UNIT: II **(DISTILLATION)**

CLASS:19

TOPIC: FRACTIONAL DISTILLATION, DISTILLATION UNDER REDUCED PRESSURE

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, *PA* and *PB* represent their partial pressures, respectively, then Dalton's law may be mathematically expressed as:

Total pressure = *PA + PB*

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

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

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

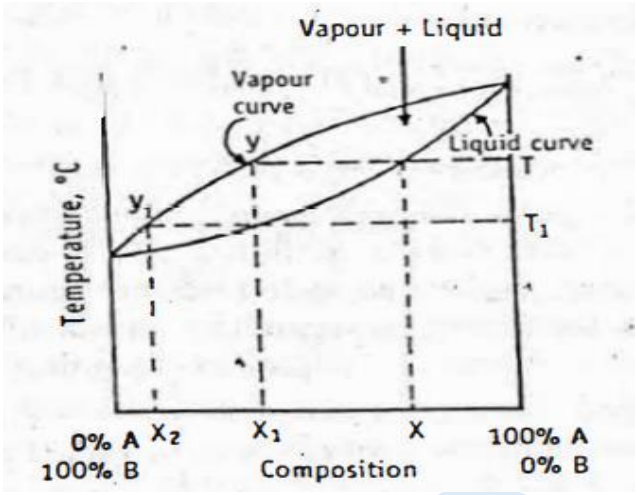
(8) The different areas correspond to the existence of liquid, vapour and liquid plus vapour phases.

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 1 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. These systems are known as *zeotropic mixtures.* Examples include benzene and toluene. carbon tetrachloride and cyclohexane, and water and methanol.

The usefulness of Figure in the design of fractional distillation is illustrated in Figure



Boiling point-composition diagram of miscible liquids.

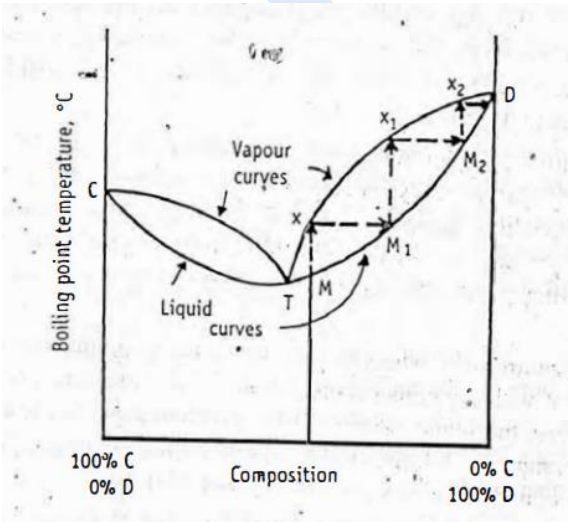
Fractional Distillation-Azeotropic Mixtures

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. 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.



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 com- ponent 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).

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).

Consider a hypothetical case (Figure) 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, which is richer in D than C. When this liquid is redistilled, the vapour has composition of x. When this vapour is condensed, the liquid has the composition of M2. 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).

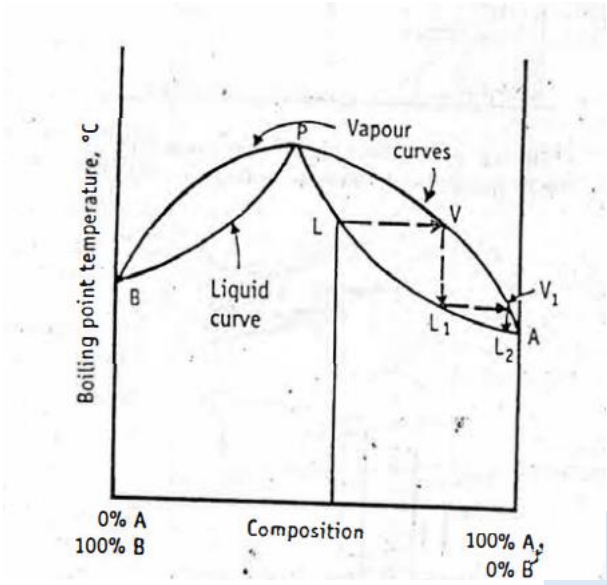
Maximum boiling point azeotropic solutions-Type III solutions (non-ideal solutions):

System that exhibits a maximum value in the boiling point-composition diagram is shown in Figure. 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).

