

DISTILLATION

Purification of Liquid Organic Compounds

***Distillation** is the process of separating the component or substances from a liquid mixture by selective evaporation and condensation.

Distillation is the most basic method used for the purification of liquids and for the separation of liquid mixtures. Distillation involves the heating of a liquid to boiling and then collecting their vapours to condense them in liquid state.

By this method,

- Separation of the liquids of the mixture, having a few degrees different boiling points,
- Separation of a liquid from non-volatile components,
- Purification of the liquid, is carried out.

Boiling point:

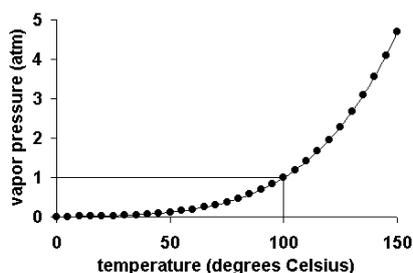
The boiling point is defined as the temperature at which the saturated vapor pressure of a liquid is equal to the surrounding atmospheric pressure.

If the liquids are heated at constant pressure, for example at atmospheric pressure, the vapor pressure increases in proportion to the heat supplied. Once the vapor pressure of the liquid is equal to the pressure of the outside atmosphere, the liquid begins to boil. The temperature at which the vapor pressure equals the atmospheric pressure of the outside is called the boiling point of the liquid.

If more heat is given to a liquid at the boiling point, the temperature of the liquid does not increase, but the heat supplied ensures that the liquid becomes vapor and the temperature remains constant until the liquid evaporates completely.

The boiling point of a substance is the temperature at which it changes state from liquid to gas throughout the bulk of the liquid. At the boiling point molecules anywhere in the liquid may be vaporized.

At any temperature a liquid partly vaporizes into the space above it until the pressure exerted by the vapour reaches a characteristic value called the vapour pressure of the liquid at that temperature. As the temperature is increased, the vapour pressure increases; at the boiling point, bubbles of vapour form within the liquid and rise to the surface. The boiling point of a liquid varies according to the applied pressure; the normal boiling point is the temperature at which the vapour pressure is equal to the standard sea-level atmospheric pressure (760 mm of mercury).



In general, the boiling point of a compound is dependent on the molecular mass of the compound and the strength of the attractive force holding the molecules together.

Factors affecting boiling point:

1. The relative strength of the four intermolecular forces is: Ionic > Hydrogen bonding > dipole dipole > Van der Waals dispersion forces. The influence of each of these attractive forces will depend on the functional groups present, but generally stronger forces means a higher boiling point.
2. Boiling points increase as the number of carbons is increased. But branching decreases boiling point.
3. Boiling point of associative polar liquids is higher than the boiling point of non associative polar liquids.

Ex: Boiling point of ethanol is higher than the boiling point of diethyl ether. Both of them have higher boiling point than the nonpolar and nonassociative propane.

Account of Boiling Point at Different Pressures

Boiling points of liquids were reported in normal atmospheric pressure (760 mmHg) in the literature.

If the liquid is distilled at a pressure other than atmospheric pressure, then boiling point varies by depending on pressure.

New boiling point is calculated according to the following formula.

$$\text{Log } p = A / T + C$$

p = vapor pressure at the absolute temperature of the liquid T

A, C = Constants

**Distillation is mainly applied in 6 different form according to the nature of the substance to be purified or removed.

1. Simple Distillation
2. Fractional Distillation
3. Steam Distillation

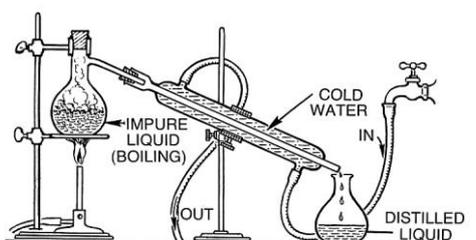
4. Vacuum Distillation
5. Molecular Distillation
6. Fractional Distillation Under Reduced Pressure

1. Simple Distillation

Distillation of the substances in simple structure, that are readily volatile and resistant to their own boiling heat, can be carried out under ordinary pressure .

For example; hydrocarbons, alcohols, esters, small molecule fatty acids, amines are purified by this method.

