the vapour pressure due to water (p_2) becomes equal to atmospheric pressure (p), that is, $p = p_1 + p_2$
Since $p_1 < p_2$, organic liquid will vapourise at a lower temperature than its boiling point.

Question 12.29:
Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Answer 12.29:
CCl_4 will not give the white precipitate of AgCl on heating it with silver nitrate. This is because the chlorine atoms are covalently bonded to carbon in CCl_4. To obtain the precipitate, it should be present in ionic form and for this, it is necessary to prepare the Lassaigne's extract of CCl_4.

Question 12.30:
Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Answer 12.30:
Carbon dioxide is acidic in nature and potassium hydroxide is a strong base. Hence, carbon dioxide reacts with potassium hydroxide to form potassium carbonate and water as

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Thus, the mass of the U-tube containing KOH increases. This increase in the mass of U-tube gives the mass of CO_2 produced. From its mass, the percentage of carbon in the organic compound can be estimated.

Question 12.31:

Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Answer 12.31:

Although the addition of sulphuric acid will precipitate lead sulphate, the addition of acetic acid will ensure a complete precipitation of sulphur in the form of lead sulphate due to common ion effect. Hence, it is necessary to use acetic acid for acidification of sodium extract for testing sulphur by lead acetate test.

Question 12.32:

An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Answer 12.32:

Percentage of carbon in organic compound = 69 %

That is, 100 g of organic compound contains 69 g of carbon.

∴0.2 g of organic compound will contain $=\frac{69\times0.2}{100}$ $=0.138\,\text{g of C}$

Molecular mass of carbon dioxide, CO_2 = 44 g

That is, 12 g of carbon is contained in 44 g of CO_2.

Therefore, 0.138 g of carbon will be contained in $\frac{44\times0.138}{12}$ = 0.506 g of CO_2

Thus, 0.506 g of CO_2 will be produced on complete combustion of 0.2 g of organic compound.
Percentage of hydrogen in organic compound is 4.8.
i.e., 100 g of organic compound contains 4.8 g of hydrogen.

Therefore, 0.2 g of organic compound will contain $\frac{4.8\times0.2}{100}=0.0096\,\text{g of H}$

It is known that molecular mass of water (H_2O) is 18 g.
Thus, 2 g of hydrogen is contained in 18 g of water.

∴0.0096 g of hydrogen will be contained in $\frac{18\times0.0096}{2}=0.0864\,\text{g}$ of water

Thus, 0.0864 g of water will be produced on complete combustion of 0.2 g of the organic compound.

Question 12.33:
A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Answer 12.33:
Given that, total mass of organic compound = 0.50 g

60 mL of 0.5 M solution of NaOH was required by residual acid for neutralisation.

60 mL of 0.5 M NaOH solution $= \frac{60}{2}\,\text{mL of } 0.5\,\text{M}$ H_2SO_4 = 30 mL of 0.5 M H_2SO_4

∴Acid consumed in absorption of evolved ammonia is (50–30) mL = 20 mL

Again, 20 mL of 0.5 MH_2SO_4 = 40 mL of 0.5 MNH_3

Also, since 1000 mL of 1 MNH_3 contains 14 g of nitrogen,

∴ 40 mL of 0.5 M NH_3 will contain $\frac{14\times 40}{1000}\times 0.5$ = 0.28 g of N

Therefore, percentage of nitrogen in 0.50 g of organic compound $= \frac{0.28}{0.50}\times 100$ = 56 %

Question 12.34:
0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Answer 12.34:
Given that,

Mass of organic compound is 0.3780 g.

Mass of AgCl formed = 0.5740 g

1 mol of AgCl contains 1 mol of Cl.

Thus, mass of chlorine in 0.5740 g of AgCl

$$= \frac{35.5\times 0.5740}{143.32}$$
$$= 0.1421\,\text{g}$$

∴ Percentage of chlorine $= \frac{0.1421}{0.3780}\times 100 = 37.59\%$

Hence, the percentage of chlorine present in the given organic chloro compound is 37.59%.

Question 12.35:
In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

Answer 12.35:
Total mass of organic compound = 0.468 g [Given]
Mass of barium sulphate formed = 0.668 g [Given]

1 mol of $BaSO_4$ = 233 g of $BaSO_4$ = 32 g of sulphur

Thus, 0.668 g of $BaSO_4$ contains $\frac{32\times 0.668}{233}\text{g}$ of sulphur = 0.0917 g of sulphur

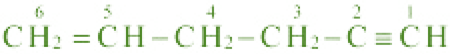
Therefore, percentage of sulphur $=\frac{0.0197}{0.468}\times 100$ = 19.59 %

Hence, the percentage of sulphur in the given compound is 19.59 %.

Question 12.36:
In the organic compound $CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}CH$, the pair of hydridised orbitals involved in the formation of: C_2 – C_3 bond is:

(a) $sp - sp^2$ (b) $sp - sp^3$ (c) $sp^2 - sp^3$ (d) $sp^3 - sp^3$

Answer 12.36:



$$\overset{6}{C}H_2=\overset{5}{C}H-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$$

In the given organic compound, the carbon atoms numbered as 1, 2, 3, 4, 5, and 6 are *sp*, *sp*, sp^3, sp^3, sp^2, and sp^2 hybridized respectively. Thus, the pair of hybridized orbitals involved in the formation of C_2-C_3 bond is $sp - sp^3$.

Question 12.37:

In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

Answer 12.37:

In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

Hence, the Prussian blue colour is due to the formation of $Fe_4[Fe(CN)_6]_3$.

Question 12.38:

Which of the following carbocation is most stable?

(a) $(CH_3)_3C.\overset{+}{C}H_2$ (b) $(CH_3)_3\overset{+}{C}$

(c) $CH_3CH_2\overset{+}{C}H_2$ (d) $CH_3\overset{+}{C}HCH_2CH_3$

Answer 12.38:

$(CH_3)_3\overset{+}{C}$ is a tertiary carbocation. A tertiary carbocation is the most stable carbocation due to the electron releasing effect of three methyl groups. An increased + I effect by three methyl groups stabilizes the positive charge on the carbocation.

Question 12.39:
The best and latest technique for isolation, purification and separation of organic compounds is:
(a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography

Answer 12.39:
Chromatography is the most useful and the latest technique of separation and purification of organic compounds. It was first used to separate a mixture of coloured substances.

Question 12.40:
The reaction:

$$CH_3CH_2I + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KI$$

is classified as :

(a) electrophilic substitution (b) nucleophilic substitution
(c) elimination (d) addition

Answer 12.40:

$$CH_3CH_2I + KOH_{(aq)} \longrightarrow CH_3CH_2OH + KI$$

It is an example of nucleophilic substitution reaction. The hydroxyl group of KOH (OH^-) with a lone pair of itself acts as a nucleophile and substitutes iodide ion in CH_3CH_2I to form ethanol.