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.

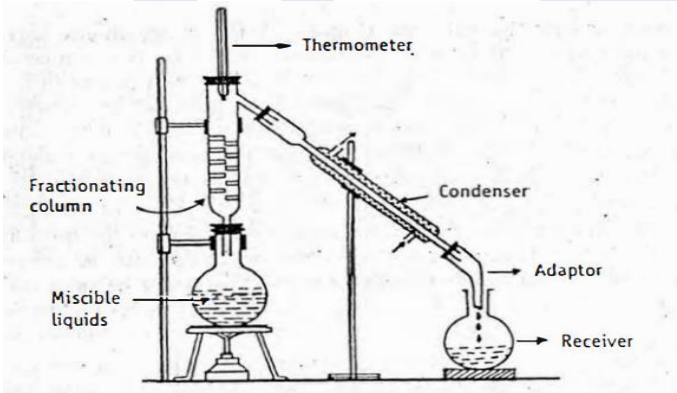
Consider a hypothetical case (Figure) in which the mixture contains more of A than B, which. is represented by L. If this mixture is distilled, the composition of vapour v is richer in A and poorer in B. At this state. the liquid residue in. the distillation flask will be richer in B and poorer in A. The vapour at v is condensed, the liquid composition is represented by L_1. If this liquid is distilled, the composition of vapour v 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



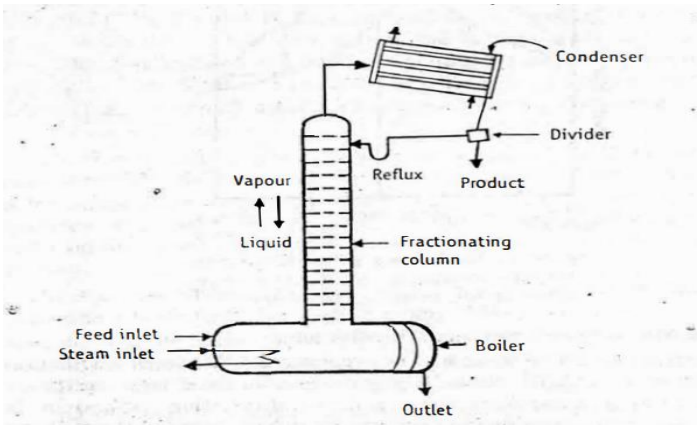
Boiling point-composition curves of a constant boiling azeotropic mixture having maximum boiling point

General Method-for Fractional Distillation

Construction: The assembly of apparatus for fractional distillation on a laboratory scale is shown in Figure(a). On a large scale. the construction of equipment for fractional distillation is shown in Figure(b). 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 arca for providing sufficient flow conditions. The broken lines across, the column represent the contacting devices

