
PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

PURIFICATION OF ORGANIC COMPOUNDS

The methods to be employed depend on the physical state of the compound.

Crystallisation : This method is based on the differences in the solubility of the organic compound and its impurities in a solvent.

- (a) **Preparation of the solution :** Organic substance is powdered and is dissolved in a suitable solvent by heating. The amount of solvent should be just sufficient to dissolve the whole of the solid on heating.

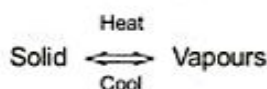
Choice of Solvent. The choice of solvent is very important in the crystallisation process. The main conditions of the solvent are:

- (i) The organic substance should dissolve in the solvent upon heating and it should get separated on cooling.
- (ii) The solvent should not dissolve the impurities.
- (iii) The solvent should not react chemically with the substance.

For example, suppose we want to purify sugar containing an impurity of common salt. This can be done by treating the mixture with ethanol around 350 K. The sugar will dissolve whereas common salt remains insoluble.

- (b) **Filtration of the solution.** The hot saturated solution is filtered preferably through a fluted filter paper placed in a glass funnel. The use of the fluted filter paper makes the filtration rapid. The jacket of the hot water funnel is heated from outside and this keeps the solution hot in the glass funnel. This will prevent the formation of crystals during filtration.
- (c) **Crystallisation.** The hot filtration is allowed to cool slowly and undisturbed in a beaker or in a crystallising dish. After some time the crystals of the pure compound are formed.
- (d) **Separation of the crystals.** The crystals formed are separated from the mother liquor by filtration. The filtration is normally done by use of Buckner funnel and a suction pump. This enables the filtration under reduced pressure and is therefore, quite fast.
- (e) **Drying of crystals.** The crystals are dried by pressing between the folds of filter paper and then placed in a stream of air oven for some time. The crystals are finally dried over sulphuric acid or calcium chloride in a desiccator.

Sublimation : Certain organic solids directly change from solid to vapour state on heating. This process is called sublimation. The vapours on cooling change back to the solid form



The sublimation process is used for the separation of those solids which sublime on heating from non-volatile solids. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid, etc. containing non-volatile impurities.

Distillation :

This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. The simple distillation involves its boiling point so that it is converted into vapours. On cooling the vapours, pure liquid is obtained.

The distillate contains pure liquid while the impurities are left behind in the distillation flask

e.g. Ether from ethyl alcohol.

Fractional Distillation :

This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards. This method may be used to separate a mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338. K).

Distillation under Reduced pressure (Vaccum Distillation) :

Certain liquids have a tendency to decompose at a temperature below their boiling points. Such liquids cannot be purified by ordinary distillation. Therefore vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.

Ex. glycerol boils with decomposition at 563K.

Steam distillation :

The process of steam distillation is used for the separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture. Thus, the process of steam distillations is used to purify the substances which

- (i) are volatile in steam but are not miscible with water
- (ii) possess sufficiently high vapour pressure at the boiling point temperature of water (100°C)
- (iii) contain non-volatile impurities.

The process of steam distillation can be applied for the separation of a mixture of o-nitrophenol and p-nitrophenol. In this process, water vapours carry along with them vapours of o-nitrophenol which is more volatile and they get condensed in the receiver; p-nitrophenol with higher b.p. remains in the distillation flask. The method can also be used for the purification of impure sample of aniline.

Chromatography :

This method is based on the differences in the rates at which the components of a mixture are adsorbed on a suitable adsorbent. There are many forms of chromatography such as column chromatography, paper chromatography, thin layer chromatography (TLC), gas chromatography, etc. The simplest method is column chromatography.

Applications of chromatographic method. This method has been used

- (i) To separate ortho and para nitro-anilines.
- (ii) To separate blue and red dyes.
- (iii) To separate and purify plant pigments and other natural products.

Types of chromatography :

Based on the principle involved chromatography is classified into different categories. Two of these are.

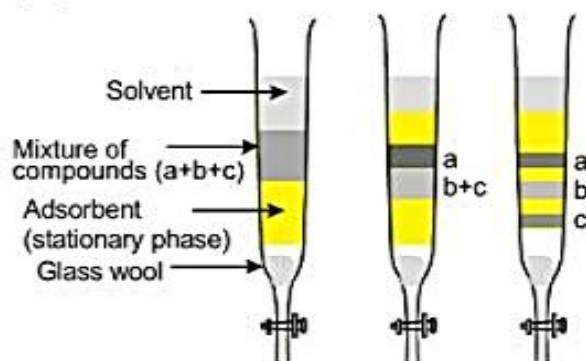
- (a) Adsorption chromatography, and
- (b) Partition chromatography

(a) Adsorption chromatography :

Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

- (i) Column chromatography, and
- (ii) Thin layer chromatography.

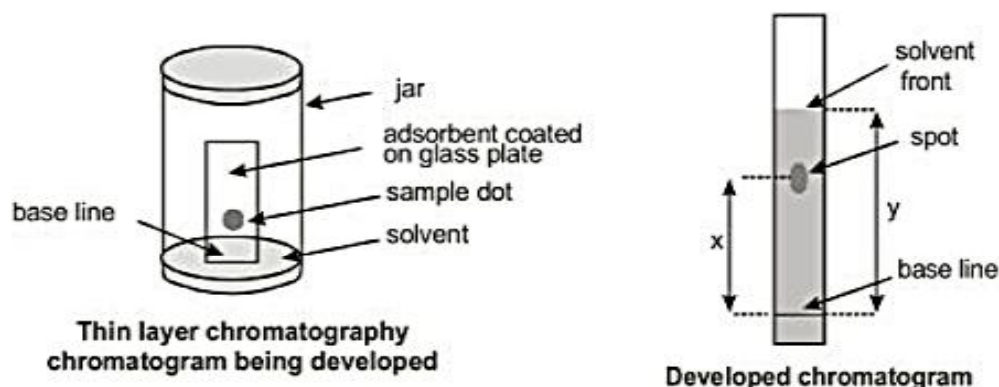
Column chromatography:



Column chromatography. Different stages of separation of components of a mixture

Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column

Thin layer chromatography :

