# SEPARATION AND PURIFICATION TECHNIQUES

General principles involved in the separation of precipitates

Precipitation is the one of the several separation techniques used in analytical chemistry. The basic principle of separation by precipitation is that **the concentration of a substance should exceed its solubility in a particular solvent.** Solubility (s) of a substance is **the amount of the substance required to give a saturated solution of the substance in a particular solvent at a particular temperature.** Thus, precipitation of a substance depends on its solubility (s) which in turn depends upon the nature of the solvent, temperature etc.

Another important principle in effective precipitation is the **solubility product** (K_{sp}). Solubility product of a sparingly soluble salt is *the product of the concentration of ions raised to suitable powers in a saturated solution.*

Let as consider a sparingly soluble salt $A_x B_y$. In its saturated solution, the following equilibrium will exist.
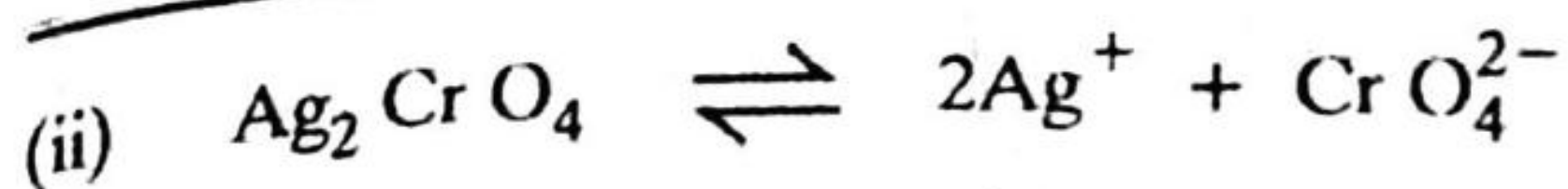
$$A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$$
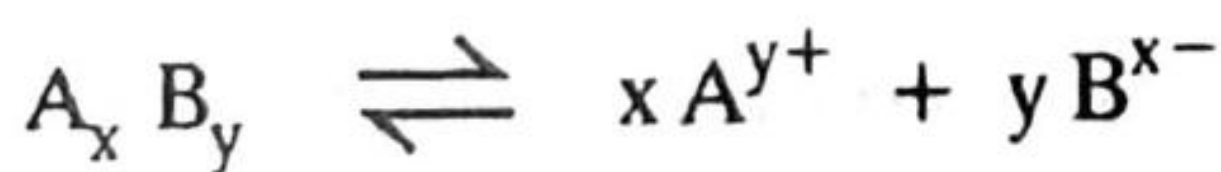
The solubility product (K_{sp}) of this salt is given by

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

For example,

(i) $$Ba\,SO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

(ii) $\quad Ag_2 Cr O_4 \rightleftharpoons 2Ag^+ + Cr O_4^{2-}$

$$K_{sp} = [Ag^+]^2 [Cr O_4^{2-}]$$

(iii) $Ca F_2 \rightleftharpoons Ca^{2+} + 2F^-$
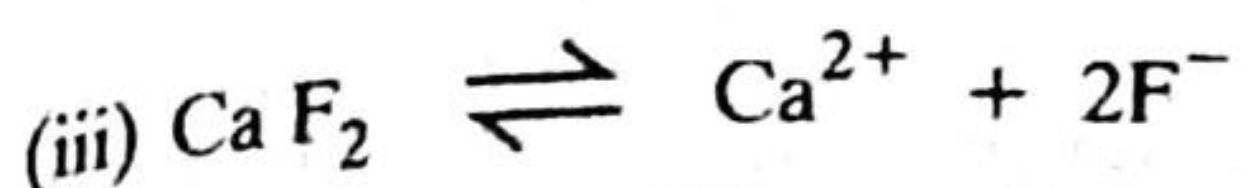
$$K_{sp} = [Ca^{2+}][F^-]^2$$