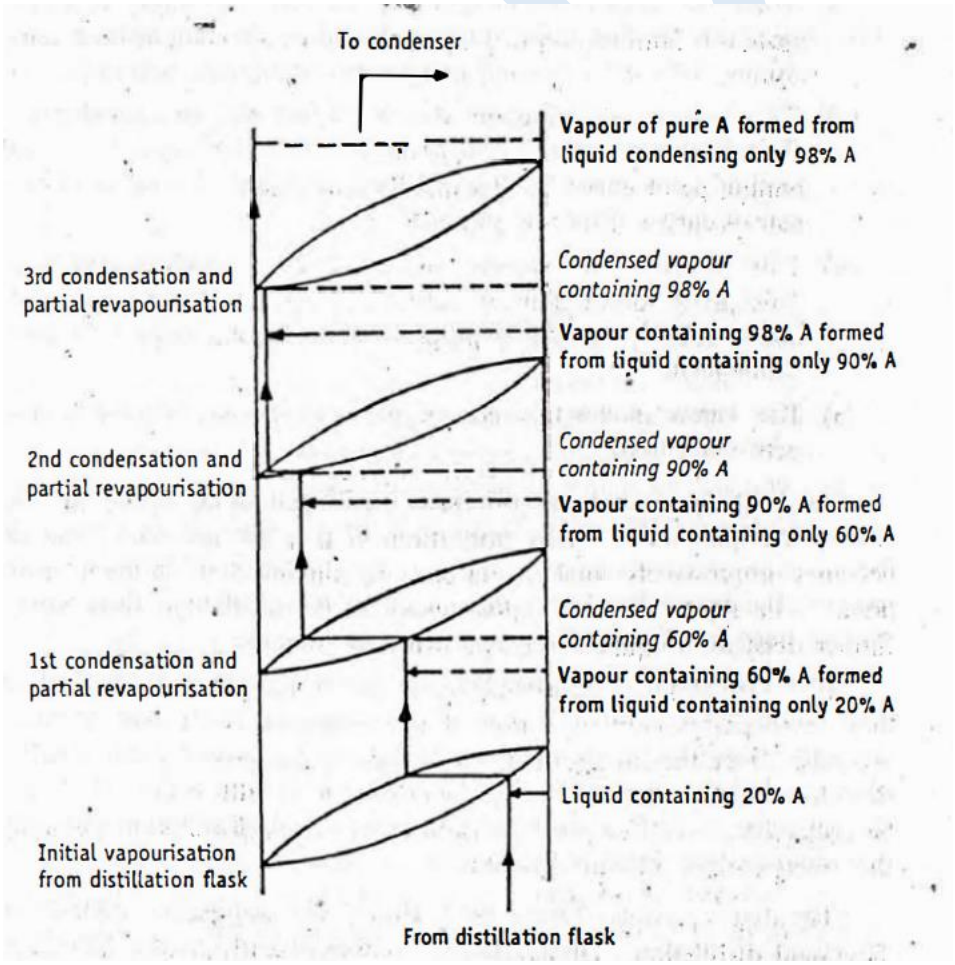


Figure(a)Assembly of apparatus for fractional distillation (on laboratory scale).



Figure(b)Assembly of apparatus for fractional distillation 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).



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, which is similar to Figure. 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). 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. 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

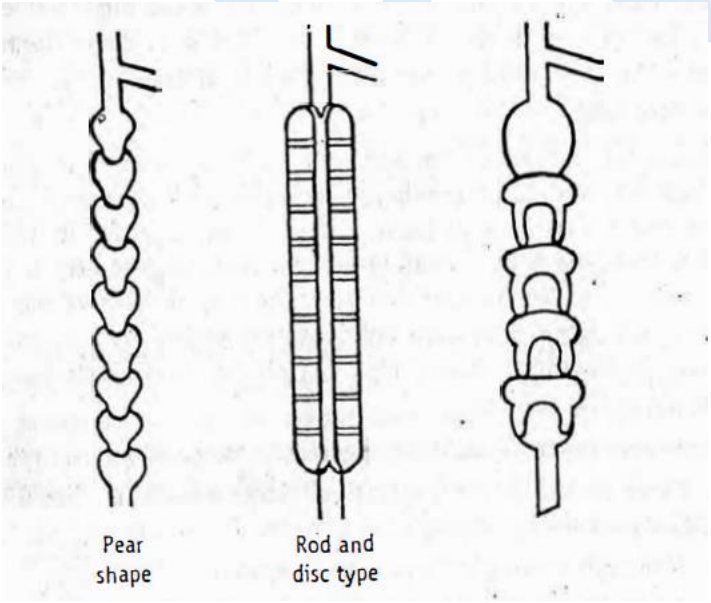
Generally, it is necessary to conduct distillation several times by appropriate means in order to separate a mixture of miscible liquids. This can be avoided by employing fractionating column for a reasonably complete separation. In fractional distillation, special type of still-heads are required so 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.