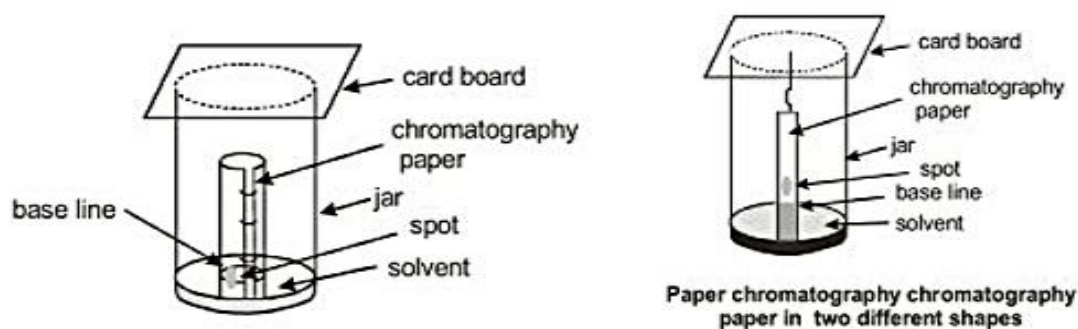


Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2 mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retention factor** i.e. R_f value

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds which are invisible to the eye but fluoresce, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine spots of compounds, which adsorb iodine will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, Amino acids may be detected by spraying the plate with ninhydrin solution

(b) Partition Chromatography :



Partition chromatography is based on continuous differential partitioning of components of mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents. This solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The qualitative analysis of an organic compound involves the detection of all the elements present in it.

Detection of Carbon and Hydrogen : A small amount of the dry and powdered substance is mixed with about double the amount of pure and dry copper oxide. The mixture is heated in a well dried hard glass tube (fig) delivery tube is packed with glass wool containing anhydrous copper sulphate (white). When the mixture is heated, the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky. The hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

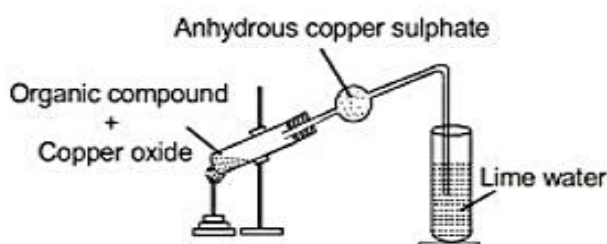
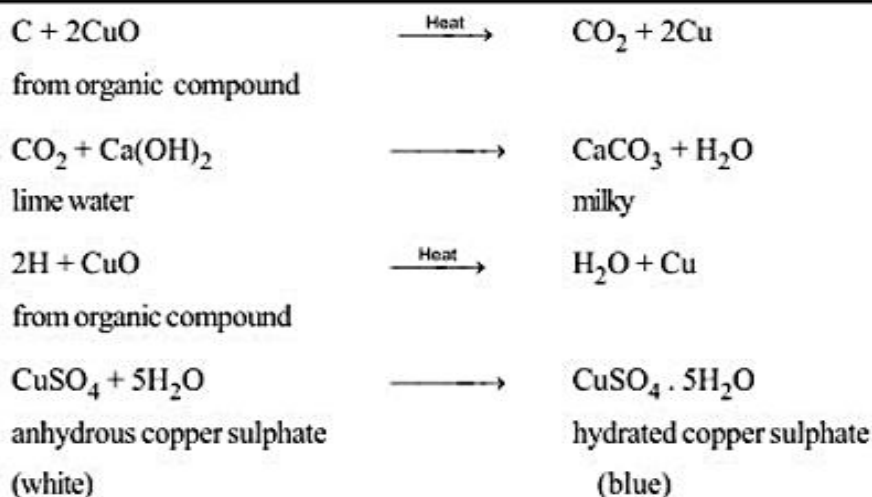


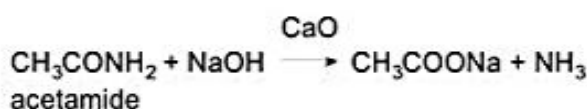
fig. Detection of carbon and hydrogen in an organic compound



This method is known as copper oxide test.

Detection of Nitrogen : Nitrogen in an organic compound is detected by the following tests :

- (a) **Soda lime test.** A pinch of an organic compound is heated strongly with soda lime ($NaOH + CaO$) in a test tube. If ammonia gas evolves, it indicates nitrogen.



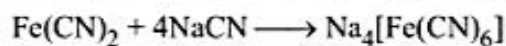
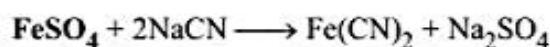
Limitation : This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate ammonia on heating with sodalime.

- (b) **Lassaigne's method :** A small piece of a dry sodium metal is heated gently in a fusion tube till it melts to a shining globule. Then, a small amount of organic substance is added and the tube is heated strongly till it becomes red hot. The red hot tube is then cooled and filtered. The filtered liquid is known as sodium extract or Lassaigne's extract.

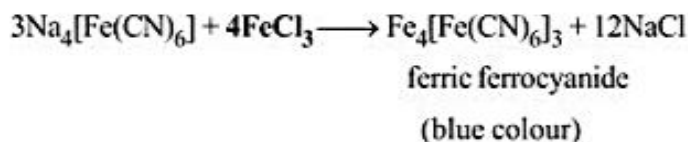
The Lassaigne's extract is usually alkaline. If not, it may be made alkaline by adding a few drops of a dilute solution of sodium hydroxide added to a part of sodium extract a small amount of a freshly prepared ferrous sulphate solution is added and the contents are warmed. A few drops of ferric chloride solution are then added to the contents and the resulting solution is acidified with dilute hydrochloric acid. The appearance of a bluish green or a blue colouration confirms the presence of nitrogen in the organic compound. The following chemical reactions occur during the test :



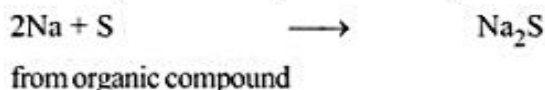
from organic
compound



sodium ferrocyanide

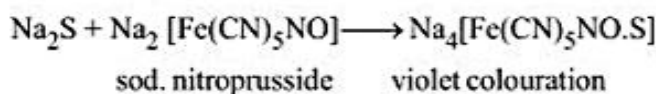


Detection of Sulphur : The sulphur in the compound reacts with sodium metal to form sodium sulphide.

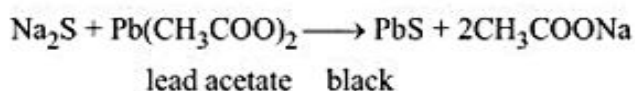


The Lassaigne's extract is divided into two parts and following tests are performed.

