11

Distillation

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Distillation is defined as the separation of the components of a liquid mixture by a process involving vaporization and subsequent condensation at another place.

The distillation process involves two steps; (a) converting a liquid into vapour phase and (b) transferring the vapour to another place and recovering the liquid by condensation. The feed liquid is known as *distilland*. The condensed liquid is known as *distillate* or *condensate*.

If one component is volatile and others are non-volatile, it is possible to separate volatile components from non-volatile components by distillation. In such cases, distillation is considered as a separation or purification method. When heat is supplied to a mixture, a more volatile liquid evaporates readily than the less volatile liquid. As a result, the condensed liquid consists of a high proportion of highly volatile liquid and less amount of less-volatile liquid. Therefore, distillation is said to be *partial separation method*. The extent of separation is governed by the properties of the components involved and the physical arrangements used for distillation.

In practice, it is difficult to distinguish three processes, namely evaporation, distillation and drying. Only working definitions help in differentiating them.

1. *Distillation* operation is used when condensed vapour is required as a product.
2. *Evaporation* operation is used when the concentrated liquid residue is needed as a product. The temperature of the liquid is maintained below its boiling point. Further vapour is not condensed, unless recovery is essential.
3. *Drying* operation is used when dried solid residue is required as a product.

Applications

Separation of volatile oils : Volatile oils are separated from cloves, anise seeds and eucalyptus leaves by the method of steam distillation.

Purification of organic solvents : Normally, simple distillation method is used for the purification of liquids having single component as a major fraction. Simple distillation method is also used for determining the boiling range of a liquid as per IP, 1996, as a method to decide the purity. Absolute alcohol (100% ethanol) can be obtained by azeotropic distillation.

Manufacture of official preparations : Spirit of nitrous ether and aromatic spirit of ammonia are prepared by simple distillation. Distilled water and water for injection are prepared as per the specifications of pharmacopoeia by simple and compression distillation methods.

Refining of petroleum products : In the petroleum industry, the crude oil is refined into different fractions using flash distillation. Each fraction is a multicomponent system. Examples are petroleum ether 60, 80 etc.

Recovery of solvents : Solvents are used for extraction of drugs from plant parts and synthetic reaction mixtures. These solvents must be recovered, in order to prevent environmental contamination. The recovered solvent may be recycled for further use.

Quality control methods : Distillation method is used for determining alcohol content in liquid dosage forms such as elixirs, as per IP, 1996. Azeotropic distillation method is used for the determination of water content in a substance using toluene according to IP, 1996.

Separation of drugs obtained from plant and animal sources : Drugs of natural origin (such as plants) are normally extracted using maceration or percolation methods. The menstruum (solvent) used for extraction is distilled off and the active constituents are separated. For

example, vitamin A is separated from fish liver oil using the method of molecular distillation.

Purification of drugs obtained from chemical process : Many chemical processes involve the conversion of raw materials into products. The products are separated from the reaction mixture and purified using the methods of distillation.

In order to handle distillation effectively and economically, it is necessary to understand the theory behind this process. Several variables are involved in the process, which are often interrelated. Theory includes the understanding of different factors influencing the distillation process. The laws of conservation of matter and conservation of energy have to be applied. This chapter deals with the theory, methods and types of equipment involved in the distillation process.

THEORY

Distillation is a process of separating and purifying the components in a liquid mixture. The primary data required to solve any distillation problem are vapour-liquid equilibrium relationship. Distillation method depends on the relative volatilities of the components present in the mixture. Some of these aspects are discussed below.

When two liquids are mixed together, they may be miscible with each other in all proportions. Such miscible liquids are known as *binary mixtures* of liquids.

Examples of binary mixtures are ethyl alcohol and water, water and acetone, benzene and carbon tetrachloride. It is essential to understand theories of ideal and real solutions (non-ideal).

Ideal Solutions

Ideal solution is defined as the one in which there is no change in the properties of the components other than dilution, when they are mixed to form a solution.

Heat is neither absorbed nor evolved during mixing. The final volume of the solution represents the additive property of the individual constituents. Example is methanol and water, which have similar properties. Ideal solution theory provides a model system to which real or non-ideal solutions can be compared. Ideal solutions are characterised by one of the important physicochemical properties of liquids namely vapour pressure.

Raoult's Law

Raoult's law expresses a quantitative relationship between the concentration and vapour pressure.

Raoult's law states that the partial vapour pressure of each volatile constituent is equal to the vapour pressure of the pure constituent multiplied by its mole fraction in the solution at a given temperature.

Since the solution is homogeneous by definition, the relative numbers of components on the surface reflect the numbers of these components in the whole of solution. These numbers can be expressed on mole fraction scale. Thus Raoult's law is appropriately suited to describe an ideal solution.

Consider a mixture of miscible liquids A and B. In this mixture:

Let partial vapour pressure exerted by A = p_A kPa.
Let partial vapour pressure exerted by B = p_B kPa.
Let vapour pressure exerted by the pure component of A = p^o_A kPa.
Let vapour pressure exerted by the pure component of B = p^o_B kPa.
Let mole fraction concentration of liquid A = X_A
Let mole fraction concentration of liquid B = X_B

Raoult's law may be mathematically expressed as:

Partial vapour pressure of a liquid = vapour pressure of pure liquid × mole fraction of the liquid

$$p_A = p^o_A X_A \quad (1)$$

$$p_B = p^o_B X_B \quad (2)$$

A mixture of ethylene chloride and benzene obeys Raoult's law. When two liquids are mixed, the vapour pressure of each one is reduced by the presence of other to the extent of dilution of each phase.

Ideal solution is defined as the one that obeys Raoult's law. Raoult's law is obeyed by only a few solutions of liquid in liquids. These solutions are also known as '*perfect*' *solutions*. The components of these solutions have a similar structure. Examples are benzene and toluene, n-hexane and n-heptane, ethyl bromide and ethyl iodide. The individual components do not have interaction of any kind or complete uniformity of attractive forces is observed.

Dalton's Law

Dalton's law of partial vapour pressures states that the total pressure exerted by a mixture of ideal gases may be considered as sum of the partial vapour pressure exerted by each gas, if alone were present and occupied the total volume.

Dalton's law is mathematically expressed as:

Total vapour pressure = partial pressure of A + partial pressure of B

$$P = p_A + p_B \quad (3)$$

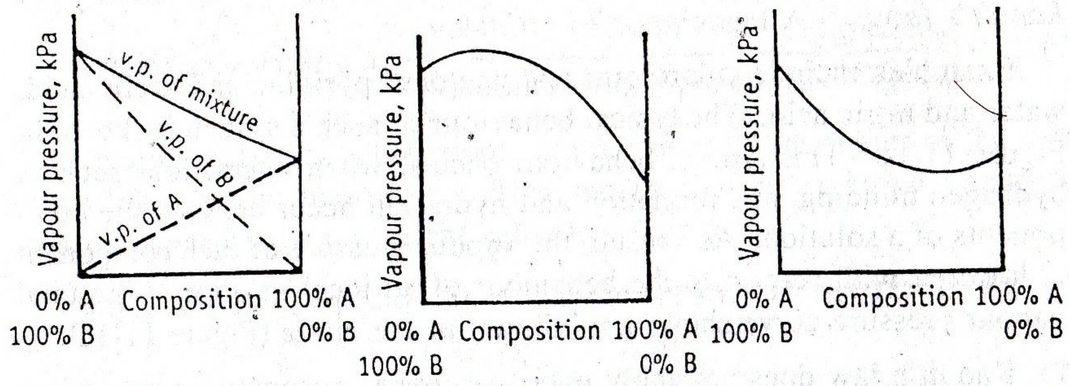
Substituting equations (1) and (2) in equation (3) gives

$$P = p^o_A X_A + p^o_B X_B \quad (4)$$

Their properties are additive, i.e., the total vapour pressure of the mixture is the weighted average of the vapour pressures of pure individual constituents. This behaviour is shown in Figure 11-1a. The following conclusions can be drawn from Figure 11-1a.

- The partial pressure of the component varies linearly from zero to full vapour pressure as the mole fraction varies from zero to one.
- The total pressure exerted by the system at a particular composition is equal to the sum of the partial pressures of its components.

Applications : According to an ideal solution, the component having relatively greater vapour pressure will be distilled first. This principle is used in simple distillation.



(a) Ideal curve-Raoult's law (b) Positive deviation from Raoult's law (c) Negative deviation from Raoult's law

Figure 11-1. Vapour-composition diagrams for different liquid-liquid systems.

Real Solutions

Most systems show varying degree of deviation from Raoult's law, depending on the nature of the liquids and the temperature. These solutions are known as *real solutions*.

Deviations are observed because solute-solute, solvent-solute and solvent-solvent interactions are unequal. Examples include carbon tetrachloride and cyclohexane, and chloroform and acetone. Mutual

interactions lead to either lowering or enhancing of the vapour pressure of the mixture with respect to ideal behaviour.

These are described as follows.

Positive deviation : In some liquid systems, the vapour pressure is greater than the sum of the partial pressures of the individual components. Such systems are said to exhibit *positive deviation from Raoult's law.*

Examples include carbon tetrachloride and cyclohexane, benzene and ethanol. The typical behaviour of such a system is shown in Figure 11-1b. This type of behaviour occurs when the components differ in their polarity, length of hydrocarbon chain and degree of association. The degree of deviation from Raoult's law decreases as the temperature increases, since the differences in the nature of components are reduced at higher temperatures. Conversely a decrease in temperature may lead to a decrease in miscibility of two components and phase separation.

Negative deviation : In some liquid systems, the vapour pressure is lower than that of the sum of the partial pressures of the individual components. Such systems are said to exhibit *negative deviation from Raoult's law.*

Examples include chloroform and acetone, pyridine and acetic acid, water and nitric acid. The typical behaviour of such a system is shown in Figure 11-1c. This type of behaviour occurs, when interactions such as hydrogen bonding, salt formation and hydration occur between the components of a solution. As a result, the vapour pressure of each component is lowered with respect to the behaviour of an ideal solution. The total vapour pressure curve shows a minimum in the curve (Figure 11-1c).

Raoult's law does not apply over the entire concentration range in a non-ideal solution. If one liquid is present in high concentrations, it is considered as a solvent. The other liquid is very dilute. Hence, Raoult's law is valid for that composition, though the liquid pair behaves non-ideal manner.

Applications : The differences in the behaviour of a mixture influence the method of distillation. The areas include fractional distillation of intermediates and drugs, purification of alcohol and other organic solvents. Complete separation of the components of a mixture by fractional distillation may not be achieved if large positive or negative deviations from Raoult's law are observed. Such solutions form so-called azeotropic mixtures. Therefore, the principles of real solutions are important in distillation.

Volatility

The *volatility* of any substance in a solution may be defined as the equilibrium partial pressure of the substance in the vapour phase divided by the mole fraction of the substance in the solution.

For example, a substance A in a liquid mixture has partial pressure p_A and its concentration in the mixture is X_A on mole fraction scale. Then volatility of A (v_A) may be mathematically expressed as:

$$\textit{Volatility of component } A,\ v_A = \frac{\text{partial vapour pressure of A}}{\text{mole fraction of A in solution}} = \frac{p_A}{X_A} \qquad (5)$$

The volatility of a material in the pure state is equal to the vapour pressure of the material.

Relative Volatility

Consider a liquid mixture containing two components A and B. In such a case, the volatility of one component is expressed in terms of the second. *Relative volatility* may be defined as:

$$\textit{Relative volatility},\ \alpha = \frac{\text{volatility of component A}}{\text{volatility of component B}} = \frac{v_A}{v_B} \qquad (6)$$

Relative volatility is commonly expressed with the higher of the two volatilities in the numerator. This means that the relative volatility should never have a numerical value less than 1.0.

Since, $v = p/X$ (equation 5), it may be substituted in equation (6)

$$\alpha = \frac{p_A/X_A}{p_B/X_B} = \frac{p_A X_B}{p_B X_A} \qquad (7)$$

According to Dalton's law, the partial vapour pressures of A and B may be expressed as:

$$p_A = Y_A.P \qquad (8)$$

$$p_B = Y_B.P \qquad (9)$$

where Y_A = mole fraction A in the vapour state
Y_B = mole fraction B in the vapour state
P = total pressure of the vapour, kPa

Relative volatility may also be expressed by substituting equations (8) and (9) in Equation (7) gives:

$$\alpha_{AB} = \frac{Y_A P.X_B}{Y_B P.X_A} = \frac{Y_A X_B}{Y_B X_A} \qquad (10)$$

Equation (10) is often gives as the definition of relative volatility.

