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DISTILLATION AND EVAPORATION

INTRODUCTION

Distillation is a process in which the liquid is vaporized, recondensed, and collected in a receiver. The liquid that has not vaporized is called the *residue*. The resultant liquid, the condensed vapor, is called the *condensate or distillate*.

Distillation is used to purify liquids and to separate one liquid from another. It is based on the difference in the physical property of liquids called *volatility*. Volatility is a general term used to describe the relative ease with which the molecules may escape from the surface of a pure liquid or a pure solid. The vapor pressure of a substance at a given temperature expresses this property. (See Fig. 21.1)
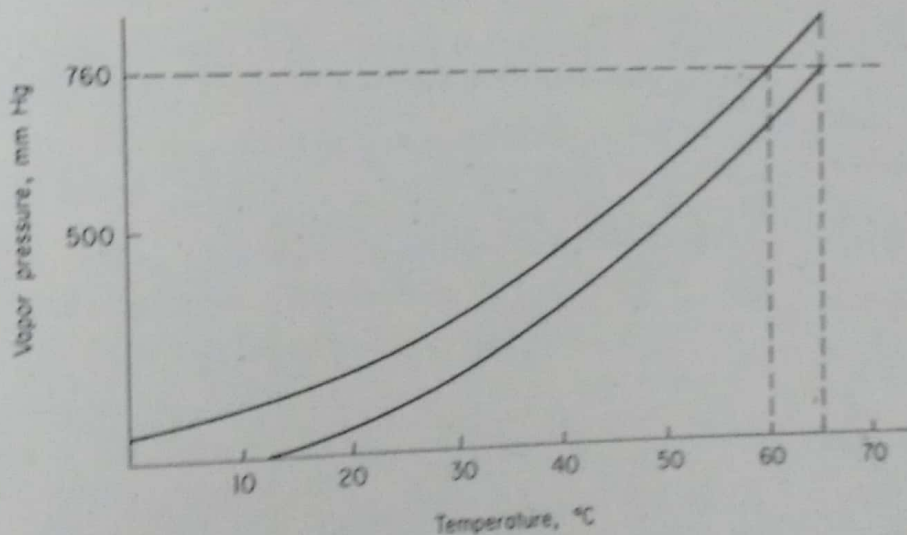

FIGURE 21.1
Dependence of vapor
pressure on temperature.

Vapor Pressure

A volatile substance is one which exerts a relatively high vapor pressure at room temperature. A nonvolatile substance is one that exerts a low vapor pressure. The more volatile a substance, the higher its vapor pressure and the lower its boiling point. The less volatile a substance, the lower its vapor pressure and the higher its boiling point.

All liquids and solids have a tendency to vaporize at all temperatures, and this tendency varies with temperature and the external pressure that is applied. When a solvent is enclosed, vaporization will take place until the partial pressure of the vapor above the liquid has reached the vapor pressure at that temperature. Fur-

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ther evaporation of the liquid can be accomplished by removing some of the vapor above it, which in turn reduces the vapor pressure over the liquid.

SIMPLE DISTILLATION

An experimental setup for simple distillation is shown in Figs. 21.2 and 21.3. The glass equipment may be standard and require corks or may have ground-glass fitted joints. To be sure your setup is correct, follow the checklist below:

1. The distilling flask should accommodate twice the volume of the liquid to be distilled.

2. The thermometer bulb should be slightly below the side-arm opening of the flask. The boiling point of the corresponding distillate is normally accepted as the temperature of the vapor. If the thermometer is not positioned correctly, the temperature reading will not be accurate. If the entire bulb of the thermometer is placed too high, above the side arm leading to the condenser, the entire bulb will not be heated by the vapor of the distillate and the temperature reading will be too low. If the bulb is placed too low, too near the surface of the boiling liquid, there may be a condition of superheating, and the thermometer will show too high a temperature.