- (i) **Sodium nitroprusside test.** The one portion of the extract, a few drops of sodium nitroprusside are added. The appearance of violet colouration indicates sulphur.



- (ii) **Lead acetate test :** The other part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirms the presence of sulphur.



Detection of Halogens :

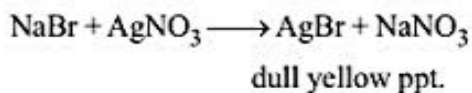
Lassaigne's test. Sodium extract is prepared as already. During fusion, sodium will combine with the halogen (from the organic compound) to form sodium halide



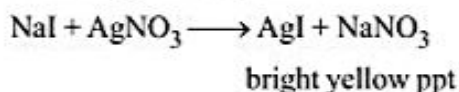
- (i) A white precipitate soluble in ammonium hydroxide solution indicates the presence of chlorine in the organic compound



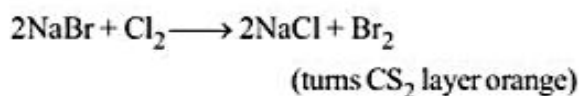
- (ii) A dull yellow precipitate partially soluble in ammonium hydroxide solution indicates the presence of bromine in the organic compound.

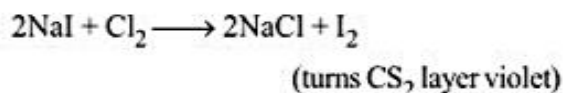


- (iii) A bright yellow precipitate, completely insoluble in ammonium hydroxide solution, indicates the presence of iodine in the organic compound.



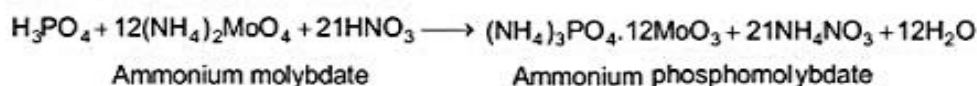
Special test for bromine and iodine.





Test of phosphorus :

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Estimation of Carbon and Hydrogen :

Principle. A known weight of the given dry organic compound is heated strongly with dry cupric oxide in an atmosphere of air or oxygen free from CO_2 . The carbon and hydrogen of the organic compound are oxidised to CO_2 and water vapour as :



(from compound)



(from compound)

Procedure :

Let the mass of organic compound taken = m g

Mass of water formed = m_1 g

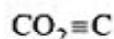
(increase in CaCl_2 U-tube)

Mass of carbon dioxide formed = m_2 g

(increase in potash tubes)

(a) Percentage of Carbon

We know that 1 mole of carbon dioxide (44 g) contains 1 gram atom of carbon (12g).



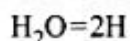
44 g of CO_2 contain C = 12 g

m_2 g of CO_2 contains C = $\frac{12}{44} \times m_2$ g

Hence Percentage of carbon = $\frac{12m_2}{44 \times m} \times 100$

(b) Percentage of Hydrogen

We know that one mole of water (18g) contains 2 gram atom of hydrogen (2g)



18g of H_2O contain H = 2g

$$\therefore m_1 \text{ g of } \text{H}_2\text{O} \text{ contains H} = \frac{2}{18} \times m_1 \text{ g}$$

$$\text{Percentage of hydrogen} = \frac{2m_1}{18 \times m} \times 100$$

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of Nitrogen :

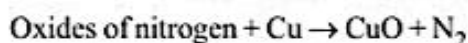
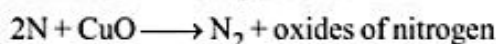
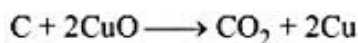
There are two methods for the estimation of nitrogen

(i) Duma's method

(ii) Kjeldahl's method

Duma's method :

Principle of the method. A known mass of an organic compound is heated with dry cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced to nitrogen by passing over a heated copper gauze. The gaseous mixture is collected over an aqueous solution of KOH when all the gases except nitrogen are absorbed. The volume of nitrogen produced is measured at room temperature and atmospheric pressure. From the volume of N_2 produced, percentage of nitrogen in the sample can be calculated.



Let the mass of organic compound = w g

The volume of nitrogen collected = $V \text{ cm}^3$

Atmospheric pressure (from barometer) = P mm of Hg

Room temperature = $t^\circ\text{C}$

Aqueous tension at $t^\circ\text{C}$ = a mm of Hg

Pressure of dry nitrogen = (P – a) mm of Hg

Let us first convert the volume of nitrogen to volume at S.T.P.

Experimental conditions S.T.P. conditions

$$P_1 = (P - a) \text{ mm Hg}$$

$$P_2 = 760 \text{ mm}$$

$$T_1 = (273 + t) \text{ K}$$

$$T_2 = 273$$

$$V_1 = V \text{ cm}^3$$

$$V_2 = ?$$

Applying gas equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\therefore V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(P - a) \times V \times 273}{760 (273 + t)} = x \text{ cm}^3 \text{ (say)}$$

Now 22400 cm^3 of N_2 at S.T.P. weight = 28 g

$$x \text{ cm}^3 \text{ of } \text{N}_2 \text{ at S.T.P. will weigh} = \frac{28}{22400} \times x \text{ g}$$

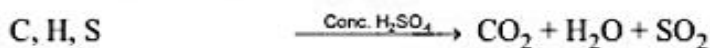
$$\therefore \text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{28x \times 100}{22400 \times w}$$

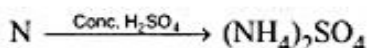
Kjeldahl's method : This method cannot be used for

- (i) Organic compounds containing nitrogen in the ring such as pyridine, quinoline, etc.
- (ii) Organic compounds containing nitrogen ($-\text{NO}_2$) and diazo ($-\text{N}=\text{N}-$) groups.

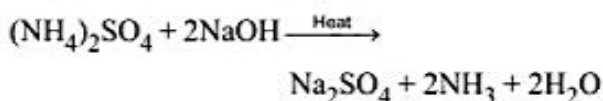
Principle : A known weight of the organic compound is heated with conc. H_2SO_4 so that nitrogen is quantitatively converted into ammonium sulphate. The solution is then heated with excess of sodium hydroxide. The ammonia gas evolved is passed into a known but excess volume of standard acid (HCl or H_2SO_4). The acid left unused is estimated by titrating the solution with standard alkali. From the amount of acid left unused the amount of acid used for neutralisation of ammonia can be calculated. From this percentage of nitrogen can be calculated.