Using equation (10), the value of relative volatility can be calculated directly from the vapour-liquid equilibrium data. For example, a mixture of methyl alcohol and water is having a total vapour pressure of 101.31 kPa (760 mmHg). This liquid contains 0.40 mole fraction of methyl alcohol and the equilibrium vapour contains 0.729 mole fraction. The data may be written as:

$$X_A = 0.4;\ Y_A = 0.729;\ X_B = 0.6;\ Y_B = 0.271$$

$$\text{Relative volatility} = \frac{0.729 \times 0.60}{0.271 \times 0.40} = 4.035$$

Sometimes, relative volatility may change with concentration especially if the binary solution do not obey Raoult's law. However, mixtures that obey Raoult's law show only a slight change in relative volatility with concentration variation.

GENERAL EQUIPMENT FOR DISTILLATION

The construction of equipment for the distillation has been described using several figures in subsequent sections. The general equipment, either for laboratory use or for industrial scale, consists of three parts.

STILL

It is a vaporizing chamber and used to place the material to be distilled. The size of the still should be such that only one-half to two-thirds full of liquid is filled. If the still is too large, superheating and some times decomposition of liquid may occur. The still is heated by a suitable means (example, steam) for the vaporisation of the volatile constituents. The temperature at which the liquid boils is of considerable importance. Therefore, provision is made to place the thermometer in the still. A condenser is attached to the still using appropriate joints.

On laboratory scale, round bottom flasks made of glass are used so that the progress of the distillation can be noticed. At the same time, the feed can be added as and when required. Stills are made of stainless steel, copper or suitable material to provide efficient heat transfer. In these stills, an observation window is provided.

Some liquids have a tendency to bump or froth, which promotes the carrying of liquid with vapour. To prevent this, a trap is inserted between distillation flask and condenser.

CONDENSER

Condenser helps in condensing the vapour. Condenser is a heat exchanger. It is kept cold by circulating water through water jacket. The boiling point and volatility of a substance are the main factors governing the choice of the condenser. The main points in the construction of a condenser are as follows.

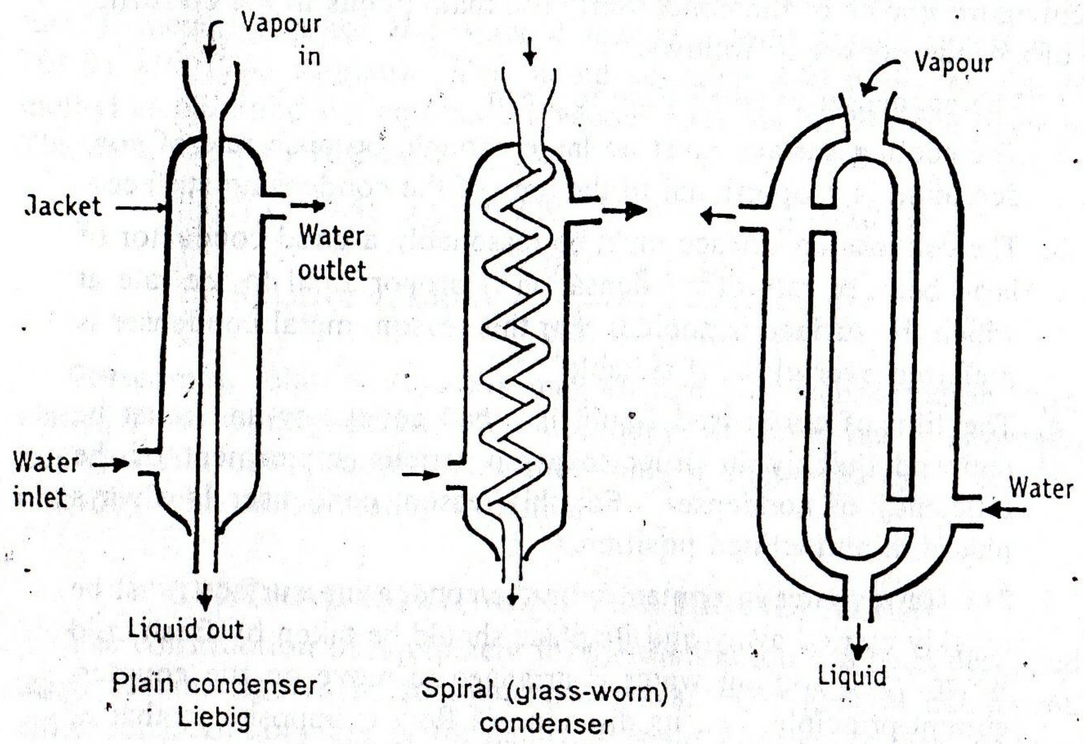
1. The condenser must be easy to clean.
2. The cooling surface must be large enough, because rate of condensation is proportional to the area of the condensing surface.
3. The condensing surface must be reasonably a good conductor of heat, because rate of condensation is proportional to the rate at which the surface is cooled. For this reason, metal condenser is preferred over glass, if suitable.
4. The film of condensed liquid is a bad conductor and must be removed quickly in order to avoid serious impairment of the efficiency of condenser. For this reason, condenser is always placed in an inclined position.
5. The warm water in contact with the condensing surface must be quickly carried away and its place should be taken by fresh cold water. The cooling water is arranged to move on the counter-current principle, i.e., its direction of flow is opposite to that of the flow of vapour to be condensed.

The condenser is connected to the receiver through a suitable adapter. *Adapter* may be employed where the receiver cannot be conveniently supported at the end of the condenser. Some times, the adapter has a provision to connect to the vacuum pump as in case of vacuum distillation. Condenser is placed in an upright or oblique position. Different types of condensers are used (Figure 11-2). Three classes of condensers are described below.

1. *Single-surface condensers* : Examples are Liebig condenser (Figure 11-2a), spiral (glass-worm condenser) (Figure 11-2b).
2. *Double-surface condensers* : The efficiency of the condensation increases. (Figure 11-2c).
3. *Multi-tubular condensers* : These are usually made of metal and used for large scale work. In the preparation of distilled water and water for injection, multi-tubular condensers are used.

The basic differences in the construction show variations in the efficiency of the condensation. Water-cooled condensers are not suitable

for liquids, which boil above 130°C. In such cases, *air condenser* may be used in place of water condenser. Air condenser is a straight tube with sufficient length (1-2 metres long), which is passed through the bung of the flask. The vapour rises in the air-cooled tube and gets condensed.



(a) Single surface condensers (b) Double surface condenser

Figure 11-2. Different types of condensers.

RECEIVER

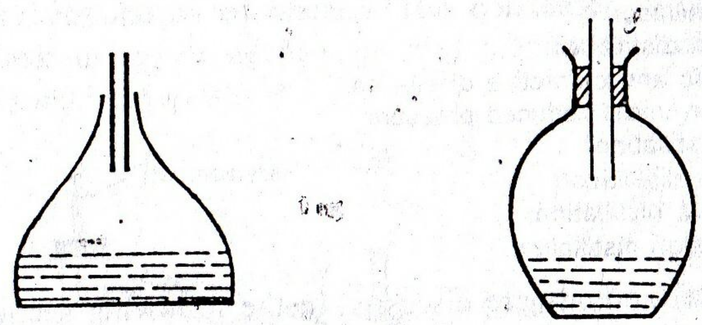
It is used to collect the distillate. It may be a simple flask (Figure 11-3a & b) or modified flasks such as Florentine receivers (Figure 11-3c & d). Some times, the receiver is immersed in an ice-bath or any other freezing mixture. This minimizes loss of volatilization. Florentine receivers are used for the separation of oil and water. These are two types.

Type I : These are used for the separation of oil heavier than water.
Type II : These are used for the separation of oil lighter than water.

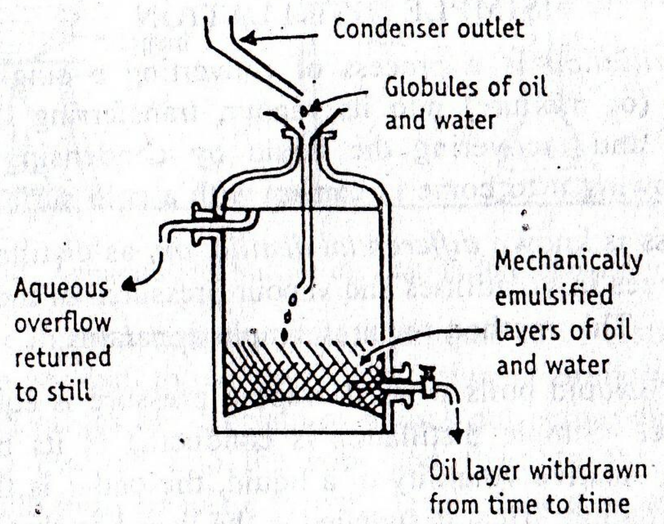
The receiver used for oil heavier than water has two taps (Figure 11-3c). The tap fitted near the bottom of vessel is used for collecting oil, while the tap fitted near the top of the vessel for water to overflow.

The receiver used for oil lighter than water is fitted with siphon at the bottom, which works when it gets filled with water (Figure 11-3d), while the tap fitted near the top is an outlet for the flow of oil.

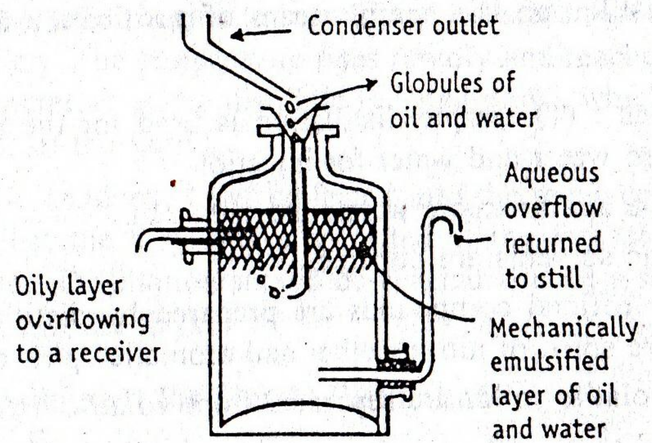
Some times, the receiver is immersed in an ice-bath or any other freezing mixture. This minimizes loss due to volatilization.



(a) Conical flask as receiver (b) Flat bottom round flask as receiver



(c) Florentine receiver for oils heavier than waters



(d) Florentine receiver for oils lighter than water

Figure 11-3. Different types of receivers.

CLASSIFICATION OF DISTILLATION METHODS

Simple distillation
Flash distillation
Fractional distillation
Azeotropic and extractive distillation
Distillation under reduced pressure
Steam distillation
Molecular distillation
Destructive distillation
Compression distillation

Some of these methods are discussed in the following sections both on laboratory scale and industrial scale along with the specific theories.

SIMPLE DISTILLATION

Simple distillation is a process of converting a single constituent from a liquid (or mixture) into its vapour, transferring the vapour to another place and recovering the liquid by condensing the vapour, usually by allowing it to come in contact with a cold surface.

This process is known *differential distillation,* as distillation is based on the differences in volatilities and vapour pressures of the components in the mixture. This method requires simple apparatus.

Principle : Liquid boils when its vapour pressure is equal to atmospheric pressure. Simple distillation is conducted at its boiling point. The higher the relative volatility of a liquid, the better is the separation by simple distillation. Heat is supplied to the liquid so that it boils. The resulting vapour is transferred to a different place and condensed. If the liquid of interest is volatile and remaining components are nonvolatile, then simple distillation is a useful means of purification and separation of liquids.

Applications : (1) Simple distillation is used for the preparation of distilled water and water for injection.
(2) Volatile and aromatic waters are prepared.
(3) Organic solvents are purified.
(4) A few official compounds are prepared by distillation. Examples are spirit of nitrous ether and aromatic spirit of ammonia.
(5) Non-volatile solids are separated from volatile liquids.