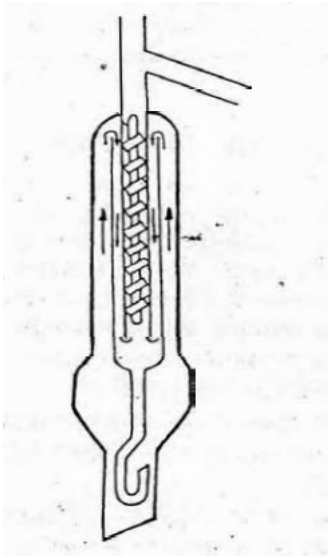


Fig (a)Different types of fractionating columns. Widmer column fig(b)

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.

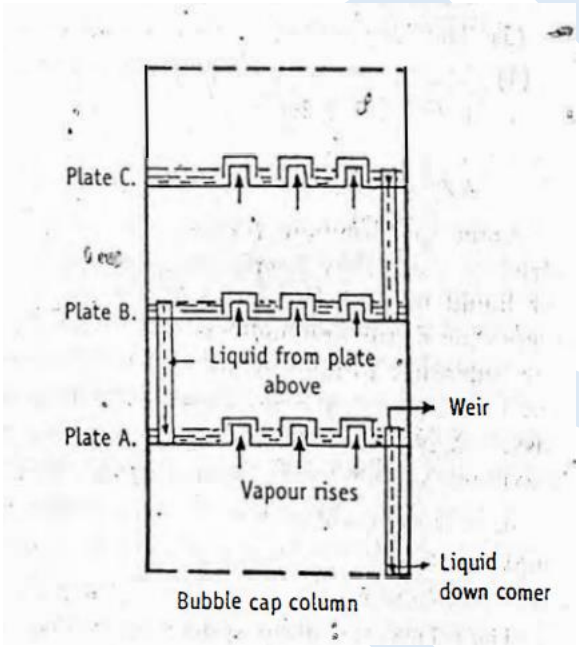
Applications: Packing must be uniform so as to obtain proper channels. If packing is irregular, mass transfer becomes less effective. Packed columns are mainly used in laboratories. · Example is Widmer column fig(b)

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.



Construction of bubble cap column for fractional distillation.

Construction: The column consists of a number of plates mounted one above the other (Figure). 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 docs 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 moisture 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 as. Azeotropic ternary mixtures with minimum boiling po int (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 tractional 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 non-volatile 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 101.3l 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:

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

According to this formula, if 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

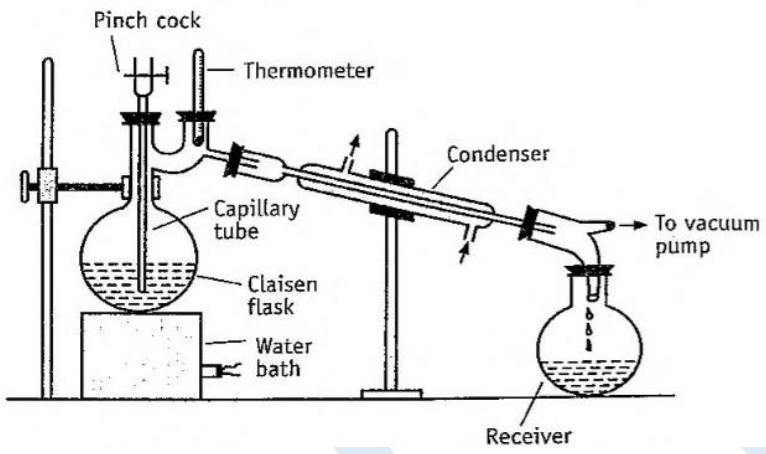
Changing physical form: In the preparation of Cascara sagrada tablets, granular extract is suitable. Drying at the atmospheric pressure yields a dense, compact residue. which is not desirable. In the initial stage the liquid extract is concentrated under atmospheric pressure or under partially reduced 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 or 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 line 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 *C!aisen flask* (Figure) 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.