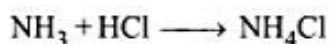
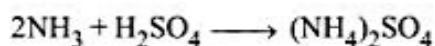


(from organic compound)



(from organic compound) ammonium sulphate





Calculations

Let the mass of organic compound = w g

Volume of standard acid taken = $V \text{ cm}^3$

Normality of acid = N_1

Let vol. of standard alkali used for neutralisation of unused acid = $V_2 \text{ cm}^3$

Normality of standard alkali = N_2

$$\underbrace{N_1 V_1}_{\text{alkali}} = \underbrace{N_2 V_2}_{\text{acid}}$$

Let this volume of $v \text{ cm}^3$

\therefore Vol. of acid used for neutralisation of ammonia

$$= (V - v) \text{ cm}^3 \text{ of } N_1 \text{ normality}$$

\therefore Ammonia liberated = $(V - v) \text{ cm}^3$ of N_1 solution

Now, 1000 cm^3 of $1N \text{ NH}_3$ solution contains nitrogen = 14 g

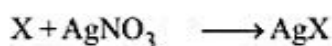
$$(V - v) \text{ cm}^3 \text{ of } N_1 \text{ NH}_3 \text{ solution contains nitrogen} = \frac{14(V - v) \times N_1}{1000} \text{ g}$$

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100 = \frac{14(V - v) \times N_1}{1000} \times \frac{100}{w} \\ &= \frac{1.4(V - v) \times N_1}{w} \end{aligned}$$

Estimation of Halogens :

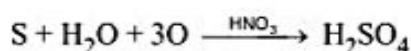
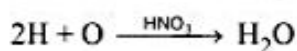
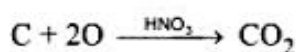
Carius method :

Principle : A known mass of the organic substance is heated with fuming HNO_3 in a Carius tube. The silver halide so obtained is separated, washed, dried and weighed. From the weight of silver halide formed, the percentage of halogen can be calculated.



Halogen

Carbon, hydrogen or sulphur present in the compound will be oxidised to CO_2 , H_2O and H_2SO_4 respectively.



Calculations :

Let the mass of organic compound be w g

Mass of silver halide formed = a g

Now, $\text{AgX} = \text{X}$

$108 + \text{X}$ parts by weight of silver halide contains X parts by weight of halogen (X is its atomic mass)

$(108 + \text{X})$ g of silver halide give halogen = X

a g of silver halide will give halogen = $\frac{\text{X}}{(108 + \text{X})} \times a$ g

$$\therefore \text{Percentage of halogen} = \frac{\text{Mass of halogen}}{\text{Mass of organic compound}} \times 100 = \frac{\text{X} \times a}{(108 + \text{X})} \times \frac{100}{w}$$

Here X is the atomic mass of halogen, e.g.

$\text{Cl} = 35.5$, $\text{Br} = 80$ (79.9 exact),

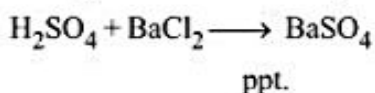
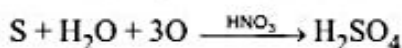
$\text{I} = 127$ (126.9 exact)

$$\text{Percentage of halogen} = \frac{\text{Atomic mass of halogen} \times \text{Mass of silver halide}}{(108 + \text{At. mass of halogen}) \times \text{Mass of organic substance}} \times 100$$

Estimation of Sulphur

Sulphur is estimated by Carius method.

Principle : A known mass of the organic compound is heated with fuming HNO_3 in a sealed tube when sulphur is quantitatively converted into sulphuric acid. It is then precipitated with barium chloride as barium sulphate. The precipitate is filtered, washed, dried and weighed. From the weight of BaSO_4 formed, the percentage of sulphur can be calculated. The main reactions are :

**Calculations :**

Let the mass of organic compound = w g

Mass of BaSO_4 formed = a g

$\text{BaSO}_4 \equiv \text{S}$

$137 + 32 + 64 = 32$

= 233

233 g of BaSO_4 contain sulphur = 32 g

a g of BaSO_4 will contain sulphur = $\frac{32 \times a}{233}$ g

$$\text{Percentage of sulphur} = \frac{\text{Mass of sulphur}}{\text{Mass of organic compound}} \times 100 = \frac{32a}{233} \times \frac{100}{w}$$

SOLVED EXAMPLES

Q.1 In Lassaigne's test when both N and S are present, blood red colour obtained is due to the formation of-

- (A) Ferric ferrocyanide (B) Ferric sulphocyanide
(C) Ferric cyanide (D) None

Ans. (B)

Sol. $3 \text{ NaCNS} + \text{FeCl}_3 \longrightarrow \text{Fe(CNS)}_3 + 3\text{NaCl}$
(Red)

Q.2 On complete combustion, 0.246g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Sol. Percentage of carbon = $\frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95 \%$

Percentage of hydrogen = $\frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58 \%$

Q.3 In Duma's method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K = 15 mm)

Sol. Volume of nitrogen collected at 300K and 715 mm pressure is 50mL

Actual pressure = 715 - 15 = 700 mm

Volume of nitrogen at STP = $\frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ mL}$

22,400 mL of N_2 at STP weight = 28g

41.9 mL of nitrogen weight = $\frac{28 \times 41.9}{22400} \text{ g}$

Percentage of nitrogen = $\frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$

Q.4 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4 . Find out the percentage of nitrogen in the compound.

Sol. 1 M of 10 mL H_2SO_4 = 1M of 20mL NH_3 1000 mL of 1M ammonia contains 14 g nitrogen

20 mL of 1M ammonia contains $\frac{14 \times 20}{1000} \text{ g}$ nitrogen

Percentage of nitrogen = $\frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0 \%$

Q.5 In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Sol. Molar mass of AgBr = $108 + 80 = 188 \text{ g mol}^{-1}$

188 g AgBr contains 80 g bromine

0.12 g AgBr contains $\frac{80 \times 0.12}{188} \text{ g bromine}$

Percentage of bromine = $\frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04 \%$

Q.6 In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Sol. Molecular mass of $\text{BaSO}_4 = 137 + 32 + 64$
 $= 233 \text{ g}$

233 g BaSO_4 contains 32 g sulphur

0.4813 g BaSO_4 contains $\frac{32 \times 0.4813}{233} \text{ g sulphur}$

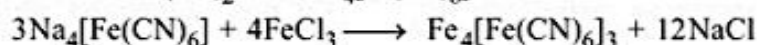
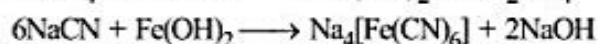
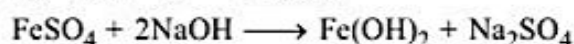
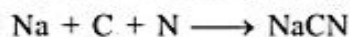
Percentage of sulphur = $\frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10 \%$