Let the solubility of the sparingly soluble salt $A_x B_y$ be s mole/lit. The relationship between the solubility (s) and the solubility product (K_{sp}) can be written as follows.
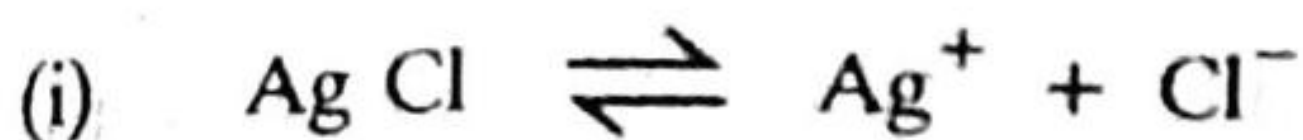
$$A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$$
$$ xs \qquad ys$$
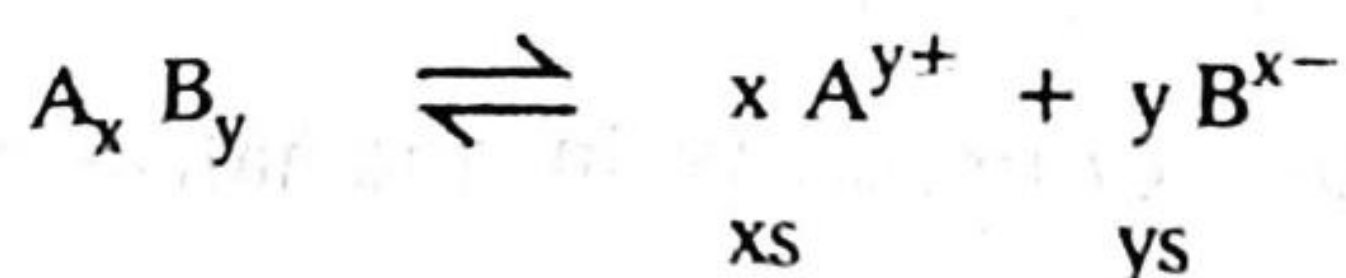
$$\therefore \quad K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

$$= (xs)^x (ys)^y$$

$$= x^x y^y s^{x+y}$$

For example ——

(i) $\quad Ag Cl \rightleftharpoons Ag^+ + Cl^-$

Here, $x = y = 1$.

$$\therefore Ksp = 1^1 1^1 (s)^{1+1} = s^2$$

(ii) $\quad Ca F_2 \rightleftharpoons Ca^{2+} + 2 F^-$
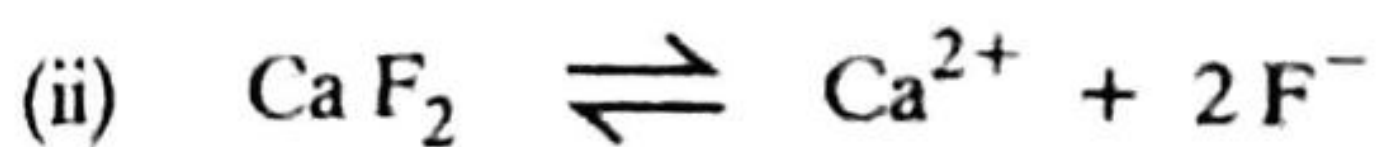
Here, $x = 1; \quad y = 2$

$$\therefore K_{sp} = 1^1 2^2 (s)^{1+2} = 4s^3$$

In the same way we can write for other sparingly soluble salts.

By employing suitable methods, when we make the ionic product to exceed solubility product, then the substance is precipitated. Using this principles, substances are separated by precipitation.
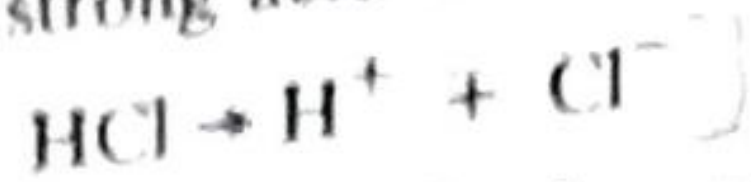
Explanation with examples

I.Precipitation of sulphides of group II in qualitative analysis

In qualitative analysis, the sulphides of group II (Cu, Cd, As, Sb, Bi and Sn) are precipitated in presence of dil. HCl. It can be explained as follows.