3. All glass-to-glass or glass-to-cork connections should be firm and tight.
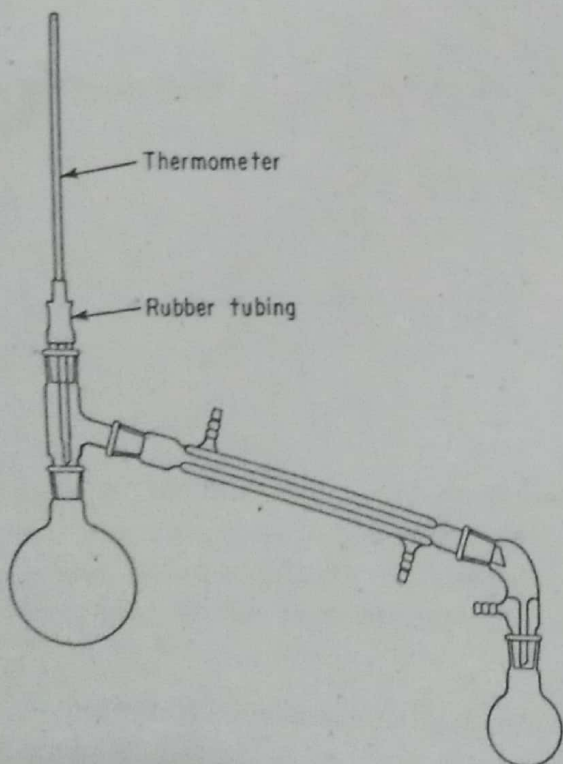

FIGURE 21.2
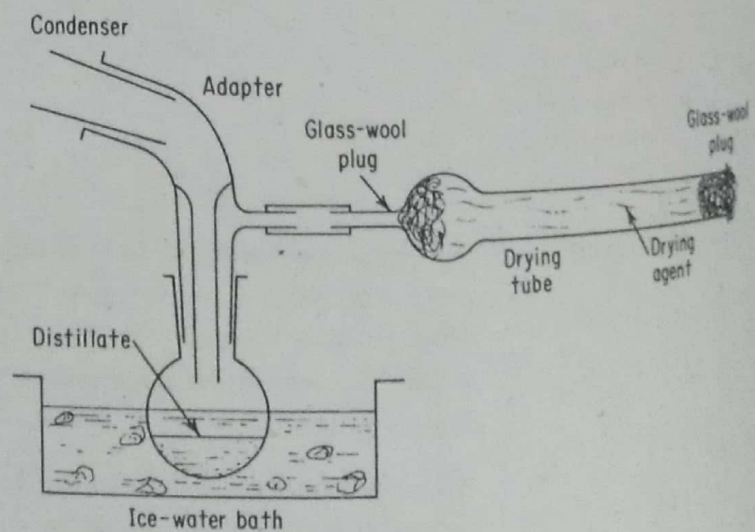Apparatus for simple distillation at atmospheric pressure.

FIGURE 21.3
Protecting a distillate from atmospheric moisture.

4. The flask, condenser, and receiver should be clamped independently in their proper relative positions on a steady base.

5. The upper outlet for the cooling water exiting from the condenser should point upward to keep the condenser full of water.

Procedure

1. Pour the liquid into the distilling flask with a funnel that extends below the side arm.

2. Add a few boiling stones to prevent bumping.

3. Insert the thermometer.

4. Open the water valve for condenser cooling.

5. Heat the distilling flask until boiling begins; adjust the heat input so that the rate of distillate is a steady two to three drops per second.

6. Collect the distillate in the receiver.

7. Continue distillation until only a small residue remains. Do not distill to dryness.

Distillation of Pure Liquids

Distillation can be used to test the purity of liquids or to remove the solvent from a solution.

The experimental setup for pure liquids is the same as that shown in Figs. 21.2 and 21.3.

1. The composition of the condensate is necessarily the same as the original liquid and is the same as the residue.

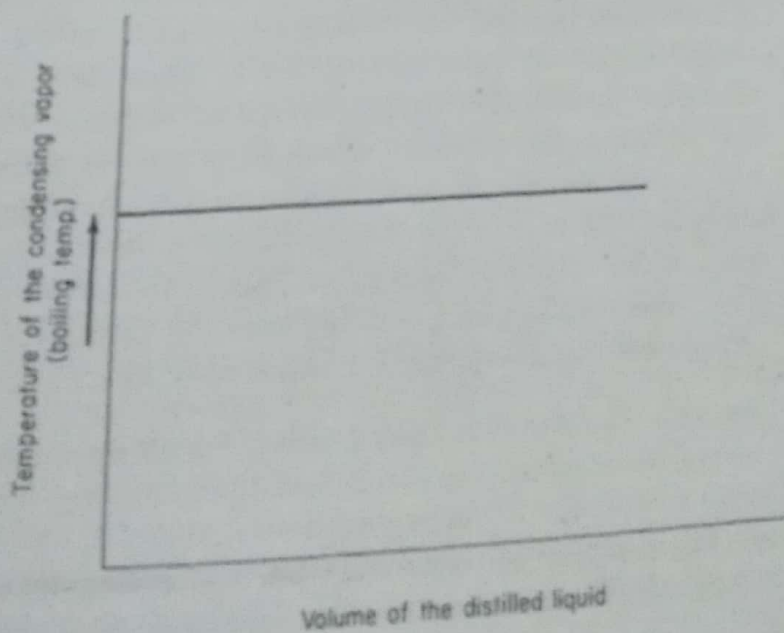2. The composition does not change (see Fig. 21.4).