Simple distillation is a procedure by which two liquids with different boiling points can be separated. Simple distillation (the procedure outlined below) can be used effectively to separate liquids that have at least 80°C difference in their boiling points. As the liquid being distilled is heated, the vapors that form will be richest in the component of the mixture that boils at the lowest temperature. Purified compounds will boil, and thus turn into vapors, over a relatively small temperature range (2 or 3°C); by carefully watching the temperature in the distillation flask, it is possible to affect a reasonably good separation. As distillation progresses, the concentration of the lowest boiling component will steadily decrease. Eventually the temperature within the apparatus will begin to change; a pure compound is no longer being distilled. The temperature will continue to increase until the boiling point of the next-lowest-boiling compound is approached. When the temperature again stabilizes, another pure fraction of the distillate can be collected. This fraction of distillate will be primarily the compound that boils at the second lowest temperature. This process can be repeated until all the fractions of the original mixture have been separated.



Basic Procedure:

1. Check the calibration of the thermometer that is to be used.
2. Fill the distillation flask. The flask should be no more than two thirds full because there needs to be sufficient clearance above the surface of the liquid so that when boiling commences the liquid is not propelled into the condenser, compromising the purity of the distillate.
3. Boiling chips should be placed in the distillation flask for two reasons: they will prevent superheating of the liquid being distilled and they will cause a more controlled boil, eliminating the possibility that the liquid in the distillation flask will bump into the condenser.
4. Heat the distillation flask slowly until the liquid begins to boil. Vapors will begin to rise through the neck of the distillation flask. As the vapors pass through the condenser, they will condense and drip into the collection receiver. An appropriate rate of distillation is

approximately 20 drops per minute. Distillation must occur slowly enough that all the vapors condense to liquid in the condenser. Many organic compounds are flammable and if vapors pass through the condenser without condensing, they may ignite as they come in contact with the heat source.

5. As the distillate begins to drop from the condenser, the temperature observed on the thermometer should be changing steadily. When the temperature stabilizes, use a new receiver to collect all the drops that form over a two to three degree range of temperature. As the temperature begins to rise again, switch to a third collection container to collect the distillate that now is formed. This process should be repeated; using a new receiver any time the temperature stabilizes or begins changing, until all of the distillate has been collected in discrete fractions.

Note: All fractions of the distillate should be saved until it is shown that the desired compound has been effectively separated by distillation.

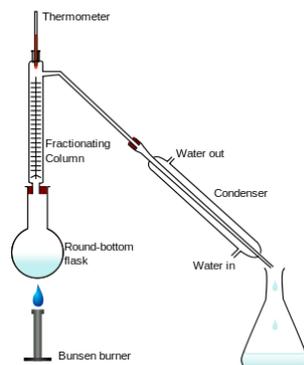
6. Remove the heat source from the distillation flask before all of the liquid is vaporized. If all of the liquid is distilled away, there is a danger that peroxides, which can ignite or explode, may be present in the residue left behind. Also, when all of the liquid has evaporated, the temperature of the glass of the filtration flask will rise very rapidly, possibly igniting whatever vapors may still be present in the distillation flask.
7. Never distill to dryness. The residue left in the distillation flask may contain peroxides, which could ignite or explode after all the liquid has distilled away.
8. Make sure that all joints are secured very tightly. If any vapor escapes at the connection points, it may come into direct contact with the heat source and ignite.
9. Never heat a closed system, the increasing pressure will cause the glass to explode. If the distillation flask has a tapered neck, the thermometer may be placed in such a way as to block to flow of vapors up the neck of the flask; in effect creating a closed system; make sure that if using a tapered neck flask, the thermometer is not resting in the lowest portion of the neck.

2.Fractional Distillation

If the boiling point of the liquids in the mixture are very close to each other then such mixtures can be purified by fractional distillation. The difference in boiling points of the mixture is usually less than 80°C. e.g. – acetone(b.p. 56°C) and methyl alcohol (b.p. 65°C). For fractional distillation, a suitable fractionating column is placed between the flask and the condenser.