Hydrogen sulphide is a weak acid and ionises to a lesser extent as follows :

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
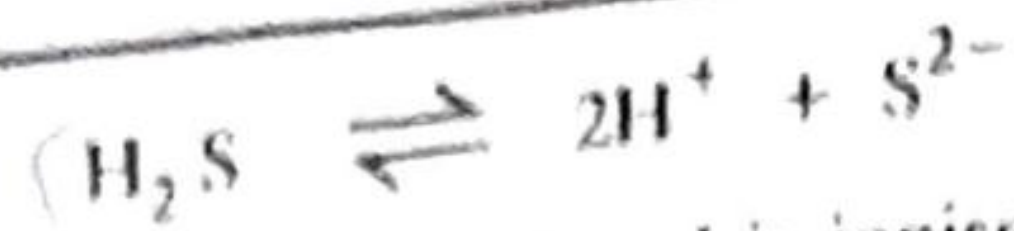
But, HCl is a strong acid and is ionised completely.

$$HCl \rightarrow H^+ + Cl^-$$

The ionisation of H_2S is further suppressed by the addition of dil. HCl due to **common ion effect.** Therefore, the concentration of S^{2-} becomes still smaller. But even this low concentration is larger than that required to exceed the solubility product of sulphides of Cu, Cd, Bi, As, Sb and Sn (The K_{sp} of CuS is 8.5×10^{-36}). Thus, these cations are precipitated as sulphides in the group II analysis.

II. Precipitation of sulphides of group IV in qualitative analysis

The solubility product of sulphides of Ni, Co, and Zn are comparatively higher (For example, K_{sp} of Ni S is 1.4×10^{-24}) than that of group II metal ions like Cu, Cd, Bi, As etc. The sulphide ion concentration in the presence of dil. HCl is insufficient for their precipitation. So, they are not precipitated in group II. The sulphides of group IV are precipitated only in the presence of NH_4OH.

In the presence of NH_4OH, the hydroxyl ions combine with H^+ ions of H_2S to give unionised water. Hence, more of H_2S ionises and thus the concentration of S^{2-} ions in solution increases. It becomes so high that the solubility product of Ni S etc. are exceeded and so they are precipitated out.

III. Precipitation of hydroxides of group III in qualitative analysis

Ammonium hydroxide is a weak base and ionises in solution to a very small extent as follows :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
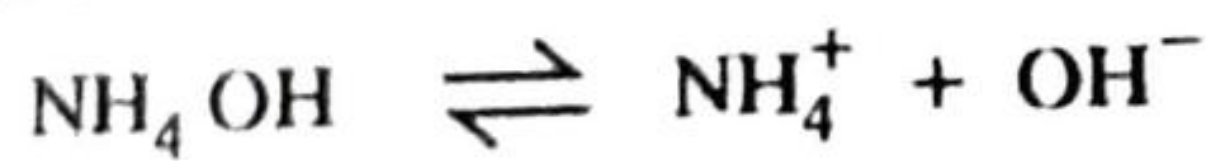
But, NH_4Cl salt is ionised completely.

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

In the presence of highly ionised NH_4Cl due to an increase in the number of NH_4^+ ions, the ionisation of NH_4OH is further suppressed due to common ion effect. Thus, the concentration of OH^- ions becomes very low. Under these conditions, the solubility product of the hydroxides of Al, Fe, Cr and Mn alone is reached (For example, the K_{sp} of $Fe(OH)_3$ is 1×10^{-38}) and these are precipitated out.

The hydroxides of Zn, Ni, Co, Mg are not precipitated from their salt solutions. It is because these hydroxides have comparatively higher K_{sp} values (K_{sp} of Zn $(OH)_2$ is 1.8×10^{-17}).

IV. Quantitative Analysis

In quantitative analysis an excess of the precipitating reagent is always employed to ensure complete precipitation.