FIGURE 21.4
Distillation curve of a pure liquid.

Temperature of the condensing vapor (boiling temp.)

Volume of the distilled liquid

3. The boiling temperature remains constant throughout the distillation.

4. Distillation establishes only the purity and boiling point of the pure liquid.

Distillation of a Solution

This process effects the separation of the nonvolatile dissolved solids because they remain in the residue and the volatile liquid is distilled, condensed, and collected.

1. The temperature of the distillate is constant throughout because it is pure.

2. The temperature of the boiling solution increases gradually throughout the distillation because the boiling solution becomes saturated with the nonvolatile solids.

When a nonvolatile substance is in the liquid being distilled, the temperature of the distilling liquid (the *head temperature*) will be the same as that of the pure liquid, since the vapor being condensed is uncontaminated by the impurity. The temperature of the pot liquid will be higher, because of the decreased vapor pressure of the solution containing the nonvolatile solute. The temperature of the pot liquid will continue to increase as the volatile component distills away, further lowering the vapor pressure of the solution and increasing the concentration of the solute.

CAUTION When evaporating a solution to recover the solute or when using electric heat or burners to distill off large volumes of solvent to recover the solute, do not evaporate completely to dryness. The residue may be superheated and begin to decompose.

Distillation of a Mixture of Two Liquids

Principle

Simple distillation of a mixture of two liquids will not effect a complete separation. If both are volatile, both will vaporize when the solution boils and both will appear in the condensate. The more volatile of the two liquids will vaporize and escape more rapidly and will form a larger proportion of the distillate. The less volatile constituent will concentrate in the liquid that remains in the distilling flask, and the temperature of the boiling liquid will rise. The more volatile of the two liquids will appear first in the distillate. When the difference in the volatilities of the two liquids is large enough, the first distillate may be almost pure. The last of the distillate collected will be richer in the less volatile component. If there is sufficient difference in the volatilities of the two liquids, the last of the distillate may be almost pure. The distillate collected between the first portion and the last portion will contain varying amounts of the two liquids. (See Fig. 21.5.)

You may separate two liquids with different volatilities by *changing the receiver* several times during the distillation, thus collecting several portions of distillate.