Q.7 In Lassaigne's test for nitrogen, the blue colour is due to the formation of-

- (A) Ferric ferrocyanide
- (B) Potassium ferrocyanide
- (C) Sodium ferrocyanide
- (D) Sodium cyanide

Ans. (A)

Sol. In Lassaigne's test substance is heated strongly with sodium metal then water extract is boiled with alkaline FeSO_4 solution and after cooling FeCl_3 solution and excess of HCl is added in it. If prussian blue or green ppt. is obtained then Nitrogen is confirmed-



sodium ferrocyanide

prussian blue or green

(ferric ferrocyanide)

Q.8 In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to-

- (A) Sodamide
- (B) Sodium cyanide
- (C) Sodium nitrite
- (D) Sodium nitrate

Ans. (B)

Sol. $\text{Na} + \text{C} + \text{N} \xrightarrow{\text{fusion}} \text{NaCN}$

Q.9 A compound which does not give a positive test in the Lassaigne's test for 'N' is-

- (A) Glycine
- (B) Phenyl hydrazine
- (C) Urea
- (D) Azobenzene

Ans. (D)

Sol. Azobenzene does not give positive test in Lassaigne's test for N.

Q.10 Liebig method is used for the estimation of-

- (A) Nitrogen (B) Sulphur
(C) Carbon and Hydrogen (D) Halogens

Ans. (C)

Sol. Liebig method is used for the estimation of carbon and hydrogen.

Q.11 The quantitative determination of halogen in an organic compound is known as-

- (A) Dumas method (B) Carius method (C) Kjeldahl method (D) Leibig method

Ans. (B)

Sol. The quantitative determination of halogen in an organic compound is called as carius method.

Q.12 0.2475g of an organic compound gave on combustion 0.4950g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are-

- (A) 54.54, 9.09 (B) 52.54, 8.09 (C) 120, 5.8 (D) None

Ans. (A)

Sol. Wt. of organic compound = 0.2475 g

Wt. of CO_2 produced = 0.4950 g

Wt. of H_2O produced = 0.2025 g

Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } \text{CO}_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } \text{H}_2\text{O}}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

Q.13 0.257 g of an organic substance was heated with conc H_2SO_4 and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 ml of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralisation at the end of the process. The percentage of nitrogen in the compound is-

- (A) 14.6 (B) 18.0 (C) 17.0 (D) 15.5

Ans. (A)

Sol. Volume of $\frac{\text{N}}{10}$ HCl taken = 50ml

Volume of $\frac{\text{N}}{10}$ NaOH used for neutralisation of unused acid = 23.2 ml

Now $N_1 V_1(\text{NaOH}) = N_2 V_2(\text{HCl})$

23.2 ml of $\frac{\text{N}}{10}$ NaOH \equiv 23.2 ml of $\frac{\text{N}}{10}$ HCl

\therefore Volume of $\frac{N}{10}$ HCl unused = 23.2 ml

\therefore Volume of $N/10$ HCl required for neutralization of NH_3 = 50 - 23.2 = 26.8 ml

26.8 ml of $\frac{N}{10}$ HCl = 26.8 ml of $N/10$ NH_3

1000 ml of 1N NH_3 solution contains nitrogen = 14 g

26.8 ml of NH_3 solution contains nitrogen = $\frac{14 \times 26.8}{10 \times 1000}$

Percentage of nitrogen = $\frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257} = 14.6\%$

Q.14 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of $BaSO_4$. The percentage of sulphur in the compound is-

- (A) 20.24 (B) 35 (C) 40 (D) 45

Ans. (A)

Sol. Mass $BaSO_4$ = 0.582 g

We know $BaSO_4 \equiv S$
 233 32

233 g of $BaSO_4$ contain sulphur = 32 g

0.582 g of $BaSO_4$ contains sulphur = $\frac{32}{233} \times 0.582$

Percentage of sulphur

$$= \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100 = \frac{32 \times 0.582}{233 \times 0.395} \times 100 = 20.24 \%$$

Q.15 Liquid which decompose below their normal boiling points can be distilled at lower temperature by-

- (A) Increasing the pressure (B) Decreasing the pressure
 (C) Heating in water bath (D) Heating in sand bath

Ans. (B)

Sol. B.pt. gets lowered at low pressure.

Q.16 A bottle containing two immiscible liquids is given to you. They may be separated by using-

- (A) Fractionating column (B) Separating funnel
 (C) Vacuum distillation (D) Steam distillation

Ans. (B)

Sol. Being immiscible liquids, they form different layers.

ENVIRONMENTAL CHEMISTRY

INTRODUCTION

- (i) Pollution may be defined as any undesirable change in the physical, chemical or biological characteristics of air, water and soil which may cause any harm to man and other living organisms of the environment.

Types of pollutants

The agents causing pollution are termed as **pollutants**.

On the basis of form of their occurrence, pollutants are divided into two categories.

- (i) **Primary pollutants** – These are present in the same form in which they are produced. eg. carbon monoxide, DDT
- (ii) **Secondary pollutants** – These are formed by reaction between the primary pollutants in the presence of sunlight eg. PAN, Ozone, HNO_3 , H_2SO_4 etc. Nitrogen oxides and hydrocarbons react photochemically to produce peroxyacetyl nitrates (PAN) and ozone.
The secondary pollutants may be more toxic than the primary ones. The phenomenon is called **synergism**.

On the basis of their degradation, pollutants are divided into two categories.

- (i) **Biodegradable Pollutants** – Pollutants which are decomposed or degraded by biological or microbial action are called biodegradable pollutants eg. domestic sewage.
- (ii) **Non-biodegradable Pollutants** – Pollutants which are not decomposed or degraded by living organisms or micro organisms are called non-biodegradable pollutants eg. DDT, glass, plastics, aluminium cans, phenolic compounds, pesticides, radioactive substances, heavy metals like mercury, lead, cadmium etc.

On the basis of their existence in nature, pollutants are divided into two categories.

- (i) **Quantitative pollutants** – These are naturally present in nature and are also added by man. These become pollutants only when their concentration reaches beyond a threshold value in the environment. eg. CO_2 .
- (ii) **Qualitative pollutants** – These are not present in nature but are added in nature only due to human activities eg. insecticides, fungicides, herbicides etc.