Laboratory Scale Apparatus for Distillation

Assembling of apparatus : The construction of a simple distillation apparatus is shown in Figure 11-4. It consists of a distillation flask with

a side arm sloping downwards. Condenser is fitted into the side arm by means of a cork. The condenser is usually water condenser, i.e., jacketed for circulation of water. The condenser is connected to a receiver flask using an adapter. On a laboratory scale, the whole apparatus is made of glass.

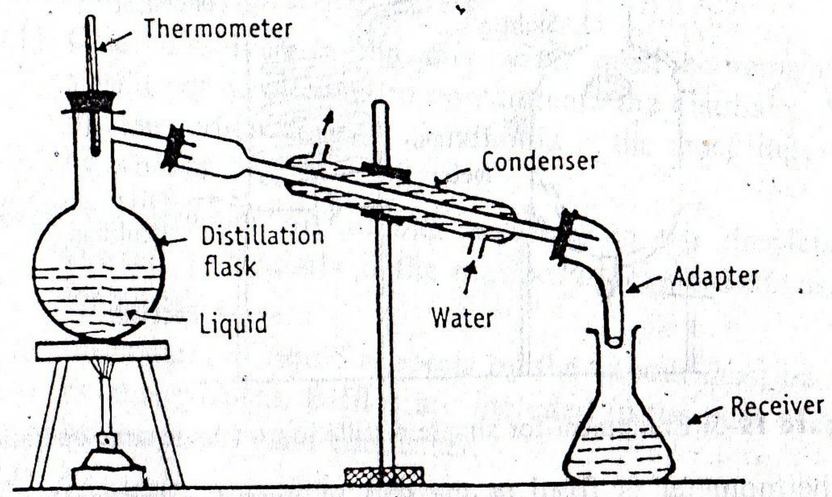


Figure 11-4. Apparatus for simple distillation (on laboratory scale).

Procedure : In the laboratory scale, the liquid to be distilled is filled into the flask to one-half to two-third of its volume. Bumping is avoided by adding small pieces of porcelain or porous pot before distillation. A thermometer is inserted into the cork and fixed to the flask. The thermometer bulb must be just below the level of the side arm. Water is circulated through the jacket of the condenser as shown in Figure 11-4.

The contents are heated gradually. The liquid begins to boil after some time. The vapour begins to rise up and passes down the side arm into the condenser. The temperature rises rapidly and reaches a constant value. The temperature of the distillate is noted down, which is equal to the boiling point of the liquid.

The vapour is condensed and collected into the receiver. The flame is adjusted so that the distillate is collected at the rate of one to two drops per second. Distillation should be continued until a small volume of liquid remains in the flask.

Large Scale Equipment for Simple Distillation

Construction : A simple still as shown in Figure 11-5 is used for large-scale distillation. It is made up of stainless steel, copper or any other suitable material. A still of this kind has a limited heating surface

and functions perfectly with volatile solvents, but is not useful for concentrating dilute solutions. Specially designed stills suited to one product or a group of products are used for frequent and continuous use.

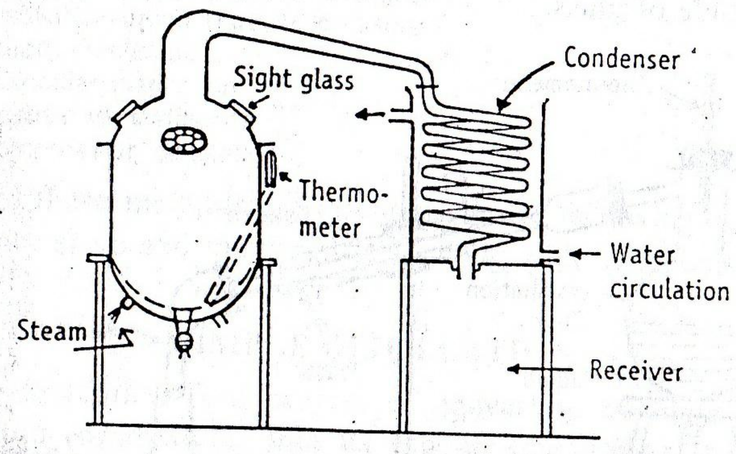


Figure 11-5. Equipment for simple distillation on large scale operation.

A thermometer is fixed to the still to note the temperature of the boiling liquid. An observation window in the hood is helpful to the operator to see the progress of the distillation and the level of the contents to be distilled. The still is connected to a condenser and then to a receiver. The still is heated using steam. Therefore, a steam inlet at the bottom of the still and an outlet for removing the condensed steam are provided.

Working : A liquid to be distilled is filled into the still to one-half to two-third of its volume. Bumping is avoided by adding small pieces of porcelain or porous pot before distillation. A thermometer is inserted into the still. Water is circulated through the jacket of the condenser as shown in Figure 11-5.

Steam is passed through the inlet. The contents are heated gradually. The liquid begins to boil after some time. The vapour begins to rise up and passes into the condenser. The temperature rises rapidly and reaches a constant value. The temperature is noted down, which is equal to the boiling point of the liquid.

The vapour is condensed and collected into the receiver. The passage of steam is regulated so that the distillate is collected at a slower rate (a few drops per second). Distillation should be continued until a small volume of liquid remains in the still.

Water stills are used for producing distilled water including water for injection on a continuous basis.

Preparation of Purified Water (BP) and Water for Injection (BP) By Distillation

The principle involved in the preparation of water for injection by distillation is same as that of the simple distillation. However, it is a special case for the following reasons.

(1) Gases dissolved in the raw water must be removed. These should not be allowed to contaminate the distillate. Such gases include carbon dioxide. Ammonia is the most important gas to be avoided.

(2) The carryover of soluble materials in the droplets must be avoided, particularly if the product is required for use as water for injection.

(3) Entrapment of liquid droplets by the vapour must be prevented. For this purpose, baffles are included in the path of the vapour between boiler and condenser.

(4) Contamination of the distillate by pyrogen from feed water must be avoided.

(5) The residue of solids must not be concentrated to a point where hydrolysis occurs. Otherwise, the distillate may be contaminated by volatile material produced during hydrolysis. For example, hydrolysis of chlorides produces hydrochloric acid.

Construction : The arrangement of an apparatus for the continuous production of distilled water or water for injection is shown in Figure 11-6. The distillation apparatus consists of a boiler, which may be made of cast iron. Baffles and condenser tubes are made up of stainless steel or monel metal. The top of the condenser jacket is open, so that gases from water can escape into atmosphere. The condenser tubes are vertical and open at both ends, as shown in Figure 11-6.

Working : Water (feed) enters at the base of the still and rises in the jacket, which contains a number of tubes. In the condenser tubes, the condensed liquid descends. The rising feed water gets heated on account of condensate in the tubes. The rate of flow is adjusted in such a way that the water gets heated to 90–95 °C, before it enters the boiler. The dissolved gases in water escape to the atmosphere. The heated water then enters the boiler, in which steam is circulated under pressure through a copper coil. The steam that is obtained by feed water cannot escape except through the condenser tubes, whose upper ends are protruded into the boiler head. The descending steam is condensed into distilled water, which flows from the lower ends of the tubes.

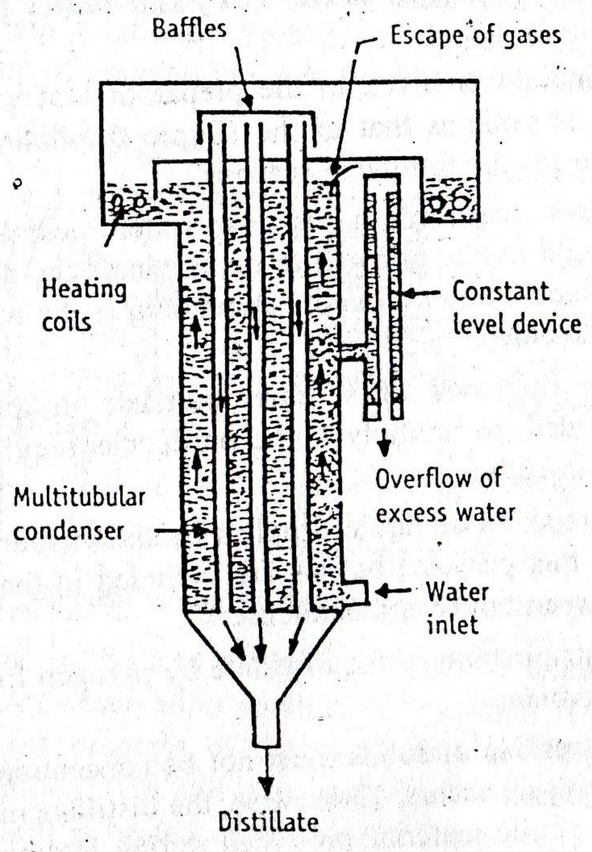


Figure 11-6. Construction of a distillation unit for the preparation of water for injection.

Advantages : This process is economical as the amount of steam used in coils is reduced on account of preheating of feed water by counter-current flow of the condensate. This also facilitates the escape of dissolved gases without any additional effort.

FLASH DISTILLATION

Flash distillation is defined as a process in which the entire liquid mixture is suddenly vaporized (flash) by passing the feed from a high pressure zone to a low pressure zone.

Flash distillation is also known as *equilibrium distillation,* i.e., separation is attempted when the liquid and vapour phases are in equilibrium. This method is frequently carried out as a continuous process and does not involve rectification.

Principle : When a hot liquid mixture is allowed to enter from a high-pressure zone into a low-pressure zone, the entire liquid mixture is suddenly vaporised. This process is known as *flash vaporisation.* During this process the chamber gets cooled. The individual vapour phase

molecules of high boiling fraction get condensed, while low boiling fraction remains as vapour. This process requires certain amount of time. Therefore, the liquid and vapour is kept in intimate contact until equilibrium is achieved. The liquid fraction is collected separately. The vapour is separated from the liquid and further allowed to condense.

Uses : Flash distillation is used for separating components, which boil at widely different temperatures. It is widely used in petroleum industry for refining crude oil.

Advantages : Flash distillation is a continuous process. It is used for obtaining a multi-component systems of narrow boiling range, especially in oil refinery. Examples are petroleum ether 60, 80 etc.

Disadvantages : Flash distillation is not effective in separating components of comparable volatility. It is not suitable for two component systems. It is not an efficient distillation when nearly pure components are required, because the condensed vapour and residual liquid are far from pure.

Equipment

Construction : The construction of a flash distillation apparatus is shown in Figure 11- 7. It consists of a pump, which is connected to a

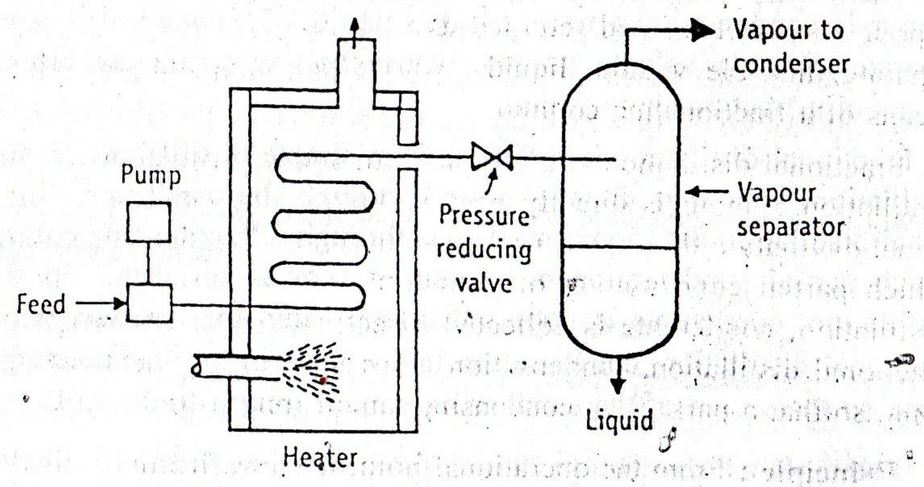


Figure 11-7. Apparatus for flash distillation.

feed reservoir. Pump helps in pumping the feed into the heating chamber which contains a suitable heating mechanism. The other end of the pipe is directly introduced into the vapour-liquid separator through a reducing valve. The vapour outlet is provided at the top of the separator and liquid outlet is provided at the bottom.