1. The first portion collected while the boiling temperature is near that of the more volatile liquid may contain that liquid with little impurity.
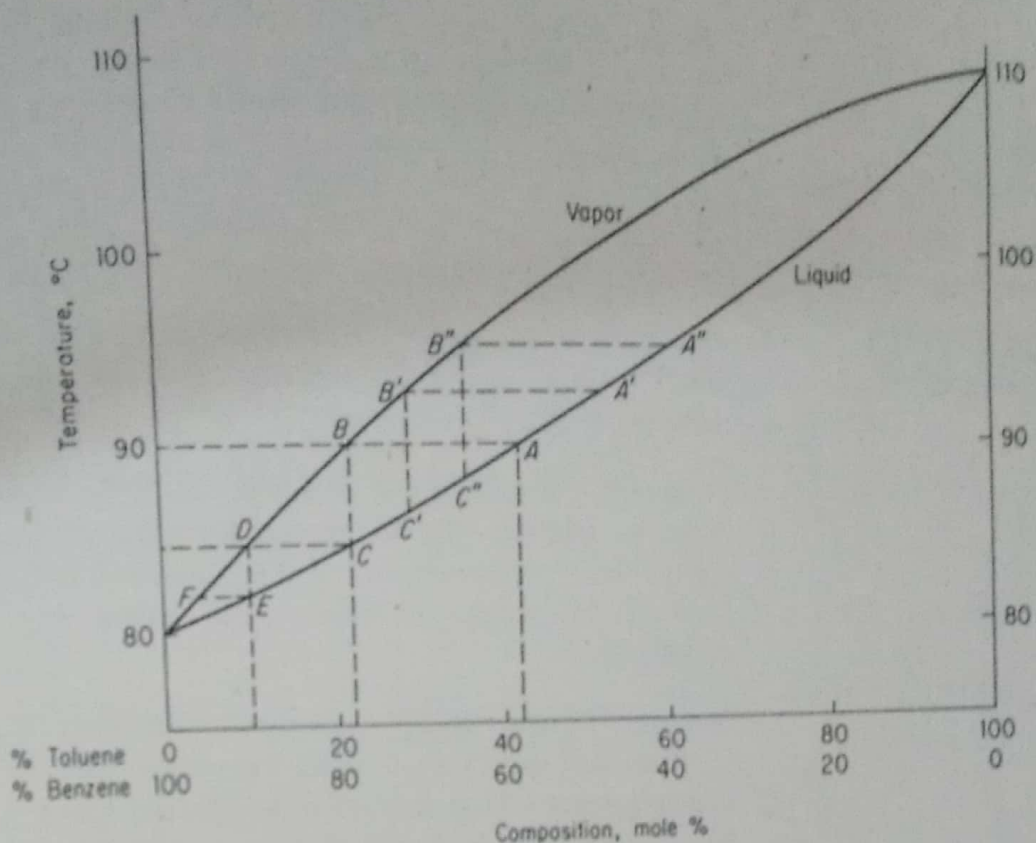
FIGURE 21.5
Boiling-point-composition
diagram for the system
benzene–toluene.

2. The last portion collected when the distillation temperature is nearly equal to
the boiling point of the less volatile liquid may contain that liquid and little of the
other. Intermediate portions will contain *both liquids in varying proportions.* You
may redistill each of the intermediate portions collected in the receiver to separate
them further into their pure components.

The lower curve of the diagram in Fig. 21.5 gives the boiling points of all mixtures
of these compounds. The upper curve gives the composition of the vapor *in equi-
librium* with the boiling liquid phase. The vapor phase is much richer in the more
volatile component, benzene, than the liquid phase with which it is in equilibrium.
Therefore, the first few drops of vapor that condense will be richer in the more
volatile component than in the less volatile one, toluene.

Rate of Distillation
(No Fractionation)

The rate of distillation is controlled by the rate of the input of heat. In normal dis-
tillations a rate of about 3 to 10 mL/min, which corresponds roughly to one to three
drops per second, is average. When liquids are to be separated by fractional distil-
lation (see Fractional Distillation, this chapter), the rate may be a great deal
smaller, depending upon the difficulty of the separation.

Concentration
of Large Volumes
of Solutions

When it becomes necessary to distill off large volumes of solvent to recover very
small quantities of the solute, it is advisable to use a large distilling flask at first.
(Never fill any distilling flask over one-half full.) When the volume has decreased,

transfer the material to a smaller flask and continue the distillation. This minimizes losses caused by the large surface area of large flasks. If the solute is a high-boiling substance, the walls of the flask act as a condenser, making it difficult to drive the material over.

AZEOTROPIC DISTILLATION

Azeotropic mixtures distill at constant temperature without change in composition. Obviously, one cannot separate azeotropic mixtures by normal distillation methods.

Azeotropic solutions are nonideal solutions. Some display a greater vapor pressure than expected; these are said to exhibit *positive deviation*. Within a certain composition range such mixtures boil at temperatures higher than the boiling temperature of either component; these are *maximum-boiling azeotropes* (see Table 21.1 and Fig. 21.6).

Mixtures that have boiling temperatures much lower than the boiling temperature of either component exhibit *negative deviation*; when such mixtures have a particular composition range, they act as though a third component were present. In Fig. 21.7, the minimum boiling point at Z is a constant boiling point because the vapor is in equilibrium with the liquid and has the same composition as the liquid does. Pure ethanol (bp 78.4°C) cannot be obtained by fractional distillation of aqueous solutions that contain less than 95.57% of ethanol because this is the azeotropic composition; the boiling point of this azeotropic mixture is 0.3° lower than that of pure ethanol.