KINDS OF POLLUTION

On the basis of environmental study pollution is of following types.

Air pollution

Water pollution

Soil pollution

Noise pollution

Radioactive pollution

Air pollution –

- (i) It is mainly caused by industries and automobiles. Automobiles are the greatest polluter of the atmosphere and are responsible for 75% of noise pollution and about 60-80% of air pollution of big cities.
- (ii) The combustion of fossil fuels (coal, oil, gas etc.) releases CO, CO₂, nitrogen oxides, fluorides, hydrocarbons etc. into atmosphere usually in the form of smoke causing air pollution.
- (iii) Particulate matters released by mills, factories and mines also cause air pollution.
- (iv) Some of the natural air pollutants are pollen grains, spores, volcanoes etc.

MAJOR AIR POLLUTANTS**Carbon monoxide –**

- (i) It is formed by incomplete combustion of fuels in various industries, automobiles etc.
- (ii) CO accounts for about 50% of total air pollution. It is largest pollutant in Delhi's air.
- (iii) CO combines with haemoglobin, produces **carboxyhaemoglobin** and therefore decreases oxygen carrying capacity leading to hypoxia, headache, decreased vision, muscular weakness, nausea, exhaustion etc.
- (iv) When 50% of haemoglobin has been transformed into carboxyhaemoglobin, then death occurs due to CO-poisoning leading to anoxia (oxygen starvation)

Carbon dioxide –

- (i) It is a **green house gas**. It is produced due to combustion of fuels, volcanic eruptions and during the process of respiration.
- (ii) Its average concentration in the atmosphere is 300 ppm (0.03%) .
- (iii) It is normally not an atmospheric pollutant, but under very high concentration it may act as a pollutant.
- (iv) It causes **Global warming** .

Sulphur dioxide (SO₂) –

- (i) It is produced during combustion of fossil fuels (mainly coal) and smelting of sulphur containing ores.
- (ii) It causes acid rain (gaseous SO₂ oxidises to SO₃, which on combination with water forms H₂SO₄).
- (iii) Acid rain is 60-70% due to SO₂ and SO₃, and 30-40% due to NO₂ and NO₃.
- (iv) Due to acid rain the leaves develop chlorotic and necrotic spots.
- (v) SO₂ corrodes stones, metals, leather, paper and fabrics. There is deterioration of colour and lustre of fabrics, stones and painted surfaces.

Hydrocarbons –

- (i) They are produced naturally (e.g. marsh gas CH₄) and by burning of petroleum.
 - (ii) Benzene (C₆H₆) is a major constituent of petrol and automobile exhaust.
 - (iii) Hydrocarbons are carcinogenic, cause irritation of eyes and mucous membrane.
 - (iv) Benzene is a known carcinogen causing **leukemia**.
-

- (v) Ethylene (C_2H_4) causes premature senescence and abscission in many plants especially in orchids and cotton,
- (vi) Methane (marsh gas) has the potential of destroy ozone.

Nitrogen oxides –

- (i) There are three oxides of nitrogen which act as air pollutants : Nitric oxide (NO), nitrogen dioxide (NO_2) and nitrogen trioxide.
- (ii) Nitrogen and oxygen combine together at high temperature in any combustion process to produce nitrogen oxides.
- (iii) These are also released by furnaces, forest fires, industries and denitrifying bacteria.
- (iv) NO is less toxic but NO_2 is a poisonous gas.
- (v) Nitrogen oxides are responsible for forming photochemical smog.

Fluorides –

- (i) Fluorides are emitted during refinement of aluminium and rock phosphates .
- (ii) Fluorides cause necrosis and chlorosis of leaf tips and leaf margins.
- (iii) In human fluorides cause mottling of teeth, weak bones, boat-shaped posture, knocking knees etc.
- (iv) Disease caused by fluoride is known as **fluorosis**.

Particulate matter –

- (i) It is the non-gaseous matter in the atmosphere.
- (ii) It consists of soot, dust, mist, fibres, fly ash, fur, spores, pollen grains etc.
- (iii) It is of two types settleable (larger than $10\ \mu m$) and suspended (less than $10\ \mu m$)
- (iv) SPM (suspended particulate matter) is classified into 3 categories –
 - (a) Aerosols (less than $1\ \mu m$)
 - (b) Dust (solid particles with more than $1\ \mu m$ diameter)
 - (c) Mist (liquid particles with more than $1\ \mu m$ diameter)
- (v) It is added in the atmosphere by burning of fuels.

Aerosols –

- (i) These are chemicals released in the air with force in the form of mist or vapour by jet planes.
- (ii) Aerosols contain **CFC (chlorofluorocarbons)** which destroy ozone layer in the stratosphere. This permitting some more harmful
- (iii) U.V. radiations to reach the earth surface, U.V. radiations cause skin cancer and increases mutation rates.
- (iv) Ozone acts as preventive shield against the U.V. rays.
- (v) Freons are several CFMS (chlorofluoromethanes) released into troposphere where they dissociates and release free chlorine that causes depletion of ozone.
- (vi) Freon or CFC also used in refrigerator, air conditioners and in making plastic foams.

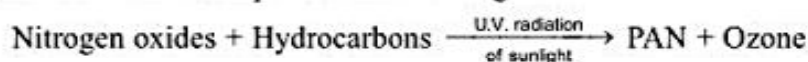
Effect of air pollutants – Air pollutants are involved in causing four major environmental effects :

- | | |
|--------------------------|-----------------------------|
| (i) Smog | (ii) acid rain |
| (iii) global warming and | (iv) ozone layer depletion. |

Smog –

- (i) The term smog was coined by Des Voeux.
- (ii) It is produced by the combination of smoke and fog.
- (iii) It causes silvering/glazing and necrosis in plants, allergies and asthma/bronchitis in human.
- (iv) Smog is of two types :
 - (a) **Classical or London smog or sulphurous smog** – It occurs at low temperature and contains H_2S , SO_2 , smoke and dust particles. It was first observed in winter months at London in 1905. It is formed due to domestic and industrial combustion of coal.
 - (b) **Photochemical smog or Los Angeles smog** – It was first observed in the mid day at Los Angeles in 1943. The cause of this smog was thought to be due to combustion of petroleum in automobiles.

Photo chemical smog occurs at high temperature over cities and towns. It is formed by the reaction of two air pollutants nitrogen oxides (mainly NO_2) and hydrocarbons (HC) that react with one another in the presence of UV radiations of sunlight to produce ozone (O_3) and PAN (peroxy acetyl nitrate) which constitute the photochemical smog.



