QUANTITATIVE ANALYSIS

Estimation of Carbon and Hydrogen

Carbon and hydrogen in an organic compound are estimated by *Leibig's method..*

Principle

A known mass of the organic compound is heated strongly in a current of dry oxygen (free from CO_2) in the presence of dry cupric oxide till the oxidation of carbon and hydrogen is complete. Carbon and hydrogen present in the compound get oxidised to carbon dioxide and water respectively.

The mass of water produced is determined by passing the gas mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated *KOH* solution. The increase in masses of calcium chloride tube and *KOH* solution give the masses of H_2O and CO_2 respectively produced.

Calculation

Mass of organic compound taken = w g,

Mass of CO_2 produced = w_2 g

Percentage of carbon $= \frac{12}{44} \times \frac{w_2}{w} \times 100$

Mass of H_2O produced = w_1 g

Percentage of hydrogen $= \frac{2}{18} \times \frac{w_1}{w} \times 100$

Estimation of nitrogen: Nitrogen in an organic compound can be estimated by two methods.

(i) *Dumas' method* and (ii) *Kjeldahl's method*

(i) Dumas' method

Principle

A known mass of the organic compound (w g) is heated with excess of dry cupric oxide (CuO) in an atmosphere of carbon dioxide. The carbon and hydrogen get oxidised to CO_2 and H_2O respectively, whereas nitrogen is stable towards oxidation and is set free. If any oxide of nitrogen is formed in the process, it is reduced to nitrogen by passing over a hot copper gauze. The mixture of gases so produced is collected over an aqueous solution of KOH. All the gases except nitrogen are absorbed in KOH solution. The volume of nitrogen gas produced is measured (V_1 mL) at room temperature (T_1 K). The pressure P_1 of N_2 is obtained by subtracting aqueous tension from the atmospheric pressure (This is because N_2 is collected over water).

Calculation

The volume of N_2 at STP is calculated using the gas equation $\frac{PV}{T} = \frac{P_0V_0}{T_0}$

where P_0 = 760 mm, T_0 is 273 K, $P = P_1$ mm, $V = V_1$ mL

$$\therefore V_0 = \frac{P_1V_1T_0}{P_0T_1} = \frac{P_1V_1 \times 273}{760 \times T_1} mL$$

Mass of 22400 mL of N_2 gas at STP = 28 g (gram molecular mass of N_2)

$\therefore$ Mass of V_0 mL of N_2 at STP $= \frac{28}{22400} \times V_0$ g

Percentage of nitrogen $= \frac{28}{22400} \times \frac{V_0}{w} \times 100$

(ii) Kjeldahl's method

Principle

A known mass of the organic compound is heated strongly with con. H_2SO_4 in a *Kjeldahl's flask.* (A small quantity of K_2SO_4 and $CuSO_4$ are also added to the flask. Potassium sulphate raises the boiling point of the mixture while copper sulphate acts as a catalyst). Then nitrogen in the organic compound gets converted quantitatively into ammonium sulphate. The solution is then heated with excess of sodium hydroxide when ammonium sulphate is decomposed into ammonia gas. The ammonia gas is then absorbed in a known excess volume of standard sulphuric acid

solution. The amount of acid left unreacted is determined by titrating the solution against standard alkali solution. From this value, the amount of acid used up by ammonia can be calculated and this would correspond to the amount of ammonia produced. The reactions involved are the following.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Calculation

Mass of organic compound taken $= w\,g$

Volume of H_2SO_4 solution taken $= V_1\,mL$

Molarity of sulphuric acid solution $= M$

Volume of H_2SO_4 solution remaining unreacted $= V_2\,mL$

$\therefore$ Volume of H_2SO_4 neutralised by NH_3 $= (V_1 - V_2)\,mL$

1 mole of H_2SO_4 requires 2 moles of NH_3 for neutralisation

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

$\therefore$ 1000 mL 1M $H_2SO_4 \equiv$ 2 mol $NH_3 \equiv 2 \times 17\,g\,NH_3 \equiv 2 \times 14\,g$ nitrogen

$$\therefore \text{ Percentage of nitrogen } = \frac{2 \times 14\,(V_1 - V_2)\,M}{1000} \times \frac{100}{w}$$

$$= \frac{\mathbf{1.4 \times M \times 2\,(V_1 - V_2)}}{w}$$

Estimation of halogens (Carius method)

A known mass of the organic compound (w g) is heated with fuming nitric acid in the presence of silver nitrate in a sealed tube called *Carius tube* . During heating the carbon and hydrogen are oxidised to CO_2 and H_2O respectively while the halogen forms a precipitate of silver halide (AgX). The precipitate is filtered, washed, dried and weighed. From the weight of silver halide formed (w g), the percentage of halogen can be calculated.

Calculation

Mass of organic compound $= w\,g$

Mass of silver halide formed $= w_1\,g$

$$\therefore \textbf{ Percentage of halogen } = \frac{\textbf{atomic mass of X (halogen)}}{\textbf{molecular mass of AgX}} \times \frac{\mathbf{w_1}}{\mathbf{w}} \times \mathbf{100}$$

Estimation of sulphur (Carius method)

A known mass of the organic compound (w g) is heated with fuming nitric acid in a Carius tube. The sulphur present in the compound is quantitatively converted into sulphuric acid, which is precipitated as barium sulphate using excess barium chloride. The precipitate of $BaSO_4$ is filtered, washed, dried and weighed. From the weight of $BaSO_4$, the percentage of sulphur in the organic compound can be calculated.

Calculation

Mass of organic compound taken = $w\,g$

Mas of $BaSO_4$ formed = $w_1\,g$

Molecular mass of $BaSO_4$ = 233

Mass of S in 233 g $BaSO_4$ = 32 g

Percentage of sulphur $= \frac{32}{233} \times \frac{w_1}{w} \times 100$