TABLE 21.1
Maximum-Boiling-Point Azeotropic Mixtures

Component A		Component B		bp of Azeotropic mixture, °C	% of B (by mass) in mixture
Substance	bp, °C	Substance	bp, °C		
Water	100.0	Formic acid	100.8	107.1	77.5
Water	100.0	Hydrofluoric acid	19.4	120.0	37
Water	100.0	Hydrochloric acid	−84.0	108.6	20.22
Water	100.0	Hydrobromic acid	−73	126	47.6
Water	100.0	Hydriodic acid	−35	127	57.0
Water	100.0	Nitric acid	86.0	120.5	68
Water	100.0	Sulfuric acid	10.5 (mp)	338	98.3
Water	100.0	Perchloric acid	110.0	203	71.6
Acetone	56.4	Chloroform	61.2	64.7	80
Acetic acid	118.5	Pyridine	115.5	130.7	65
Chloroform	61.2	Methyl acetate	57.0	64.8	23
Phenol	181.5	Aniline	184.4	186.2	58
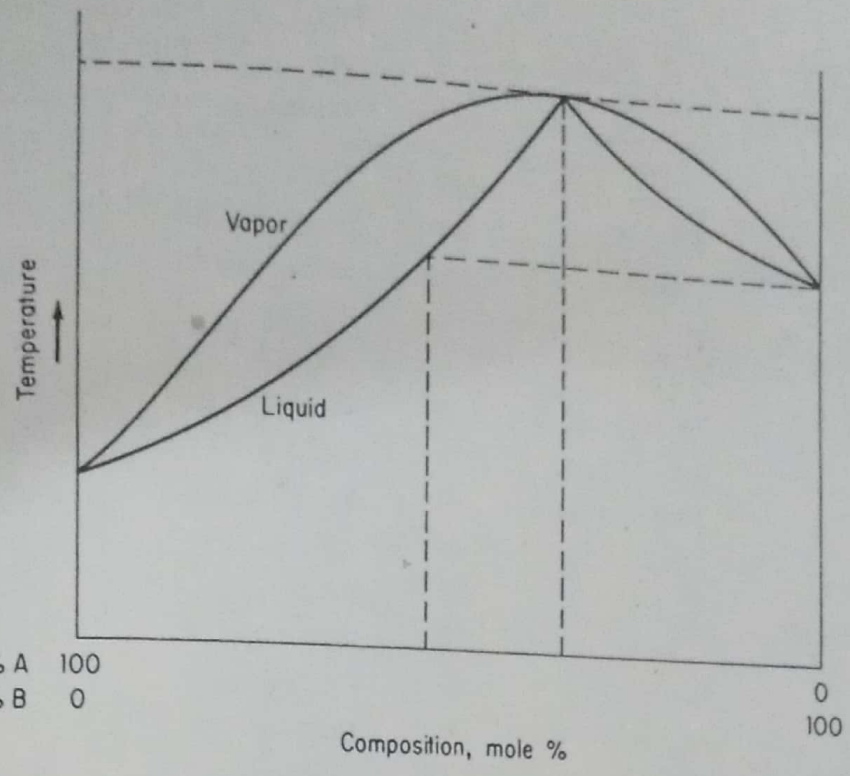
FIGURE 21.6
Maximum-boiling-point azeotrope.

% A 100
% B 0

0
100

Composition, mole %
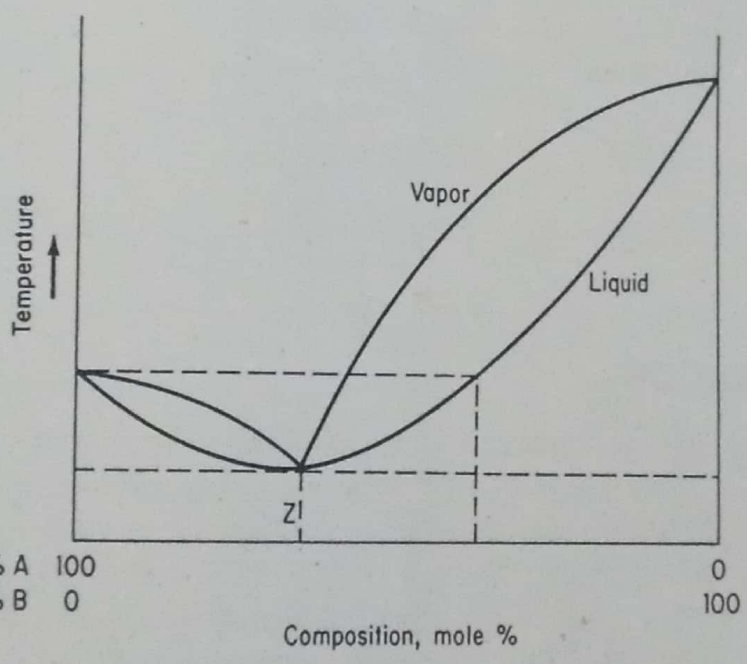
FIGURE 21.7
Minimum-boiling-point azeotrope.