Working : The feed is pumped through a heater at a certain pressure. The liquid gets heated, which enters the vapour-liquid separator through a pressure-reducing valve. Due to the drop in pressure, the hot liquid flashes, which further enhances the vaporisation process. The sudden vaporisation induces cooling. The individual vapour phase molecules of high boiling fraction get condensed, while low boiling fraction remains as vapour. The mixture is allowed for a sufficient time, so that vapour and liquid portions separate and achieve equilibrium. The vapour is separated through a pipe from above and liquid is collected from the bottom of the separator.

By continuously feeding into the still, it is possible to obtain continuous flash distillation. The operating conditions can be adjusted in such a way that the amount of feed exactly equals the amount of material removed. Therefore, vapour and liquid concentrations at any point remain constant in the unit.

FRACTIONAL DISTILLATION

Fractional distillation is a process in which vaporisation of liquid mixture gives rise to a mixture of constituents from which the desired one is separated in pure form.

This method is also known as *rectification*, because a part of the vapour is condensed and returned as a liquid. This method is used to separate miscible volatile liquids, whose boiling points are close, by means of a fractionating column.

Fractional distillation is different from simple distillation. In simple distillation, vapour is directly passed through the condenser. In fractional distillation the vapour must pass through a fractionating column in which partial condensation of vapour is allowed to occur. In simple distillation, condensate is collected directly into the receiver, while in fractional distillation, condensation takes place in the fractionating column, so that a part of the condensing vapour returns to the still.

Principle : From the operational point of view, fractional distillation is a mass transfer process involving counter-current diffusion of the components at each equilibrium stage.

When a liquid mixture is distilled, the partial condensation of the vapour is allowed to occur in a fractionating column. In the column, ascending vapour from the still is allowed to come in contact with the condensing vapour returning to the still. This results in enrichment of the vapour with the more volatile component. By condensing the vapour

and reheating the liquid repeatedly, equilibrium between liquid and vapour is set up at each stage, which ultimately results in the separation of a more volatile component.

Applications : Fractional distillation is used for the separation of miscible liquids such as acetone and water, chloroform and benzene.

Disadvantage : Fractional distillation cannot be used to separate miscible liquids, which form azeotropic mixtures.

Theory : According to the principles of colligative properties, when a substance is dissolved in a liquid, the vapour pressure of solvent is lowered. When two miscible liquids are mixed, each may be considered as a solution of one in the other. The vapour pressure of each component is lowered. The pressure exerted by each one is known as *partial pressure*.

According to *Dalton's law*, the total pressure exerted by a gaseous mixture is the sum of the individual partial pressures of the component gases. If A and B are two miscible liquids and, p_A and p_B represent their partial pressures, respectively, then Dalton's law may be mathematically expressed as:

$$Total\ pressure = p_A + p_B$$

Like other gas laws, Dalton's law holds strictly good only when the partial pressures are not too high. Dalton's law is important because it permits the estimation of total vapour pressure, which should be equal to atmospheric pressure so as to reach the boiling point. At boiling point, the vaporization is maximum.

Based on the boiling point behaviour, the binary mixtures are classified into three classes.

Boiling Point—Composition Curves of Mixtures

Since repeated vaporisation and condensation processes are involved simultaneously, the composition of liquid and vapour phases change continuously. Hence, boiling point-composition curves are helpful in predicting whether the separation is possible or not, if possible, whether it is easy or difficult. These are helpful in designing the equipment for fractional distillation.

Boiling point–composition curves are constructed as follows:

(1) Mixtures of liquid A and liquid B are prepared in different proportions.

(2) Boiling point of each mixture is determined.

(3) Liquid composition of each component is analysed at its boiling point.

(4) Vapour composition of each component is analysed at its boiling point.

(5) The boiling points are plotted on *y*-axis against composition of the mixture (*x*-axis). The resulting plot is shown in Figure 11-8.

(6) The upper curve represents the vapour phase composition.

(7) The lower curve represents the liquid phase composition.

(8) The different areas correspond to the existence of liquid, vapour and liquid plus vapour phases.

The curves represent the equilibrium condition. Therefore, they are helpful in drawing conclusions regarding the composition of components at any given temperature.

Fractional Distillation–Type I Miscible Liquids (for Ideal Solutions)

Fractional distillation is suitable for a system when the boiling point of the mixture is always intermediate between those of pure components. There is neither a maximum nor a minimum in the composition curves as shown in Figure 11-8. These systems are known as *zeotropic mixtures*. Examples include benzene and toluene, carbon tetrachloride and cyclohexane, and water and methanol.

The usefulness of Figure 11-8 in the design of fractional distillation is illustrated in Figure 11-10.

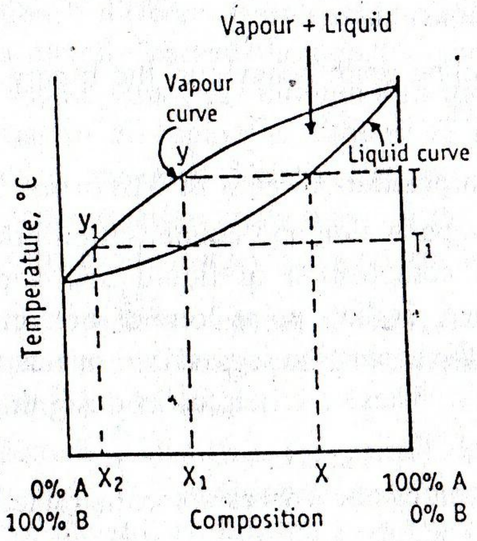


Figure 11-8. Boiling point–composition diagram of miscible liquids.

Fractional Distillation—Azeotropic Mixtures

Many liquid mixtures cannot be separated completely into pure components by simple distillation, because the volatilities of the components are equal. Such a mixture is known as an azeotrope (*Greek*: boil unchanged)

Azeotropic solution is a solution which distils unchanged at a constant temperature.

Such solutions are also known as *constant boiling mixtures*. An example of this type is 89.43 mol % mixture of ethanol and water at atmospheric pressure. This mixture has a relative volatility of 1.0, further purification cannot be obtained by conventional distillation. These solutions deviate from the Raoult's law to a large extent.

Minimum boiling point azeotropic solutions–Type II solutions (non-ideal solutions) : System that exhibits a minimum value in the boiling point-composition curve is shown in Figure 11-9. Such a system is known as *azeotropic mixture* with a maximum vapour pressure or minimum boiling point. Examples include chloroform and acetone, pyridine and acetic acid, and water and nitric acid.

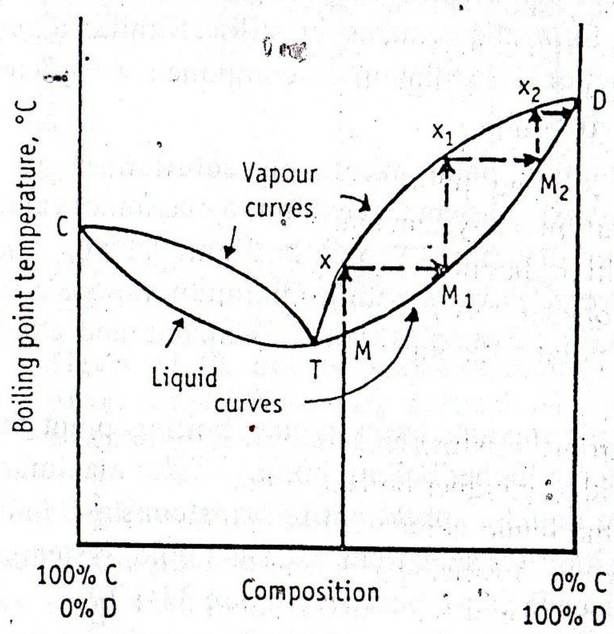


Figure 11-9. Boiling point-composition curves of a constant boiling azeotropic mixture having minimum boiling point.

The azeotropic mixture has a lower boiling point than that of the component with the least boiling point. At the minimum boiling point temperature, the liquid composition remains constant and is equal to the vapour

composition (arising from such a liquid system). This is indicated by coincidence at the trough (Figure 11-9).

All mixtures of compositions lying between C and T (trough) can be separated by continuous fractional distillation. In this process, pure liquid C is recovered from the still and a mixture with constant composition (as of T) is obtained as a distillate from the condenser. In a similar way, all mixtures of compositions lying between T and D can be separated by continuous fractional distillation. In this process, pure liquid D is recovered from the still and mixture with constant composition (as of T) as condensate.

Since vapour gives constant composition of mixture, liquid curve (i.e., liquid present in the still) should be considered for the analysis (Figure 11-9).

Consider a hypothetical case (Figure 11-9) in which the mixture contains more of D than C, which is represented by *M*. If the mixture is distilled, the vapour has a composition of *x*. When this vapour is condensed, the liquid composition is represented by M_1, which is richer in D than C. When this liquid is redistilled, the vapour has composition of x_1. When this vapour is condensed, the liquid has the composition of M_2. Thus on repeated distillation (fractional distillation), the liquid D will be in pure form and remains in still. Similar arguments can be proposed for fractional distillation of component C by considering left-side curves to T (trough).

Maximum boiling point azeotropic solutions–Type III solutions (non-ideal solutions) : System that exhibits a maximum value in the boiling point-composition diagram is shown in Figure 11-10. Such a system is known as *azeotropic mixture* with a minimum vapour pressure or maximum boiling point. Examples include benzene and ethanol, water and ethanol.

The azeotropic mixture has a higher boiling point than that of the component with the higher boiling point. At the maximum boiling point temperature, the liquid composition remains constant and is equal to the vapour composition (arising from such a liquid system). This is indicated by coincidence at the peak, P (Figure 11-10).

All mixtures of compositions lying between P (peak) and A give pure liquid A as distillate and a mixture of A and B with constant composition in the still. In a similar way, all mixtures of compositions lying between B and P give pure B as distillate and a mixture of A and B with constant composition in the still.

Consider a hypothetical case (Figure 11-10) in which the mixture contains more of A than B, which is represented by *L*. If this mixture is distilled, the composition of vapour *v* is richer in A and poorer in B. At this state, the liquid residue in the distillation flask will be richer in B and poorer in A. The vapour at *v* is condensed, the liquid composition is represented by L_1. If this liquid is distilled, the composition of vapour v_1 is further richer in A and poorer in B. Thus on repeated distillations (i.e., fractional distillation), the liquid A in pure form can be obtained as a distillate. But the residue remained in the still is always the mixture of A and B of constant composition. Similar arguments can be proposed for fractional distillation of component B by considering left-side curves to P.

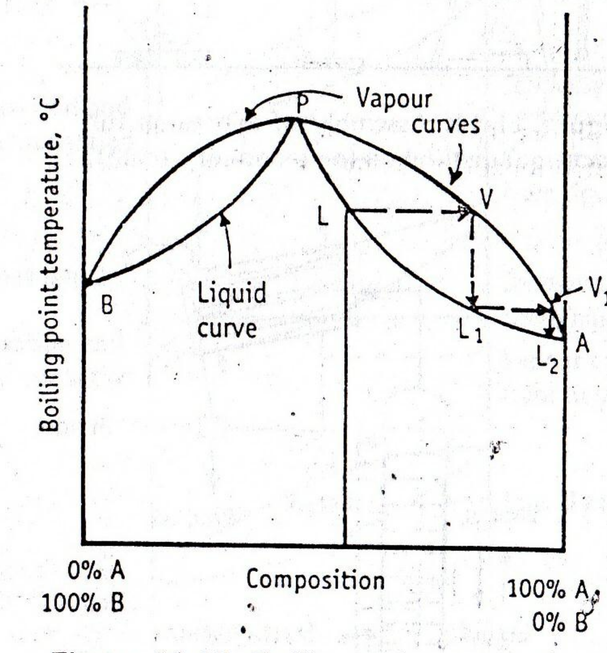


Figure 11-10. Boiling point-composition curves of a constant boiling azeotropic mixture having maximum boiling point.

General Method for Fractional Distillation

Construction : The assembly of apparatus for fractional distillation on a laboratory scale is shown in Figure 11-11. On a large scale, the construction of equipment for fractional distillation is shown in Figure 11-12. The fractionating column is inserted between the still and the condenser. A provision is made for the supply of heat (usually a steam coil) at the bottom of the column. At the top of column, a condenser is provided. The column has a large area for providing sufficient flow conditions. The broken lines across the column represent the contacting devices.