For example, in the precipitation of barium chromate, a small quantity of $Ba\,Cr\,O_4$ may be left out in solution if equal quantities of reactants are used.

$$Ba\,Cl_2 + K_2\,Cr\,O_4 \rightleftharpoons 2KCl + Ba\,Cr\,O_4$$
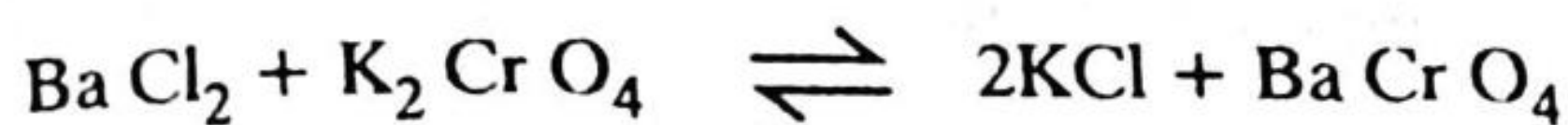
If a little excess of $K_2\,Cr\,O_4$ is used, the ionic product $[Ba^{2+}]\,[Cr\,O_4^{2-}]$ far exceeds the solubility product of $Ba\,Cr\,O_4$ and it is precipitated completely.

Solvent Extraction

It is a separation technique employed to separate a solid or liquid present in a mixture by extracting it with a solvent.

Principle: The substance to be extracted should be soluble in a particular solvent while all the other constituents in the mixture should be insoluble. After the extraction, the solvent should be easily separable.

Superiority of solvent extraction over precipitation methods

(i) 100 % separation is possible in solvent extraction method, whereas in precipitation methods, there is a possibility of some substance remaining in the mixture.

(ii) The procedural portion is simple.

(iii) In solvent extraction methods, a small amount of solvent is enough as it is recovered and recycled.

Uses of solvent extraction

Solvent extraction is used to separate ——

(i) Dissolved substances from their solutions.

(ii) One constituent from a solid mixture.

(iii) Unwanted impurities from substances.

Nernst Distribution law

Separation of a substance from a solution in a solvent from other dissolved substances, using another solvent is achieved using solvent extraction which is based on Nernst distribution law.

Law : *At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio.*

The ratio of the concentrations in the solvents is called the **partition coefficient** or **distribution coefficient, K_D.**

Let C_A and C_B be the concentrations of the solute in liquids A and B at constant temperature, then $C_A/C_B = K_D = $ constant.

Larger the value of K_D, more efficient is the extraction.

When a solute distributes itself between two solvents without dissociation or association, it is possible to calculate the weight of the solute which can be removed by a series of extraction.

If V_i ml of a solution contains W g of a solute and if the solute is repeatedly extracted with v ml of another solvent, the weight of the solute W_n remaining in the first solvent after n extraction is given by,

$$W_n = W \left[\frac{K_D V_i}{K_D V_i + v} \right]^n$$

Here, K_D is the distribution coefficient.

From the above equation we find that

(i) In order to make W_n as small as possible for a given value of K_D, n should be as large as possible.

(ii) nv is equal to the total volume of the extracting liquid available and is a constant. Hence, if n should be large, then v should be small.

(iii) For a given volume of extracting solvent, the extraction process is more efficient when the extracting solvent is added in small portions instead of using the whole of it in one lot. This is explained with the following worked example.

WORKED EXAMPLE

The partition coefficient of a solute (A) between water and ether is 10. Calculate how much solute A would be extracted from 1 lit of

water containing 20 g of the solute if extracted with 200 ml of ether in (i) one lot (ii) using 100 ml ether in two stages.