% A 100
% B 0

0
100

Composition, mole %

Other examples are:

1. A mixture of 32.4% ethyl alcohol and 67.6% benzene (bp 80.1°C) boils at 68.2°C.

2. A ternary azeotrope (bp 64.9°C) is composed of 74.1% benzene, 18.5% ethyl alcohol, and 7.4% water. (See also Table 21.2.)

Absolute ethyl alcohol can be obtained by distilling azeotropic 95.5% ethyl alcohol with benzene. The water is removed in the volatile azeotrope formed.

The procedure is described above under Distillation of Pure Liquids.

TABLE 21.2
Minimum-Boiling-Point Azeotropic Mixtures

Component A		Component B		bp of Azeotropic mixture, °C	% of A (by mass) in mixture
Substance	bp, °C	Substance	bp, °C		
Water	100.0	Ethyl alcohol	78.3	78.15	4.4
Water	100.0	Isopropyl alcohol	82.4	80.4	12.1
Water	100.0	n-Propyl alcohol	97.2	87.7	28.3
Water	100.0	tert-Butyl alcohol	82.6	79.9	11.8
Water	100.0	Pyridine	115.5	92.6	43.0
Methyl alcohol	64.7	Methyl iodide	44.5	39.0	7.2
Ethyl alcohol	78.3	Ethyl iodide	72.3	63.0	13
Methyl alcohol	64.7	Methyl acetate	57.0	54.0	19
Ethyl alcohol	78.3	Ethyl acetate	77.2	71.8	31
Water	100.0	Butyric acid	163.5	99.4	18.4
Water	100.0	Propionic acid	140.7	100.0	17.7
Benzene	80.2	Cyclohexane	80.8	77.5	55
Ethyl alcohol	78.3	Benzene	80.2	68.2	32.4
Ethyl alcohol	78.3	Toluene	110.6	76.7	68
Methyl alcohol	64.7	Chloroform	61.2	53.5	12.5
Ethyl alcohol	78.3	Chloroform	61.2	59.4	7.0
Ethyl alcohol	78.3	Methyl ethyl ketone	79.6	74.8	40
Methyl alcohol	64.7	Methylal	42.2	41.8	18.2
Acetic acid	118.5	Toluene	110.6	105.4	28

FRACTIONAL DISTILLATION

Principle

The separation and purification of a mixture of two or more liquids, present in appreciable amounts, into various fractions by distillation is *fractional distillation*. It consists essentially in the systematic redistillation of distillates (fractions of increasing purity). Figures 21.8, 21.9, and 21.10 are distillation curves showing how two liquids separate. Fractionations can be carried out with an ordinary distilling flask; but, where the components do not have widely separated boiling points, it is a very tedious process. A fractionating column (Fig. 21.11) is essentially an apparatus for performing a large number of successive distillations without the necessity of actually collecting and redistilling the various fractions. The glass column is filled with pieces of glass, glass beads, metal screening, or glass helices (Fig. 21.12). Some columns are more efficient than others.

