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.

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

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

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

$$(X = Cl, Br, I)$$

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

Lassaignes's extract + Ferrous sulphate

↓ Conc. sulphuric acid

Prussian blue colour
(Ferriferro cyanide)

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

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

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

Prussian blue colour

(b) Test for sulphur

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

$$S^{2-} + Pb^{2+} \longrightarrow PbS$$

$$(Black)$$

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

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.

$$S^{2-} + \left[Fe(CN)_5NO\right]^{2-} \longrightarrow \underset{\text{(Violet)}}{\left[Fe(CN)_5NOS\right]^{-4}}$$

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.

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

(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.

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

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

$$\text{Organic compound} \xrightarrow{\text{Conc.}H_2SO_4} (NH_4)_2SO_4$$
$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$
$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

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

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

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.

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

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

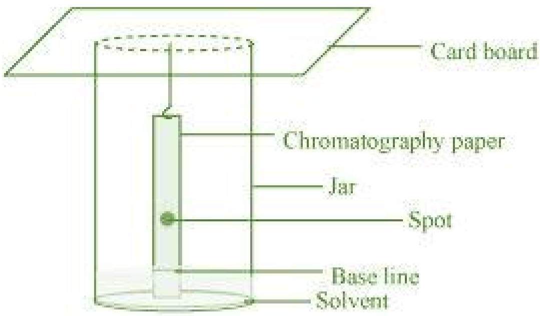
$$\text{Thus, percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m}\%$$

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

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN$$
$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S$$

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

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

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 $= \frac{69 \times 0.2}{100} = 0.138 \text{ g of C}$

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 $\frac{44 \times 0.138}{12}$ = 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 $\frac{4.8 \times 0.2}{100} = 0.0096 \text{ g of H}$

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 $\frac{18 \times 0.0096}{2} = 0.0864 \text{ g}$ 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 $\frac{32 \times 0.668}{233}$ 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.