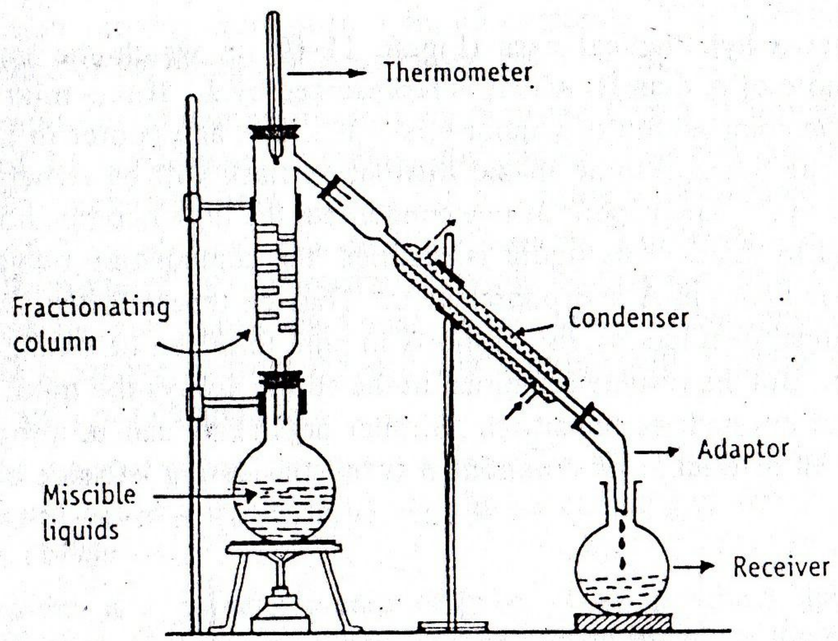


Figure 11-11. Assembly of apparatus for fractional distillation (on laboratory scale).

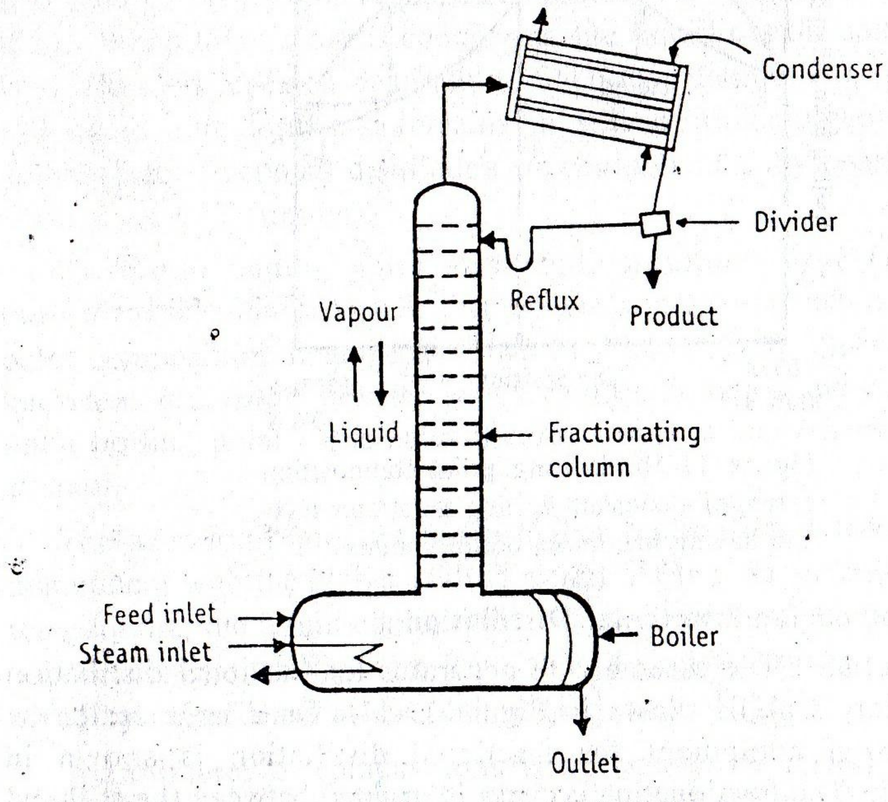


Figure 11-12. Fractional distillation apparatus for large scale operation.

Working : The mixture to be distilled is fed to the boiler and heated usually by steam. The sequence of events occurring in the

fractionating column can be illustrated using the following general example (Figure 11-13).

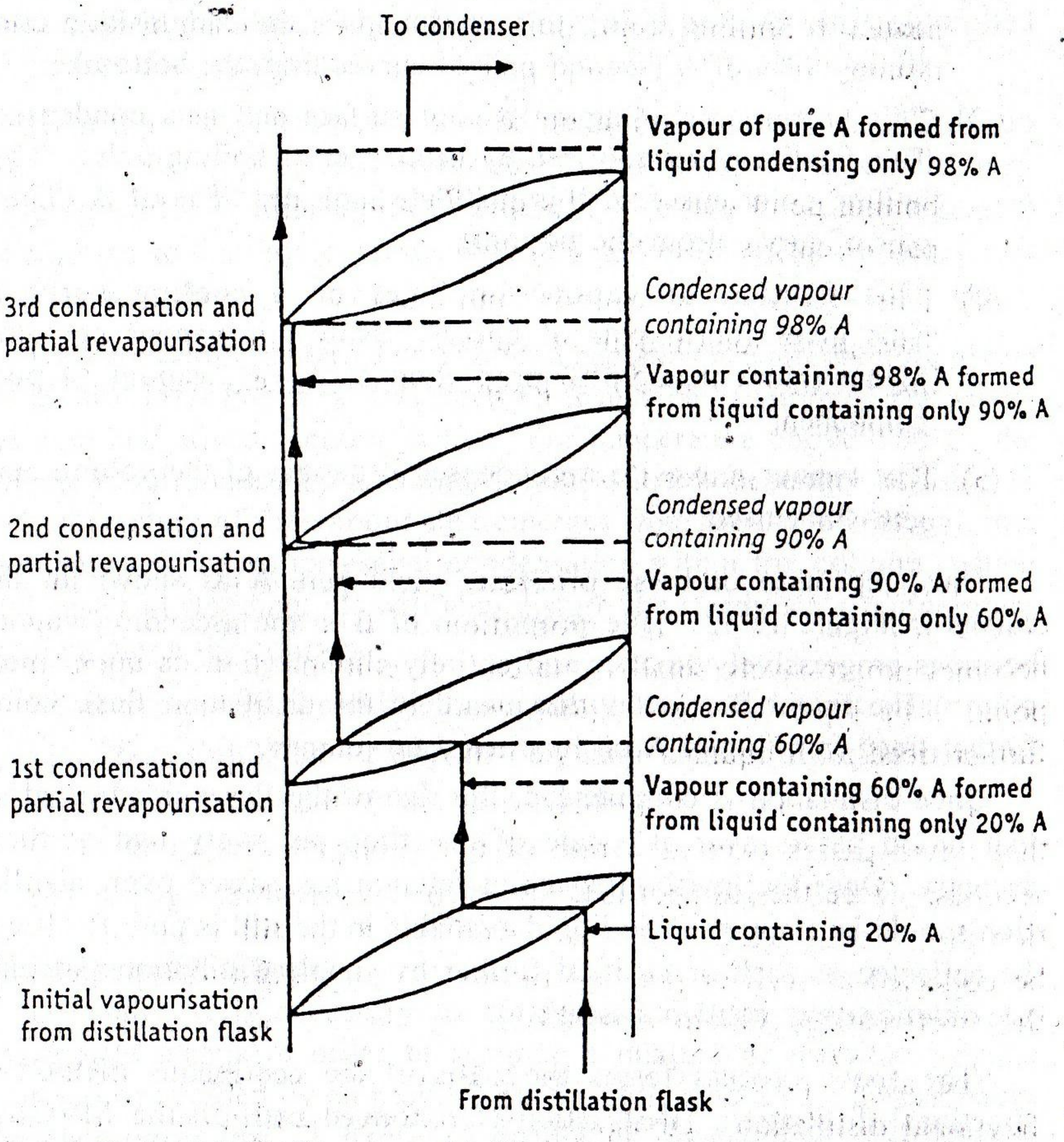


Figure 11-13. Sequence of boiling point–composition diagrams to illustrate the fractional distillation of a mixture of components.

Consider a mixture of two miscible liquids A and B containing 20% of A and 80% B. Liquid A (More Volatile Component, MVC) is having a lower boiling point than B (Less Volatile Component, LVC). These liquids do not produce constant boiling point mixture. The boiling point composition curves of this mixture are shown in Figure 11-13, which is similar to Figure 11-8, but written several times so as to represent the steps (i.e., in fractions) in fractional distillation.

(1) When the boiling point of the mixture is reached, the vapour-composition curves are drawn as shown by lowest pair of curves

(Figure 11-13). These curves indicate that the vapour contains 60% of A.

(2) When this vapour is condensed, the resulting liquid is again heated to boiling point, this vapour gives the composition containing 90% of A (second pair of curves from the bottom).

(3) This vapour impinging on a cool surface and gets condensed. This fraction is revaporised by heating to its boiling point. This boiling point curve of this distillate indicates 98% of A (Third pair of curves from the bottom).

(4) This fraction of vapour impinges on a cooling surface. This gives fourth pair of curves. Now this vapour contains higher (more than 98%) proportion of A, i.e., vapour of pure component.

(5) The vapour moves to a condenser at the top of the column and gets condensed.

Thus, repetition of these processes yield pure A as shown in the curves in Figure 11-13. The proportion of B in the ascending vapour becomes progressively smaller and entirely eliminated at its upper most point. The liquid B trickles downward to the distillation flask being further freed from liquid A on its downward journey.

Once distillation is commenced, the size of the flame is adjusted so that liquid passes over at a rate of one drop per every two or three seconds. Once the low boiling point fraction has passed over, distillation should be stopped. The liquid available in the still is pure B. It can be collected as such or purified further by simple distillation (keeping the fractionating column assembly).

The above process forms the basis of the continuous method of fractional distillation. Distillation is continued until all the MVC has been distilled off from the top as the product and the LVC is left in the still as a separate product.

Efficiency of the Fractional Distillation

The efficiency of separation of a mixture may be expressed in several ways.

Length of the fractionating column : A state of dynamic equilibrium is required for the separation. A maximum degree of separation of the components is obtained along the length of the column.

Reflux ratio : *Reflux ratio* is the quotient of the amount of liquid returning through the column to the amount collected into the receiver during the same interval of time. A column operating under total reflux will not yield distillate. The reflux ratio should be high. It is controlled by means of a suitable still.

Heat input : Heat input to the still should be controlled. If it is too little, the packing is insufficiently wetted. If it is too high, velocity may be too great for equilibrium to be attained. The size of the flame should be adjusted so that liquid passes over at a rate of one drop for every two or three seconds.

Column temperature : For a column operating at a temperature above 60°C, heat loss should be prevented by insulation. Examples are asbestos cord and silver vacuum jacket. For temperature above 100°C, the column is surrounded by a heating jacket, which is generally adjusted to the temperature of the vapour that emerges from the top of the column. Heat loss will cause excessive condensation within the column, which may result in flooding. It will also disturb the steady state temperature gradient along the column.

Other experimental conditions necessary for good separation are:

(1) There should be a comparatively large amount of liquid continuously returning through the column.

(2) Thorough mixing of liquid and vapour.

(3) A large active surface of contact between liquid and vapour.

Fractionating Columns

Generally, it is necessary to conduct distillation several times by appropriate means in order to separate a mixture of miscible liquids. This can be avoided by employing fractionating column for a reasonably complete separation. In fractional distillation, special type of still-heads are required so that condensation and revaporisation are affected continuously. These are known as *fractionating columns.*

A fractionating column is essentially a long vertical tube in which the vapour passes upward and gets partially condensed. The condensate flows down the column and is returned eventually to the flask. The columns are constructed so as to offer the following advantages simultaneously.

(1) It offers a large cooling surface for the vapour to condense.

(2) An obstruction to the ascending vapour allows easy condensation. The obstruction also retards the downward flow of liquid, which is a high boiling component.

Fractionating columns can be divided into two groups.