The separation of mixtures by this means is a refinement of ordinary separation by distillation. Thus a series of distillations involving partial vaporization and condensation concentrates the more volatile component in the first fraction of distillate and leaves the less volatile component in the last fraction or in the residual liquid. The vapor leaves the surface of the liquid and passes up through
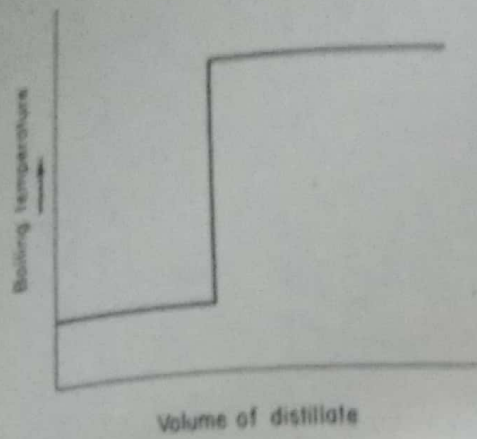
FIGURE 21.8
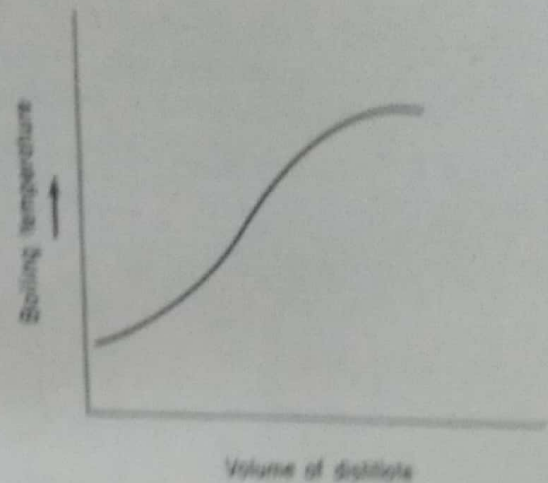Curve for the ideal separation of two components.

FIGURE 21.9
Curve for the actual separation, in a simple distillation apparatus, of two components that have boiling points close together.
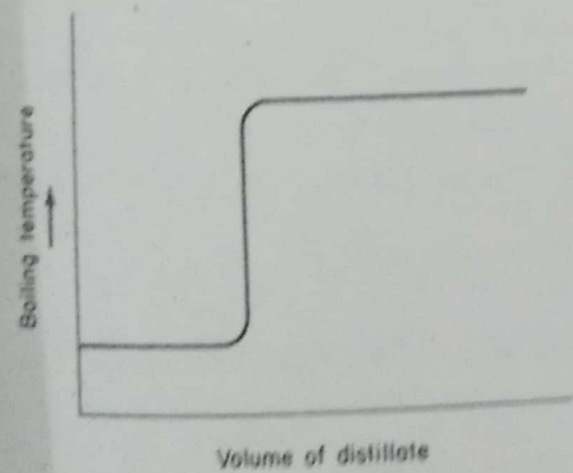

FIGURE 21.10
Curve for the actual separation of two liquids, which have boiling points close together, when the separation is carried out in a fractional distillation apparatus with an efficient column.
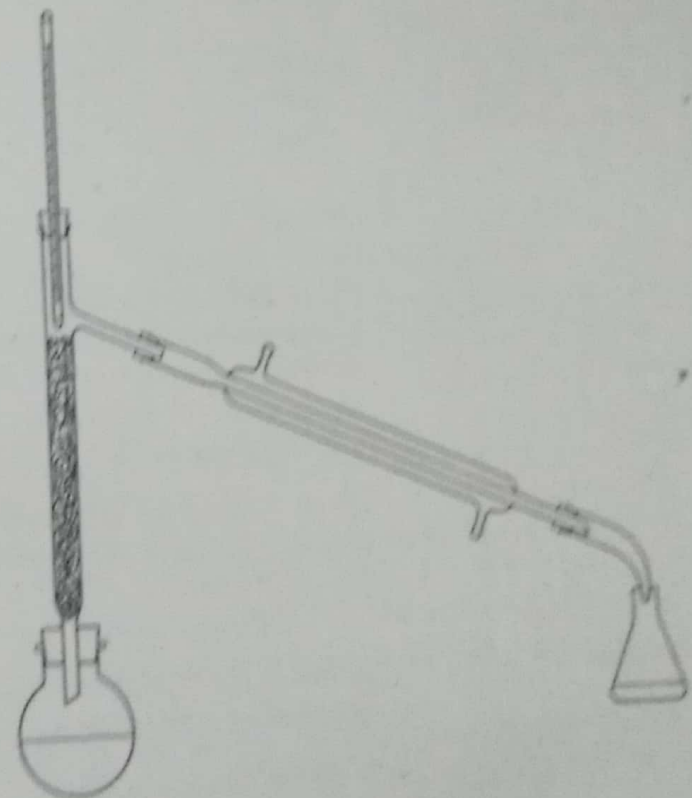

FIGURE 21.11
Fractional distillation apparatus, for use under vacuum or at atmospheric pressure. Column should be packed.