I. Using 200 ml ether in one lot

The amount of solute that remains unextracted at the end of one extraction, W_1 is given by,

$$W_1 = W \left(\frac{K_D V}{K_D V + v} \right)^1$$

Here, $W = 20$ g; $K_D = \frac{1}{10} = 0.1$; $V = 1000$ ml; $v = 200$ ml.

$$\therefore W_1 = 20 \left(\frac{0.1 \times 1000}{0.1 \times 1000 + 200} \right)$$

$$= 20 \left(\frac{100}{100 + 200} \right) = 20 \times \frac{100}{300} = 6.67 \text{ g}.$$

$\therefore$ The amount of solute extracted $= 20 - 6.67 = $ **13.33 g.**

II. Using 100 ml ether in two extractions

$$W_2 = W \left(\frac{K_D V}{K_D V + v} \right)^2$$

Here, $W = 20$ g; $K_D = \frac{1}{10} = 0.1$; $V = 1000$ ml; $v = 100$ ml

$$W_2 = 20 \left(\frac{0.1 \times 1000}{0.1 \times 1000 + 100} \right)^2$$

$$= 20 \times \left(\frac{100}{200} \right)^2 = 20 \times (\tfrac{1}{2})^2 = 20 \times \frac{1}{4} = 5 \text{ g}$$

$\therefore$ The amount of solute extracted $= 20 - 5 = $ **15 g**

Hence, the second process (two steps extraction) is more efficient.

ELECTROPHORESIS

The colloidal particles carry specific charge. *When current is passed through colloidal solution, the colloidal particles migrate and when the dispersion medium does not migrate, the phenomenon is known as electrophoresis.* This can be demonstrated by Burton tube experiment. (Fig 4.1).

This consists of a U - tube provided with a stop cock through which it is connected to a funnel shaped reservoir. A small amount of water is first placed in the U - tube and a reasonable quantity of the colloid is taken in the reservoir. The stop cock is then slightly opened and the reservoir is gradually raised so as to introduce the colloid into the U - tube gently. The water is displaced upwards producing a sharp boundary in each arm. A voltage of 50 to 200 volts is then applied by means of platinum electrodes which are immersed in water layer only.
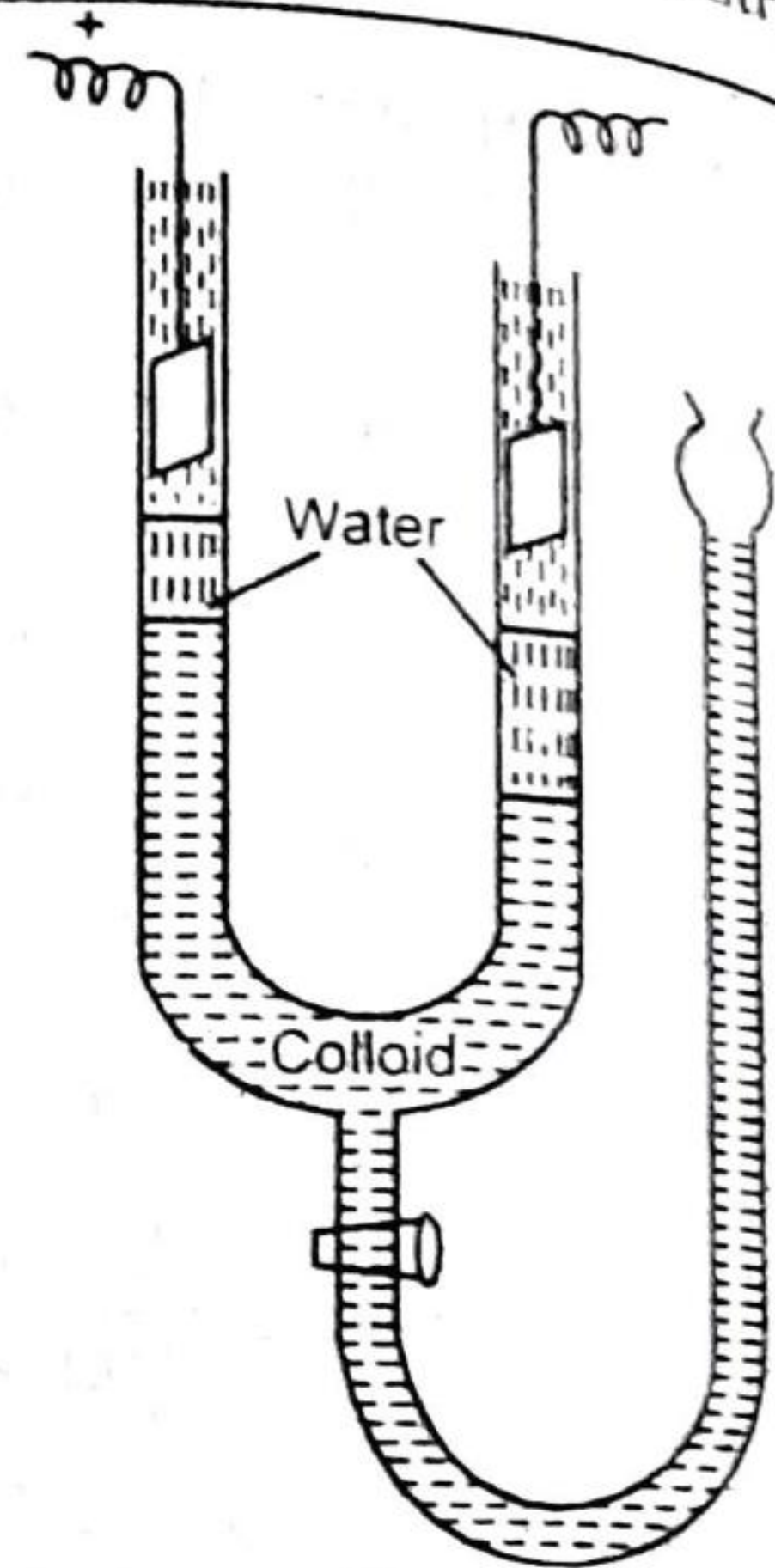
Electrophoresis