Packed columns : In this type, some form of packing is used in the column to affect the necessary liquid/vapour contact. The packing may consist of single turn helices (spirals) of wire or glass, glass rings, cylindrical glass beads, stainless steel rings etc. The height of packing is equivalent to *one theoretical plate*. Some types of fractionating columns are shown in Figure 11-14.

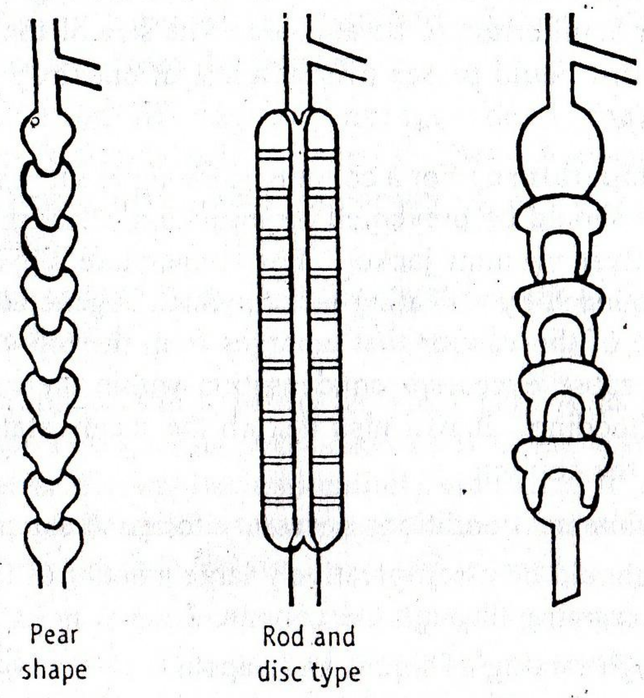


Figure 11-14. Different types of fractionating columns.

Construction : Packed column consists of a tower containing a packing that becomes wetted with a film of liquid, which is brought into contact with the vapour in the intervening spaces.

The same type of fractionating columns can be obtained in various lengths.

(a) A long fractionating column is necessary when the boiling points of the constituents are lying fairly close together.

(b) A short fractionating column is necessary when the boiling points of the constituents differ considerably.

Applications : Packing must be uniform so as to obtain proper channels. If packing is irregular, mass transfer becomes less effective. Packed columns are mainly used in laboratories. Example is Widmer column. (Figure 11-15).

Plate columns : Many forms of plates are used in the fractionating columns. These can be divided into two types, which are commonly used in pharmacy.

(a) Bubble cap plates

(b) Turbo grid plates

Bubble cap column is used in large distillation plants and is described below.

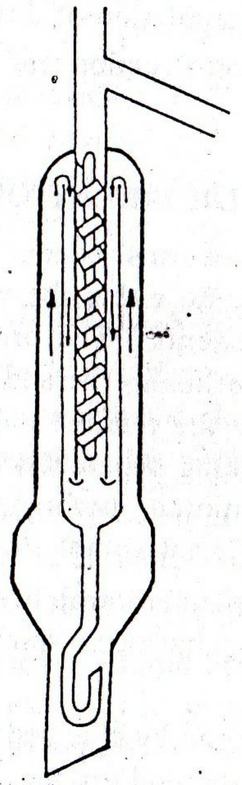


Figure 11-15. Widmer column.

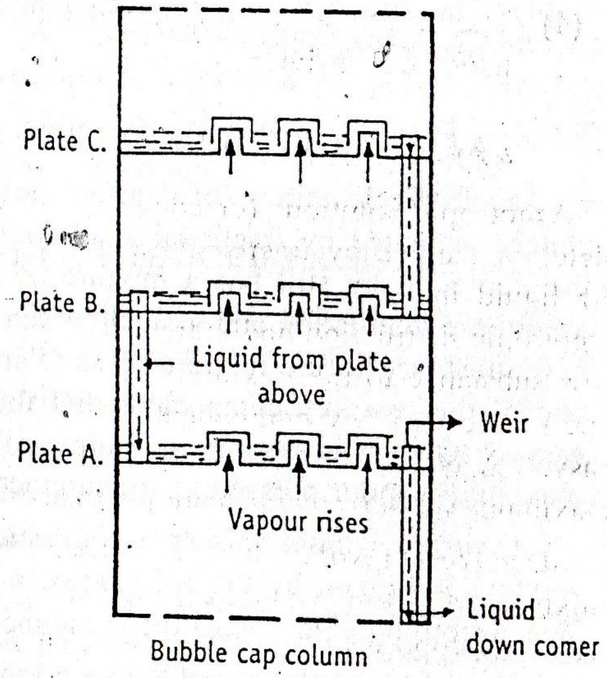


Figure 11-16. Construction of bubble cap column for fractional distillation.

Construction : The column consists of a number of plates mounted one above the other (Figure 11-16). The plates have a weir leading to a downcomer. Caps are present on each plate, which allow the vapour to escape by bubbling through the liquid.

Working : Ascending vapour from the still passes through the bubble-caps on plate A and the rising vapour will be richer in the more volatile component. This vapour passes through the liquid on plate B and partially condensed. The heat of condensation partially vaporizes the liquid. The process of condensation and vaporisation will be repeated at plate C and so on all the way up the column. Each bubble-cap plate has the same effect as a separate still.

Advantages : The bubble cap plate is effective over a wide range of vapour-liquid proportions and velocities. There is an excellent contact as the vapour bubbles through the liquid.

Disadvantages : (1) A layer of liquid on each plate results in considerable hold-up of liquid over the entire column.

(2) The need to force the vapour out of the caps through the liquid led to a large pressure drop through the column.

(3) The column does not drain even after completion of distillation.

(4) The structure is complicated making construction and maintenance expensive.

AZEOTROPIC AND EXTRACTIVE DISTILLATION

Azeotropic solutions (or constant boiling solutions) cannot be completely separated by fractional distillation, because either the vapour or the liquid in the still has a mixture of components. The principle of azeotropic distillation and extractive distillation lies in the addition of a new substance to the mixture so as to increase the relative volatility of one of the two key components and thus making separation relatively easy. Azeotropic ternary mixtures with minimum boiling point (or maximum vapour pressure) are pharmaceutically important.

Azeotropic distillation is a distillation method in which azeotropic mixture is broken by the addition of a third substance, which forms a new azeotrope with one of the components.

The relative volatility of the liquid mixture can be changed by adding a third substance. For example, benzene is added to the azeotropic mixture of water and ethyl alcohol. Benzene breaks the mixture water-ethyl alcohol and forms a new azeotrope between benzene and ethyl alcohol. The volatility of the water (more polar liquid) is enhanced. On distillation, water distills at 65.85°C leaving alcohol and benzene behind. The boiling point of this binary mixture is 68.2°C and benzene gets distilled leaving pure alcohol behind. It can be distilled off at 78.3°C. The benzene can be recycled. Thus, using fractional distillation method, absolute alcohol can be prepared.

When glycerin is added to the above mixture, the vapour pressure of water is lowered. Practically pure ethanol can be obtained from the fractionating tower.

In *extractive distillation*, the third substance added to the azeotropic mixture is relatively nonvolatile liquid compared to the components to be separated.

The third component is withdrawn at the base of the fractionating column.

Example is separation of toluene from paraffin hydrocarbons of approximately same molecular weights. The separation of toluene and *iso*-octane (example for hydrocarbon) is difficult. In the presence of phenol, the relative volatility of *iso*-octane increases, therefore, separation of toluene is relatively easy. In another example, furfural is added for the separation of butadiene from its mixture containing butane and butene.

Applications : The liquor from fermentation process is a common source of ethanol and contains approximately 8 to 10%. Absolute alcohol can be prepared by azeotropic distillation. Petroleum refineries and distilleries use these types of distillation.

DISTILLATION UNDER REDUCED PRESSURE

Distillation under reduced pressure may be stated as a distillation process in which the liquid is distilled at a temperature lower than its boiling point by the application of vacuum.

Vacuum pumps, suction pumps, etc. are used to reduce the pressure on the liquid surface. Distillation under reduced pressure is based on the principle of simple distillation with some modifications.

Principle : Liquid boils when vapour pressure is equal to the atmospheric pressure, i.e., pressure on its surface. If the external pressure is reduced by applying vacuum, the boiling point of liquid decreases. Therefore, the liquid boils at a lower temperature. This principle is illustrated using an example of water. Water boils at 100°C at an atmospheric pressure of 101.31 kPa (760 mm Hg). At 40°C, the vapour pressure of water is approximately 9.33 kPa (70 mm Hg). Hence, the external pressure is reduced to 9.33 kPa (70 mm Hg) where water boils at 40°C. The net result is an increase in the rate of mass transfer into vapour.

The important factor in evaporation is:

$$\text{Mass of vapour formed} \propto \frac{\text{vapour pressure of evaporating liquid}}{\text{external pressure}}$$

According to this formula, water is allowed to evaporate at 40°C and 9.33 kPa (70 mm Hg) pressure, the mass of vapour formed in unit time is approximately 11 times, i.e. 760/70 for water.

Applications : Distillation under reduced pressure is essential and finds a number of applications.

Preventing degradation of active constituents : During extraction, concentration or processing at higher temperatures, the active constituents may undergo decomposition (inactivation). A few examples are given below. Hence extraction and concentration should be done at a lower temperature (≈55°C) under reduced pressure.

Category	*Reaction*	*Examples*
Enzymes	Inactivation	malt extract, pancreatin
Vitamins	Oxidation	thiamine, ascorbic acid
Glycosides	Hydrolysis	anthraquinones
Alkaloids	Racemization	hyocyamine to atropine
Tannins	Precipitation	phlobatanins to phlobaphenes

Changing physical form : In the preparation of *Cascara sagrada* tablets, granular extract is suitable. Drying at the atmospheric pressure yields a dense, compact residue, which is not desirable. In the initial stage, the liquid extract is concentrated under atmospheric pressure or under partially reduced pressure, until the residue has the consistency of treacle. The pressure is then quickly reduced, where upon the treacly semi-solid swells up due to sudden evolution of water vapour. This produces a light porous mass, which can readily be passed through a sieve to form a granular powder.

Disadvantages : In vacuum distillation, persistent foaming occurs. This may be overcome by adding capryl alcohol to the liquid or by inserting a fine air capillary tube in the second neck of the Claisen flask. The stream of air is drawn in and breaks the rising foam. The above method is not suitable for the preparation of semisolid or solid extracts.

Distillation Under Reduced Pressure

Assembling of apparatus : It consists of a double-neck distillation flask known as *Claisen flask* (Figure 11-17). Thick walled glass apparatus with interchangeable standard glass joints are used for vacuum distillation. In one of the necks of the Claisen flask, a thermometer is fitted. The second neck prevents splashing of the violently agitated liquid. Bumping occurs readily during vacuum distillation. Placing a fine capillary tube in the second neck of the flask can prevent bumping.

The capillary tube is dipped in the boiling liquid, so that a stream of air bubbles is drawn out. Water bath or oil bath is used for heating.

The Claisen flask is connected to a receiver through a condenser. Vacuum pump is attached through an adapter to the receiver. A small vacuum gauge (manometer) should be inserted between the pump and the receiver.

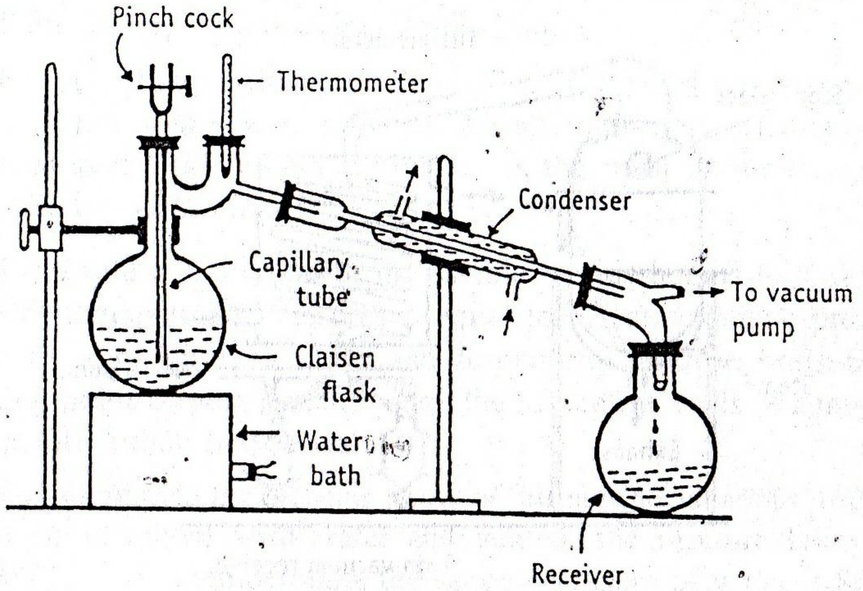


Figure 11-17. Assembly of apparatus for distillation under reduced pressure (on laboratory scale).