Glass beads
(a)

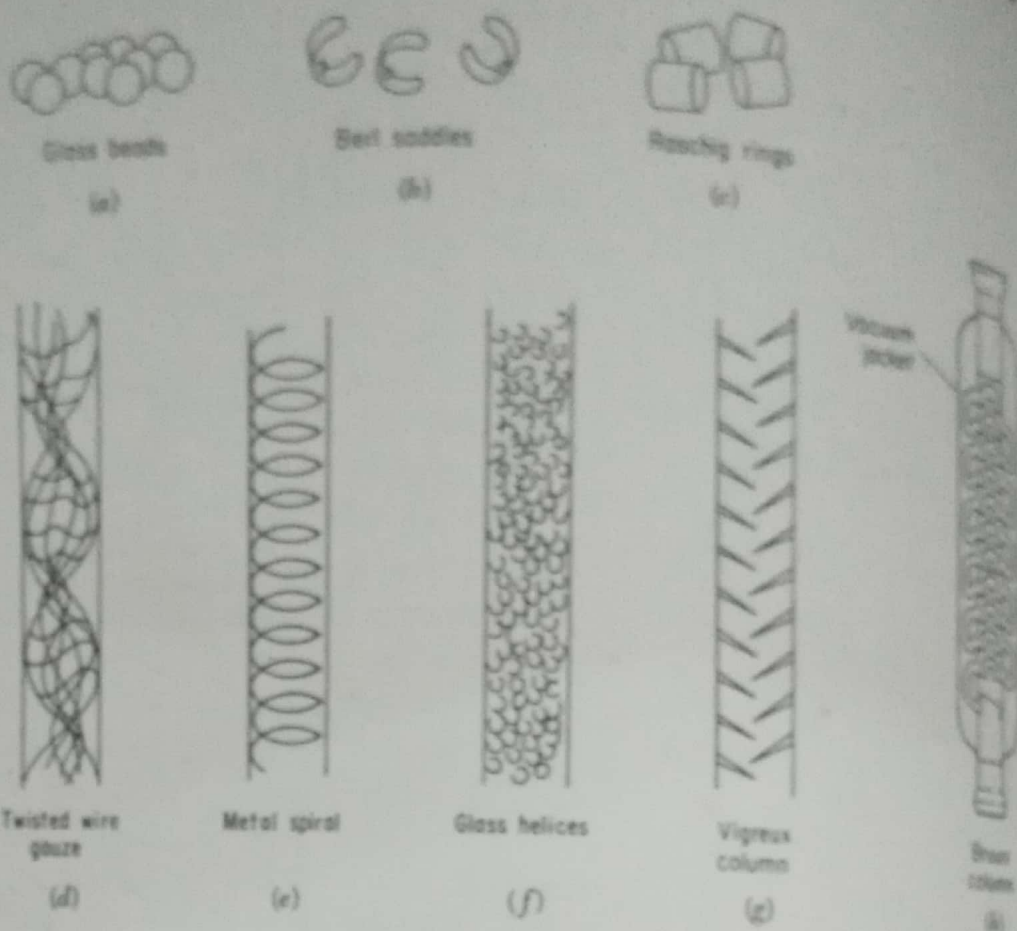Berl saddles
(b)

Raschig rings
(c)

FIGURE 21.12
Packings for fractionating columns. Some (a,b,c) are shown loose; others (d,e,f) are shown in place. In the Vigreux (g) and Bruun (h) columns, the packings are built in.

Twisted wire gauze
(d)

Metal spiral
(e)

Glass helices
(f)

Vigreux column
(g)

Bruun column
(h)

the packing of the column. There it condenses on the cooler surfaces and redistills many times before entering the condenser. Each minute distillation causes a greater concentration of the more volatile liquid in the rising vapor and an enrichment of the residue which drips down through the column in the less volatile components.

By means of long and efficient distillation columns (see Fig. 21.11), two liquids may be completely separated.

Procedure

1. Select the type of fractionating column to be used, one that offers a large surface contact inside (see Fig. 21.12).

2. Set up the equipment.

3. Open the inlet cooling-water valve.

4. Apply heat.

5. Keep a large volume of liquid condensate continually returning through the column.

6. Distill slowly to effect efficient separation (See caution, p. 509.)