Ozone and PAN are commonly referred to as oxidants.

Breathing ozone affects the respiratory and nervous system, resulting in headache, respiratory distress and exhaustion. It also causes irritation in eyes and asthma. The ozone is known to destroy crops of potato, alfalfa and spinach to the extent of 50%. It also damages leaves of tobacco, tomato and pine as also the grape fruits. Besides, the PAN also blocks Hill reaction of photosynthesis.

Acid rain –

- (i) The coal and oil burned by power plants release SO_2 into the air.
- (ii) Automobile exhaust puts NO_2 in the air.
- (iii) Both SO_2 and NO_2 are converted to acids (H_2SO_4 and HNO_3 respectively) when they combine with water vapour in the presence of O_2 in the atmosphere. These acids return to the earth as acid rain.
 - (A)

$\text{NO} + \text{O}_3$	\longrightarrow	$\text{NO}_2 + \text{O}_2$
$\text{NO}_2 + \text{O}_3$	\longrightarrow	$\text{NO}_3 + \text{O}_2$
$\text{NO}_2 + \text{NO}_3$	\longrightarrow	N_2O_5
$\text{N}_2\text{O}_5 + \text{H}_2\text{O}$	\longrightarrow	2HNO_3
 - (B) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{No. Soot or Metal ions}} 2\text{SO}_3$
- (iv) The pure rain has a pH of about 5.6 while the acid rain has pH below 5.6.
- (v) Acid rain is actually a mixture of H_2SO_4 and HNO_3 (usually 60-70% H_2SO_4 and 30-40% HNO_3)
- (vi) Acid rain affects the ability of the trees to tolerate cold temperatures and the weakened trees are killed by cold conditions or become more susceptible to diseases.
- (vii) Acid rain leaches lead, mercury and calcium, from the soils and rocks and discharges them into rivers and lakes. The metals may become concentrated in fish and then passed on to people through food chain.
- (viii) Acid rain also damages building materials, including steel, paint, plastics, cement and marble.

Green house effect and Global warming –

- (i) The sunlight that reaches to the earth, warms both atmosphere and the earth surface. The earth's atmospheric system then radiates the heat as infra-red radiations.
- (ii) Gases like CO_2 , CH_4 , CFCs, NO_2 are strong absorbers of long-wave or infra-red radiations emitted by the surface of the earth, and warm the earth's atmosphere. This is called the **green house effect** because it is like the glass panel of a green house that allows sunlight to pass through and then traps the resulting heat inside the structure.
- (iii) CO_2 is the principal green house gas responsible for warming of the earth.
- (iv) CO_2 is rising into the atmosphere slowly as a result of large scale burning of fossil fuels (coal, oil etc), volcanic activities and respiration
- (v) 50% of the increase in earth's temperature is due to CO_2 , 20% is due to CFCs and remaining 30% is due to other gases.

Ozone layer depletion –

- (i) The ozone layer present in the stratosphere acts as an ultraviolet absorbant thus protecting the earth from its harmful effect.
- (ii) Depletion/destruction of ozone layer is primarily caused by CFCs (Chlorofluoro carbons) and halons(halocarbons $\text{C}_x\text{F}_x\text{Br}_x$)
- (iii) CFCs are heat transfer agents used in refrigerators, air conditioners, fire extinguishers.
- (iv) Halons are antifire agents used in fire extinguishes .
- (v) The CFCs react with ozone and thus cause thinning of ozone layer which permits more UV radiations to reach the surface of earth.

WATER POLLUTION

Water pollution is defined as the addition of some substances (organic, inorganic , biological, radio logical) or factor (eg. heat) which degrades the quality of water so that, it either becomes health hazard or unfit for use.

Kinds of water pollution –

The water pollution may be physical, chemical or biological.

- (a) **Physical pollution** – It involves the changes in the physical properties of water eg. colour, taste, odour, temperature, turbidity etc.
- (b) **Chemical pollution** – It is caused due to change in the chemical properties of water. They mainly include the pH, dissolved O_2 , inorganic or organic chemicals, heavy metals etc.
Inorganic chemicals include fluorides, chlorides, phosphates and nitrates. Organic chemicals include phenols, dyes, pesticides and chlorocompounds.
- (c) **Biological pollution** – It is caused due to the presence of living organisms in water such as algae, fungi, bacteria, viruses, protozoans, insects etc.

Sources of water pollution and effects of water pollutants –

Water pollution is a serious health hazards in India, especially in villages. It is estimated that 50-60% of Indian population suffers from diseases caused by it. 30-40% of all deaths are believed to be due to it.

The principal sources of water pollution and effects of water pollutants are as follows.

Domestic wastes and sewage

- (i) Sewage containing human faeces, urine, kitchen and cloth washings, organic waste, industrial waste etc. is usually poured into water bodies which cause water pollution.
- (ii) The villagers often wash their animals, cloths and take bath in the same pond. Such water get contaminated with infectious agents for cholera, typhoid, dysentery, Jaundice and skin diseases.
- (iii) Sewage provide food for decomposers, so the population of decomposers increases.
- (iv) Decomposers/microorganisms causing decomposition of sewage take up most of the oxygen present dissolved in water. So in this water BOD (Biological oxygen demand or Biochemical oxygen demand) increased very much.
- (v) BOD is the amount of oxygen in milligrams required by microorganisms for five days to metabolise waste present in one litre of water at 20°C .

Industrial effluents (or industrial discharges)

Industries usually discharge waste water into ponds, lakes and rivers. Industrial waste water contains heavy metals (mercury, lead, copper, arsenic and cadmium), inorganic pollutants (acids, alkalies and bleaching liquors), organic pollutants (phenol, naphtha, proteins, aromatic compounds, cellulose fibres etc.) Industrial effluents are the most hazardous pollutants on land and water.

(a) Mercury (Hg) –

- (i) It is released during combustion of coal, smelting of metallic ores, paper and paint industries.
- (ii) Mercury is highly persistent . In water it gets changed into water soluble dimethyl form $[(CH_3)_2Hg]$ and enters the food chain (undergoes biomagnification).
- (iii) It kills fish and poisons the remaining fauna. Human beings feeding on such poisoned animals develop a crippling deformity called **minamata disease** which is characterised by impairment of various senses, diarrhoea, haemolysis, meningitis and death.
- (iv) The minimata disease was first detected in Japan.
- (v) Mercury inhibits chromosomal disjunction during gamete formation. So it brings about genetic changes also.