The movement of the particles can be readily followed by observing the position of the boundary by means of a naked eye or a lens or a cathetometer. When the particles are negatively charged, as in the case of $As_2 S_3$ colloid, the boundary on the negative electrode side is seen to move down and that on the positive electrode side to move up showing that the particles move towards the positive electrode.

APPLICATIONS

(i) By noting the direction of motion of the particles in the electric field, it is possible to determine the sign of the charge carried by the particles.

(ii) It is also possible by this technique to determine the rate at which colloidal particles migrate in an electric field.

(iii) The sign of charge on bacteria and viruses can be determined

(iv) Rubber can be electrodeposited on metal objects as in electroplating.

(v) Biomolecules like proteins, carbohydrates, nucleic acids can be separated using electrophoresis from their solutions.

PURIFICATION OF ORGANIC SOLIDS

Soxhlet Extraction: *It is the extraction of a solid with an organic solvent, in which the impurities are insoluble using the Soxhlet extractor* (Fig. 4.2)

Principle : (The substance to be extracted should be soluble in a particular solvent while all other constituents in the mixture should be insoluble. After the extraction, the solvent should be easily separable.)

Procedure : (Soxhlet extractor consists of a glass cylinder C with a side tube T and a siphon, S. A water condenser is attached at the top of C.) (The sample from which the solid to be extracted is powdered. It is placed in a thimble made up of a thick filter paper. The thimble is placed at the bottom of the water condenser.) The extracting solvent is taken in the boiling flask. The solvent is boiled. Its vapour rises through T