Procedure : The liquid to be distilled is filled one-half to two-third volume of the flask. Small pieces of porcelain are added to the liquid for facilitating distillation and prevent bumping. The capillary tube and thermometer are kept in place in the flask (Figure 11-17). The required vacuum is applied. The contents are heated gradually. The temperature rises and liquid gets vaporised rapidly due to vacuum. The vapour passes through the condenser. The condensate is collected in the receiver. The temperature is noted down, which would be less than the boiling point of the liquid.

When a large volume of a liquid is to be distilled under reduced pressure, it is more convenient to distil comparatively small volumes at a time.

Large Scale Apparatus Using Vacuum Stills for Distillation Under Reduced Pressure

Construction : The general construction of a large scale equipment for distillation under reduced pressure is shown in Figure 11-18. The

vacuum jacketed still is generally made of stainless steel, copper or any other material, which can withstand a high vacuum. An observation window in the hood is helpful to see the progress of the distillation and also the level of the liquid contents. The still is fitted with a drainpipe at the bottom and an air vent. The still is connected to a condenser. A thermometer is incorporated in the still. Vacuum pump through vacuum gauge is connected as shown in Figure 11-18.

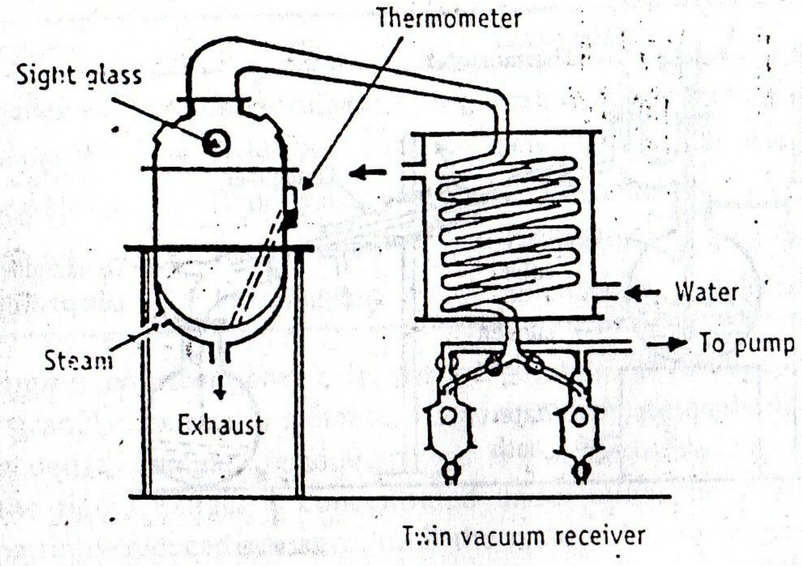


Figure 11-18. Assembly of apparatus for distillation under reduced pressure (on industrial scale).

Working : The still is filled with the liquid to be distilled through an attachment of a pipe with a tap. The other end of the pipe is connected to a reservoir of liquid, so that it can be filled at a controlled flow rate. Vacuum is created by means of a vacuum pump. Using the steam, the liquid is gradually heated. The temperature rises and the liquid gets vaporised rapidly due to vacuum. The vapour passes through the condenser and the condensate is collected into a receiver.

Normally two receivers are fitted with suitable arrangement of cocks, so that they can be used alternatively, the distillate being collected from one, while the other is connected to the still under vacuum. Therefore distillation need not be stopped.

Distillation is stopped while the contents of the flask are sufficiently fluid to run off through the drain pipe at the bottom. When spongy powdery mass is desired, the still can be provided with a stirring arrangement, which also hastens vaporization. According to the requirements, the capacity may be a few litres to thousands of litres.

STEAM DISTILLATION :

Steam distillation is a method of distillation carried with the aid of steam and is used for the separation of high-boiling substances from non-volatile impurities.

High-boiling liquids cannot be purified by simple distillation, since the constituents in the mixture tend to decompose at higher temperatures. In such cases, steam distillation is employed. Steam distillation is used for the separation of immiscible liquids.

For substances, which are insoluble in water and not decomposed by heat, steam distillation provides an alternative to distillation under reduced pressure. Steam distillation is the most common example of *differential distillation.*

Principle : A mixture of immiscible liquids begins to boil when the sum of their vapour pressures is equal to the atmospheric pressure. In case of a mixture of water and turpentine, mixture boils below the boiling point of pure water, though the turpentine boils at a much higher temperature than that of water.

For example, the boiling point of turpentine is about 160°C. But when it is mixed with water and heated, the mixture boils at about 95.6°C. At this temperature, the vapour pressure of water is 86.245 kPa (647 mm Hg) and that of turpentine is 15.06 kPa (113 mm Hg). The sum of the vapour pressures is 101.31 kPa (760 mm Hg) which is normal atmospheric pressure. Thus, high boiling substances may be distilled at a temperature much below its boiling point, when water (steam) is used.

For volatile substances, which are miscible with water, steam distillation involves the same principle as fractional distillation.

Applications : (1) Steam distillation is used for the separation of immiscible liquids. Example is toluene and water.

(2) This method is used for extracting most of the volatile oils such as clove, anise and eucalyptus.

(3) It is useful in purification of liquid with high boiling point, for example essential oil of almond.

(4) Camphor is distilled by this method.

(5) Aromatic waters are prepared by this method.

Advantages : Volatile oils can be separated at a lower temperature in steam distillation, without any decomposition and loss of aroma. If a substance has low volatility, it can be satisfactorily distilled, provided its

molecular weight is considerably higher than water.

Disadvantages : Steam distillation is not suitable when immiscible liquid and water react with each other

Apparatus Used for Laboratory Scale

Assembly of apparatus : The assembly of apparatus for steam distillation on laboratory scale is shown in Figure 11-19. It consists of a

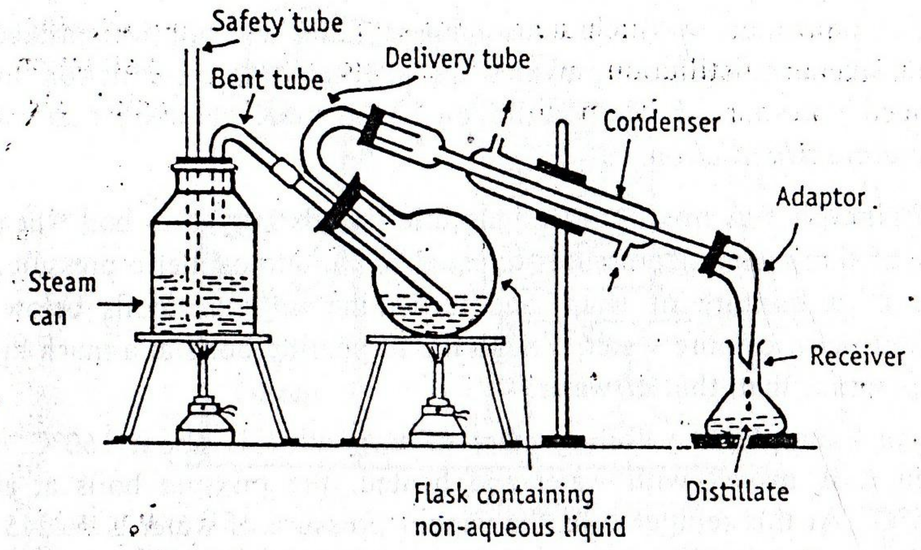


Figure 11-19. Assembly of apparatus for steam distillation (on laboratory scale).

metallic '*steam can*' fitted with a cork having two holes. Through one of the holes, a long tube is passed so as to reach almost the bottom of the steam generator. This tube acts as a safety tube, so that in case the pressure inside the steam generator becomes too much, water will be forced out of it and the pressure will be relieved. Moreover, when steam starts coming out from the safety tube, it indicates that the steam can is almost empty. Through another hole, a bent tube is passed. The other end of the bent tube is connected to the flask containing non-aqueous liquid (for example, crude containing volatile oil) through a rubber bung. This tube should reach almost the bottom of the flask.

Through the other hole of the rubber bung, a delivery tube is inserted which connects the flask and the condenser. The condenser is connected to a receiver flask using an adaptor. Provisions are made to heat the *steam can* and flask.

Procedure : The non-aqueous liquid is placed in the flask. A small quantity of water is added to it. *Steam can* is filled with water. The

steam generator and the flask are heated simultaneously, so that a uniform flow of steam passes through the boiling mixture. The mixture gets heated. The steam carries the volatile oil and passes into the condenser, which is cooled by cold water. The condensed immiscible liquid is collected into the receiver.

Distillation is continued until all the non-aqueous liquid has been distilled. In the receiver, water and organic liquid form two separate layers, which can be easily separated using a separating flask.

For volatile substances, which are miscible with water, distillation with steam would involve the same principle of fractional distillation.

Equipment Used on Industrial Scale

Construction : Steam distillation unit is diagrammatically shown in Figure 11-20. It consists of a jacketed still with a perforated plate which forms a false bottom. Manholes are provided at the top and side for charging and discharging. A Florentine receiver is placed between the still and condenser. The condenser is cooled by circulating cold water.

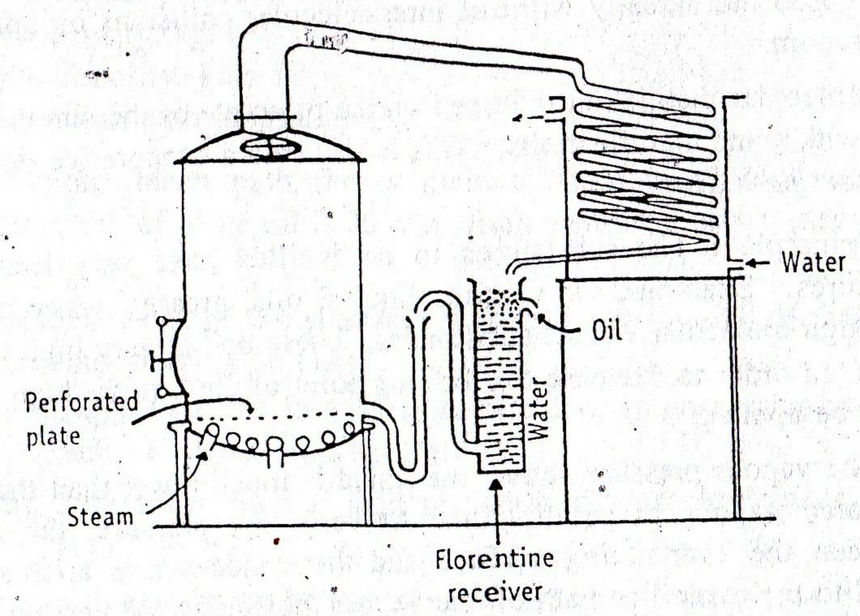


Figure 11-20. Assembly of apparatus for steam distillation (on industrial scale).

Working : The material from which the volatile oil has to be extracted is placed in the still above the perforated plate. Steam is admitted to the jacket of the still. The water and material present in the still are heated to boiling. Simultaneously steam is also injected below the materials through a steam pipe from the jacket. The steam carries the volatile oil and gets condensed in the condenser, which is cooled by

cold water. The condensate is collected into the Florentine receiver. Most volatile oils are lighter than water and well separated from the distillate as an upper layer and removed from the upper spout. The water can run off from the spout on the left and returns to the still.

Some volatile oils are heavier than water in which case the separation is reversed. Oil is collected from the lower spout.

Variants : (1) For volatile substances, which are miscible with water, distillation method combines the principles of the steam and fractional distillations.

(2) If the specific gravity of the oil is near 1.0, then separation does not take place. In such cases, it may be necessary to collect the whole of the distillate. Further it is extracted with an (volatile) organic solvent. The solvent should be distilled off to get the volatile oil.