(b) Lead (Pb) –

- (i) The sources of lead pollution are smelters, battery industry, paint, chemical and pesticide industry, automobiles exhausts etc.
- (ii) Lead is pollutant of air, soil and water.
- (iii) It is used as anti-knock reagent in petrol and released by automobile exhausts.
- (iv) Lead is a persistant pollutant and may show biological amplification or biomagnification.
- (v) It is a mutagenic and causes anemia, headache, vomitting, colic, loss of muscle power, bluish lines around the gums, loss of appetite and damage of liver, kidney and brain.

(c) Cadmium (Cd) –

- (i) It is added to the environment by metal industries, welding and electroplating, pesticides and phosphate industries.
- (ii) Cd shows biological amplification and accumulates inside kidneys, liver, pancreas and spleen.
- (iii) It causes hypertension, anemia, diarrhoea and damages liver and kidneys.

Oil

- (i) During extraction and transportation of oil from the sea to different parts, some of the oil spreads over the surface of water. Refineries also discharge a lot of oil present in their effluents into rivers.
- (ii) Oil spreading on the surface of water prevents its oxygenation and inhibits photosynthetic activity of aquatic plants. Animal life is destroyed due to reduced availability of oxygen, food and toxic effects of oil.
- (iii) Oil spilled over the surface of water may catch fire and hence kill all organic life.

Thermal pollution

- (i) Hot water is produced by many industries, power generation plants and thermal power plants.
- (ii) Thermal pollution is caused by addition of hot water effluents in water bodies, it brings about rise in water temperature.
- (iii) Warmer water contains less oxygen. Therefore, there is decrease in the rate of decomposition of organic matter.
- (iv) In hot water green algae are replaced by less desirable blue green algae.
- (v) Many organisms fail to reproduce in hot water e.g. Salmon, Trout.

SOIL POLLUTION

- (i) Unfavourable alteration of soil by addition or removal of substances and factors which decrease soil productivity, quality of plant products and ground water is called soil pollution.
- (ii) The soil pollutants include pesticides, fertilizers, industrial wastes, salts, radio-nuclides, tin, iron, lead, copper, mercury, aluminium, plastics, paper, glass, broken bottles, discarded food etc.

Types of Soil pollution

Soil pollution is of two main types

Negative soil pollution

Positive soil pollution

Negative soil pollution –

- (i) It includes over use of soil and erosion.
- (ii) Soil erosion is caused by water and wind.
- (iii) Water erosion of soil is found near the hills where high speed flooding removes top soil.
- (iv) Soil erosion also occurs by high speed winds which bring sand particles from dry desert.

Positive soil pollution – It is caused by addition of undesirable substances (eg. pesticides, fertilizers, industrial waste, air pollutant washed down from atmosphere through rain)

(A) Pesticides –

- (i) These include insecticides (kill insects), fungicides (kill fungi), algicides (kill algal blooms), weedicides or herbicides (kill weeds), rodenticides (kill rodents).
- (ii) Pesticides are generally broad-spectrum and affect other animals, man and even plants. They are hence, also called **biocides**.
- (iii) DDT (dichloro diphenyl trichloroethane), BHC (benzene hexachloride or gamaxine), aldrin, dieldrin, endrin, heptachlor etc. are chlorinated hydrocarbons used as pesticides.

- (iv) Dieldrin is five times more toxic than DDT when ingested and 40 times more poisonous when absorbed.
- (v) Endrin is the most toxic amongst chlorinated hydrocarbons.

(B) Fertilizers –

- (i) The fertilizers contain plant nutrients particularly N,P and K , but the soil also gets polluted mainly due to organic pollutants present as impurities.
- (ii) Excessive use of fertilizers cause soil deterioration through decrease of natural microflora (nitrogen fixing, nitrifying bacteria)
- (iii) Fertilizers added to soil enter the crop plants. Nitrogen fertilizers produce toxic concentration of nitrate in the leaves and fruits. When these leaves and fruits are eaten, nitrates changed into nitrites by the activity of bacteria in the alimentary canal. The nitrites enter the blood and combine with haemoglobin to form methaemoglobin. As a result oxygen transport is reduced. It gives rise to disease known as **methaemoglobinaemia**. In infants it produces **cyanosis (blue baby syndrome)**

(C) Industrial wastes –

- (i) Wastes of the industries are dumped over the soil. They contain a number of toxic substances including cyanides, acids, chromates, alkalies and metals like mercury, copper, zinc, lead, cadmium etc.
- (ii) The industrial pollutants increase the toxicity level of the soil.
- (iii) Heavy metals destroy useful micro organisms of the soil.
- (iv) In 1970 some 200 people died in Japan by Cd pollution of soil due to **itai-itai disease**.

NOISE POLLUTION

- (i) Various kinds of undesirable loud sounds, which disturb our environment are called noise pollutants.
- (ii) Noise pollution is produced by loud sounds of various machines, loudly played radio, automobiles, thundering of jet planes, loud speakers etc.
- (iii) The intensity of noise is measured in decibels (or dB).
- (iv) The sound above 80 dB causes noise pollution.
- (v) Moderate conversation produces 60 dB sound, loud conversation 70dB.

SOLVED EXAMPLES

Q.1 Eutrophication causes reduction in-

- (A) Dissolved salts (B) Dissolved hydrogen
(C) Dissolved oxygen (D) All the above

Ans. (C)

Sol. Dissolved oxygen

Q.2 The smog is essentially caused by the presence of

- (A) O_2 and O_3
(B) Oxides of sulphur and nitrogen
(C) O_2 and N_2
(D) O_3 and N_2

Ans. (B)

Sol. Oxides of sulphur and nitrogen

Q.3 Which are quantitative pollutants out of the following

- (A) CO_2 (B) P_2O_5 (C) N_2O_5 (D) NO_2

Ans. (A)

Sol. CO_2 become pollutants only when their concentration reaches beyond a threshold value in the environment.

Q.4 Which are secondary pollutants in the following

- (A) O_3 (B) CO_2 (C) CO (D) Cl_2

Ans. (A)

Sol. These are formed by reaction between primary pollutants in the presence of sunlight.

Q.5 Which have Non-biodegradable pollutants in the following

- (A) DDT (B) Domestic sewage (C) CO_2 (D) NO_2

Ans. (A)

Sol. Pollutants which are not decomposed or degraded by living organisms or micro-organism.