Soxhlet Extractor
Fig. 4.2

and enters the water condenser. The vapours condense there. The condensed solvent falls on the sample in the thimble. The substance to be extracted dissolves while the impurities do not. The solution is filtered by the thimble and collects in the cylinder C. When C becomes full, the solution reaches the flask through S. The solvent becomes vapour again and rises up through T. The extracted solid remains in the flask.
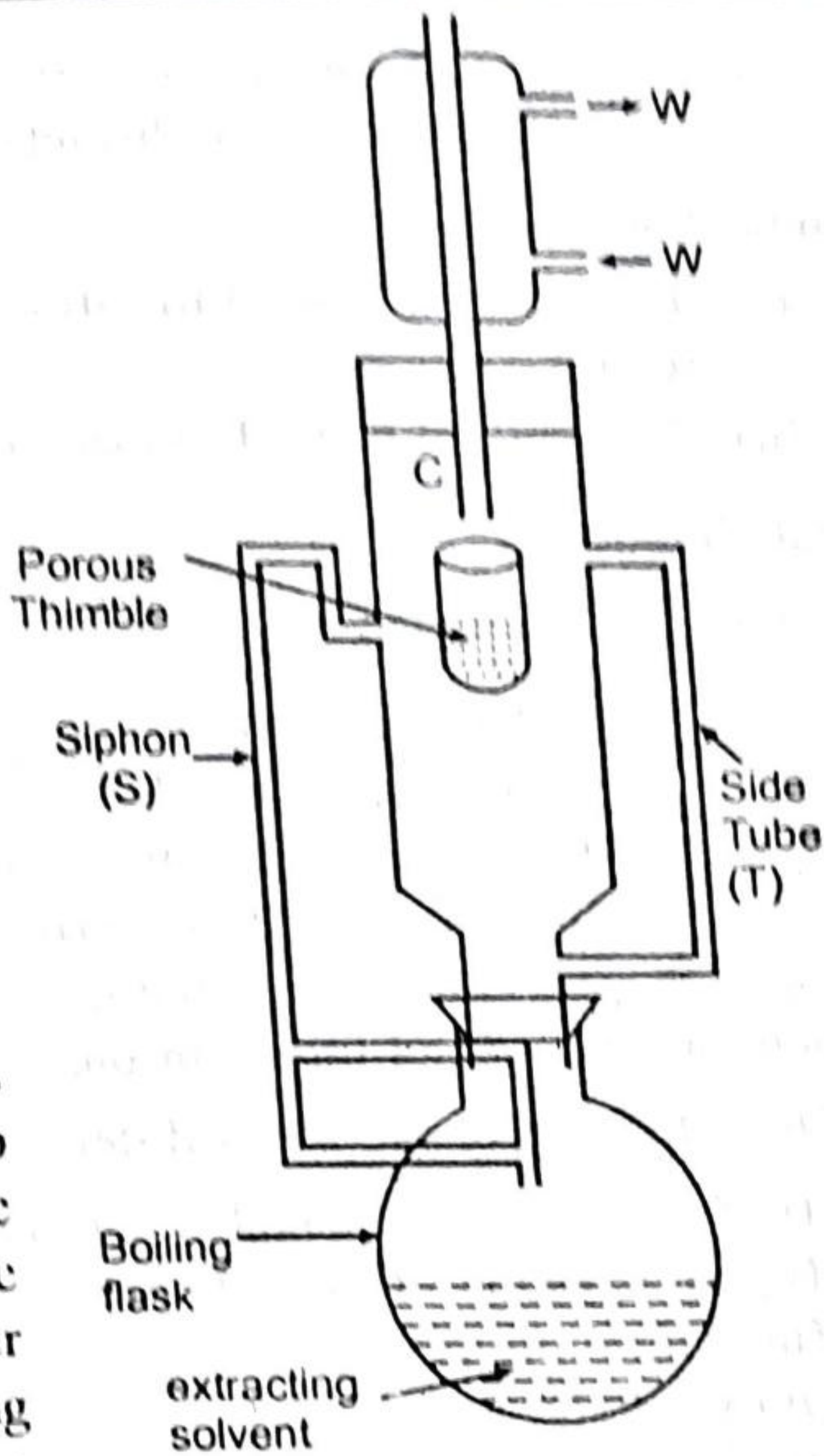
(Thus, the solvent extracts the solid continuously from the sample and brings it to the flask. Finally, the solution from the flask is distilled. The solvent distills off, leaving behind the organic substance.

Advantages

(i) This method provides a thorough contact and heating with the solvent.

(ii) A small quantity of the solvent is enough to extract a maximum amount of solid as the solvent is recycled.

6