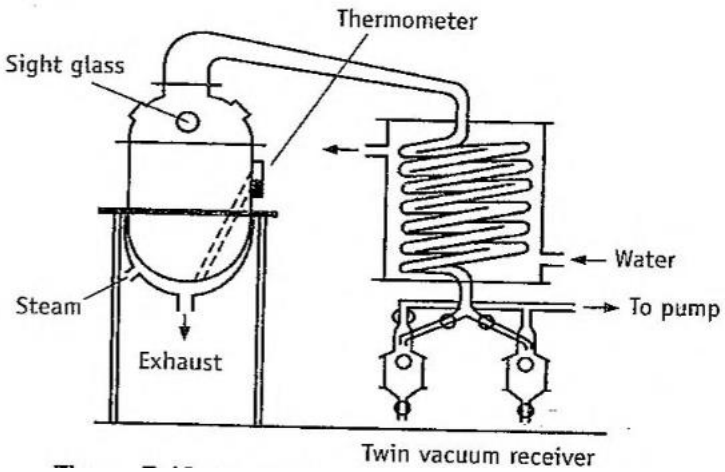
Assembly of apparatus for distillation under reduced pressure (on laboratory scale)

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). 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:



Assembly of apparatus for distillation under reduced pressure (on industrial scale).

The general construction of a large scale equipment for distillation under reduced pressure is shown in Figure. 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 sec 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.

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 the condensate 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 oft through the drain pipe at the bottom. When spongy powdery 1nass 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.

MCQ Each carry 1 mark

1. Absolute alcohol is prepared by one of the following methods

a. Azeotropic distillation

b. Simple distillation

c. Steam distillation

d. Vacuum distillation

2. The Fractional distillation is always different from the distillation due to the presence of which of the following?

(A). Condenser

(B). Fractionating column

(C). Distillation flask

(D). Conical flask

3. Much suitable for the fractional distillation process is _____

(A). None of the mentioned

(B). Water bath

(C). Oil bath

(D). Glycerine bath

4. How the simple fractional tube is packed?

(A). With the Plastic beads

(B). With the Glass beads

(C). With the Metal beads

(D). With the Wooden beads

5. The beads are provided in a fractional column for which of the following?

(A). Vapours to condense

(B). Vapours to evaporate

(C). Vapours to generate

(D). All of the mentioned

6. Which of the following is the incorrect statement?

(A). The Fractionating columns are always available in different designs and size

(B). Fractional distillation is the process of separating the different gases from the air

(C). The Fractionating columns are always available according to the one fixed standard

(D). The simple fractionating column is a tube always packed with the glass beads

7. The gases that cannot be separated from air using fractional distillation are_____

(A). Helium

(B). Argon

(C). Oxygen

(D). Nitrogen

8. What is The difference in the boiling point of 2 liquids in fractional distillation?

(A). Less than 25 K

(B). Equal to 25 K

(C). Greater than 25 K

(D). None of the mentioned

9. The Fractional distillation is a process of separation of which of the following?

(A). 2 immiscible liquids

(B). 1 miscible and 1 immiscible liquid

(C). 2 miscible liquids

(D). None of the mentioned

10. What is the Number of steps that are required for the separation of two liquids in fractional distillation?

(A). 3.

(B). 1

(C) 2

(D). 4

Each carry 2 marks

1. What exactly does "distillation under reduced pressure" mean? Give examples
2. What is the purpose of distillation under lower pressure? In distillation under reduced pressure, what is the name of the flask that is used?
3. Name the materials commonly used in packing of fractionating columns.
4. Describe the construction of any one fractionating column

Each carry 5 marks

1. Explain with relevant procedure the separation of an azeotropic mixture.
2. What are constant boiling mixtures? Draw typical boiling diagrams for constant boiling mixtures
3. Describe one fractionating column of your choice. List its advantages and disadvantages

Each carry 10 marks

1. Describe Fractional Distillation-Azeotropic Mixtures