MOLECULAR DISTILLATION

Molecular distillation is defined as a distillation process in which each molecule in the vapour phase travels mean free path and gets condensed individually without intermolecular collisions on application of vacuum.

Molecular distillation is based on the principle of the simple distillation with some modifications. This is also called evaporative *distillation* or *short path distillation.*

Principle : The substances to be distilled have very low vapour pressures. Examples are viscous liquids, oils, greases, waxy materials and high molecular weight substances. These boil at very high temperatures. In order to decrease the boiling point of the liquids, high vacuum must be applied.

The vapour pressure above the liquid is much lower than that of the saturated vapour in equilibrium. At very low pressure, the distance between the evaporating surface and the condenser is approximately equal to the mean free path of the vapour molecules. Molecules leaving the surface of the liquid are more likely hit the condenser surface than to collide with other molecules. Little or no re-condensation takes place at the surface of the liquid.

Applications : Molecular distillation is used for the purification and separation of chemicals of low vapour pressure.

(1) Purification of chemicals such as tricresyl phosphate, dibutyl phthalate and dimethyl phthalate.

(2) More frequently used in the refining of fixed oils.

(3) Vitamin A is separated from fish liver oil. Vitamin E is concentrated by this method from fish liver oils and other vegetable oils.

(4) Free fatty acids are distilled at 100°C. Steroids can be obtained between 100°C and 200°C, while triglycerides can be obtained from 200°C onwards. Proteins and gums will remain as non-volatile residues. Thus, the above mixture can be separated by molecular distillation.

Theory : The *mean free path of a molecule* is defined as the average distance through which a molecule can move without coming into collision with another.

The mean path (λ) can be expressed mathematically as:

$$\lambda = \eta\sqrt{\frac{3}{p\rho}} \qquad (11)$$

where p = vapour pressure, kPa
ρ = density, kg/m^3
η = viscosity, Pa·s
λ = mean path length, m

For example, mean path (heavy molecules) of butyl phthalate is about 30 mm and of olive oil is 20 mm when measured at a pressure of 0.1 pascal.

The characteristics of the substance influence the method of distillation. According to equation (11):

(a) Liquids having low viscosity and density posses long mean path. Distillation is simple.

(b) Substances having high pressures possess low mean free path.

The mean free path can be increased by decreasing the viscosity (η), which can be obtained at high temperature and low pressure. Thus, nonvolatile substances may become volatile and distillation is possible.

It is necessary to design the equipment based on the requirement of the molecular distillation. Some of them are as follows.

(1) The evaporating surface must be close to the condensing surface. This ensures the molecules to come in contact with the con-

denser as soon as they leave the evaporating surface. For this reason, this process is also known as *short path distillation.*

(2) The molecular collisions should be minimized because they change the direction of the path of molecules. In other words, intermolecular distances should be fairly high. It can be achieved under very high vacuum, usually of the order of 0.1 to 1.0 pascals.

(3) The liquid surface area must be as large as possible so that the vapour is evolved from the surface only, but not by boiling. Thus this process is also called *evaporation distillation.*

Based on the method of formation of the liquid film, apparatus may be divided into two types.

Falling Film Molecular Still or Wiped Film Molecular Still

Principle : In this method, vaporisation occurs from a film of liquid flowing down a heated surface under high vacuum. The vapour

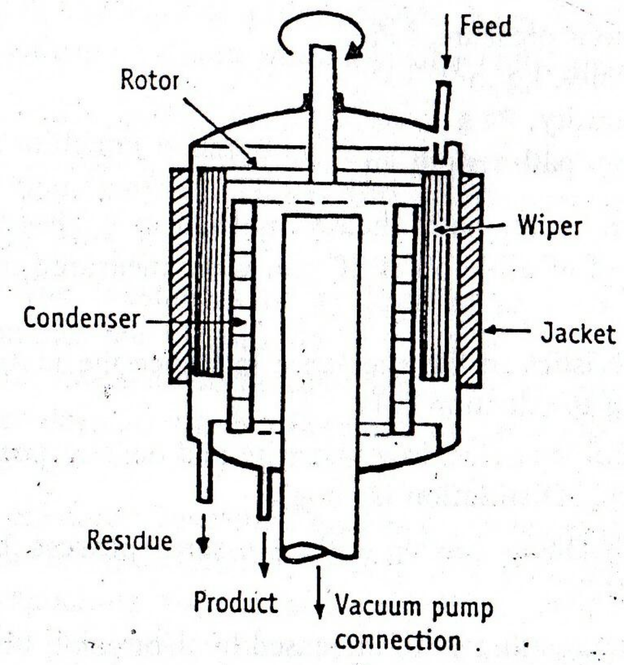


Figure 11-21. Wiped film molecular still.

(molecules) travels a short distance and strikes the condenser nearby. Each molecule is condensed individually. The distillate is subsequently collected.

Construction : The construction of a wiped film molecular still is shown in Figure 11-21. The vessel has a diameter of one metre. The

walls of the vessel are provided with suitable means of heating (jacket). Wipers are provided adjacent to the vessel wall. Wipers are connected to a rotating head through a rotor. The condensers are arranged very close to the wall (evaporating surface) as shown in Figure 11-21. Vacuum pump is connected to a large diameter pipe at the centre of the vessel. Provisions are made for collecting the distillate and the undistilled liquid residue at the bottom.

Working : The vessel is heated by suitable means. Vacuum is applied at the centre of the vessel and wipers are allowed to rotate. The feed is entered through the inlet of the vessel. As the liquid flows down the walls, it is spread to form a film by PTFE (polytetrafluoroethylene) wipers, which are moving at a rate of 3 metre per second. The velocity of the film is 1.5 metres per second. Since the surface is already heated, the liquid film evaporates directly. The vapour (molecules) travels its mean free path and strikes the condenser. The condensate is collected into a vessel. The residue (undistilled or mean free path not travelled) is collected from the bottom of the vessel and re-circulated through the feed port for further distillation. Capacity is about 1000 litre per hour.

Centrifugal Molecular Still

Principle : In this method, liquid feed is introduced into a vessel, which is rotated at very high speed (centrifugal action). On account of heating, vaporisation occurs from a film of liquid on the sides of the vessel. The vapour (molecules) travels a short distance and gets condensed on the adjacent condenser. Each molecule is condensed individually. The distillate is subsequently collected.

Construction : The construction of a centrifugal molecular still is shown in Figure 11-22. It consists of a bucket-shaped vessel having a diameter of about 1 to 1.5 metre. It is rotated at high speed using a motor. Radiant heaters are provided externally to heat the fluid in the bucket. Condensers are arranged very close to the evaporating surface. Vacuum pump is connected to the entire vessel at the top. Provisions are made for introducing the feed into the centre of the bucket, for receiving the product and residue for re-circulation.

Working : Vacuum is applied at the centre of the vessel. The bucket shaped vessel is allowed to rotate at high speed. The feed is introduced from the centre of the vessel. Due to centrifugal action of the rotating bucket, liquid moves outward over the surface of the vessel and forms a film. Since, the radiant heaters heat the surface, the liquid evaporates directly from the film. The vapour (molecules) travels its mean free path

and strikes the condenser. The condensate is collected into another vessel. The residue is collected from the bottom of the vessel and is re-circulated through the feed port for further distillation.

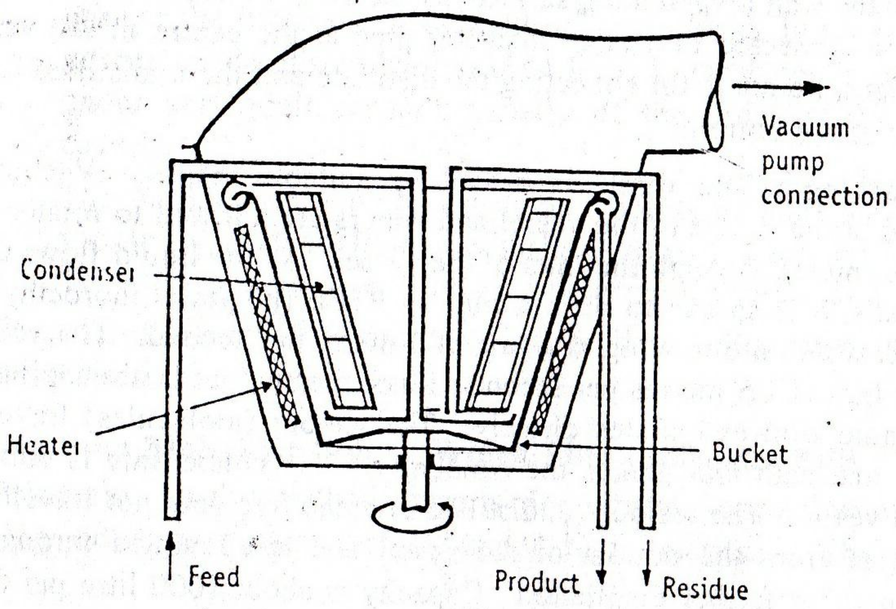


Figure 11-22. Centrifugal molecular still.

Disadvantages : Construction and operation are more complicated compared to falling film molecular still.

DESTRUCTIVE DISTILLATION

Destructive distillation is a distillation method in which the distillate is decomposition products of the constituents of the organic matter burnt in the absence of air.

This process is also known as *dry distillation.* It is not useful in laboratory practice, but one of the most important industrial processes for obtaining many valuable products from wood, coal, and animal matter. It involves the heating of dry organic matter in a suitable vessel in the absence of air, until all volatile substances are driven off. The distillate is the decomposition products. Wood distillation industry and coal carbonisation industry provide many useful materials.

COMPRESSION DISTILLATION

Compression distillation method was developed to meet the needs of Navy and Army for fresh water, which is obtained from sea-water. The product obtained is quite pure and pyrogen-free. Therefore, it meets the

requirements of the pharmaceutical industry. It is economical from the standpoint of consumption of fuel and water.

The feed water is heated in an evaporator for boiling. The vapour produced in the tubes is separated from entrained distilland in a separator. The vapour is then conveyed to a compressor, which compresses it and raises its temperature to about 118°C. It then flows to the steam chest where it is condensed on the outer surface of the tube. During condensation, heat is released which is allowed for heating of the fresh feed in the tubes to the boiling point. The vapour is condensed and drained off as distillate.

Glossary of Symbols

P = Total vapour pressure of the mixture, kPa.
p = Partial vapour pressure of a liquid, kPa.
p^o = Vapour pressure exerted by pure solvent, kPa.
v = Volatility of the component, kPa.
X = Mole fraction of component in liquid state.
Y = Mole fraction of component in gaseous state.
α = Relative volatility.
ρ = Density, kg/m^3.
η = Viscosity, Pa·s.

QUESTION BANK

Each question carries 2 marks

1. Describe Raoult's law. What is its significance?
2. What are constant boiling mixtures? How are they separated?
3. What is meant by constant boiling mixtures? Give two examples.
4. Name the materials commonly used in packing of fractionating columns.
5. List the requisite characteristics that a packing material should possess.
6. Differentiate between plate towers and packed towers.
7. Describe the construction of any one fractionating column.
8. Distinguish between drying and distillation. Explain differential distillation.
9. Distinguish between 'stripping section' and 'rectifying section' of a rectifying column.
10. Name the characteristics of a packing material for use in fractionating columns.
11. Name different types of rectifying columns.
12. Define distillation. Mention two applications of it as per IP.
13. Differentiate between differential distillation and rectification.
14. Define 'ideal plate' and 'relative volatility'.
15. Define 'flash distillation'. List applications.

Each question carries 5 marks

1. Explain with relevant procedure the separation of an azeotropic mixture.
2. What is meant by steam distillation? What are its special advantages?
3. Describe the principles and applications of steam distillation.
4. What are constant boiling mixtures? Draw typical boiling diagrams for constant boiling mixtures.
5. Describe the construction of bubble cap column. What are its advantages?
6. Describe a bubble cap rectifying column. What are the specific drawbacks of bubble cap columns.
7. Describe one fractionating column of your choice. List its advantages and disadvantages.
8. Describe the construction and working of a distillation apparatus for the preparation of distilled water.

Each question carries 10 marks.

1. Explain the principle and procedure of molecular distillation. What are its applications?
2. Distinguish between plate columns and packed towers. Describe the types of packing for rectifying columns. How is absolute alcohol made?