Since the procedures of simple distillation are so similar to those involved in fractional distillation, the apparatus that are used in the procedures are also very similar. The only difference between the equipment used in fractional distillation and that used in simple distillation is that with fractional distillation, a packed fractionating column is attached to the top of the distillation flask and beneath the condenser. This provides the surface area on which rising vapors condense, and subsequently revaporize.

The fractionating column is used to supply a temperature gradient over which the distillation can occur.



In an ideal situation, the temperature in the distillation flask would be equal to the boiling point of the mixture of liquids and the temperature at the top of the fractionating column would be equal to the boiling point of the lower boiling compound; all of the lower boiling compound would be distilled away before any of the higher boiling compound. In reality, fractions of the distillate must be collected because as the distillation proceeds, the concentration of the higher boiling compound in the distillate being collected steadily increases. Fractions of the distillate, which are collected over a small temperature range, will be essentially purified; several fractions should be collected as the temperature changes and these portions of the distillate should be distilled again to amplify the purification that has already occurred.

Raoult's law

Raoult's law states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present:

$$P_{\text{solution}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

P= vapour pressure

X= number of moles

Ideal solutions are uniform mixtures of components that have physical properties connected to their pure components. These solutions are supported by [Raoult's law](#) stating that interactions between molecules of solute and molecules of solvent are the same as those molecules each are by themselves. An example of ideal solutions would be benzene and toluene.

Azeotropes fail to conform to this idea because, when boiling, the component ratio of unvaporized solution is equal to that of the vaporized solution. So an azeotrope can be defined as a solution whose vapor has the same composition its liquid. Mixtures of liquids called **azeotropes** can be encountered that mimic the boiling behavior of pure liquids. These mixtures when present at specific concentrations usually distill at a constant boiling temperature and can not be separated by distillation.

Examples of such mixtures are 95% ethanol-5% water (bp 78.1 °C), 20% acetone-80% chloroform (bp 64.7 °C), 74.1% benzene, 7.4% water, 18.5 % ethanol (bp 64.9).

The azeotropic composition sometimes boils lower than boiling point of its components and sometimes higher. Mixtures of these substances at compositions other than those given above behave as mixtures.

Azeotropic mixtures can be separated into their components by various methods.

The most important of these methods are;

1. Another liquid is added to the azeotrope mixture for to reduce the vapor pressure ratio and the mixture can be distilled.

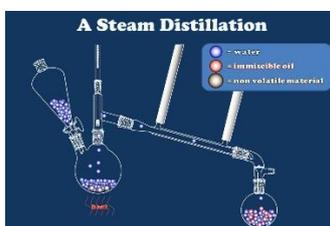
2. Some of the components present in the azeotropic mixture can be removed from the mixture by chemical reactions.

3. Steam Distillation

Steam distillation is a separation process used to purify or isolate temperature sensitive materials, like natural aromatic compounds. Steam or water is added to the distillation apparatus, lowering the boiling points of the compounds. These compounds should be immiscible with water. The goal is to heat and separate the components at temperatures below their decomposition point.

The advantage of steam distillation over simple distillation is that the lower boiling point reduces decomposition of temperature-sensitive compounds.

Steam distillation is useful for the purification of organic compounds, although vacuum distillation is more common. When organics are distilled, the vapor is condensed. Because water and organics tend to be immiscible, the resulting liquid generally consists of two phases: water and the organic distillate.

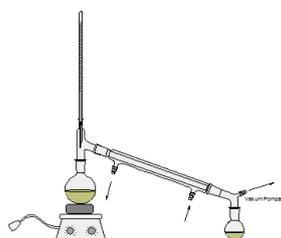


Steam distillation is the preferred method used to isolate essential oils. It is also used for "steam stripping" in petroleum refineries and to separate commercially important organic compounds, such as fatty acids.

4. Vacuum Distillation

Distillation under reduced Pressure (or) Vacuum distillation. It is used for organic compounds which decompose at or below their boiling points. Example: Glycerol. The boiling point of a liquid is the temperature at which the total vapour pressure is equal to the external pressure. This means that by lowering the pressure the boiling point of the liquid can be lowered.

If we have an organic substance which decompose at its boiling point, we can make it to boil at a temperature lower than its boiling point. All that we have to do is to create a partial vacuum. Under reduced pressure, the substance boils at a much lower temperature and distills over undecomposed.



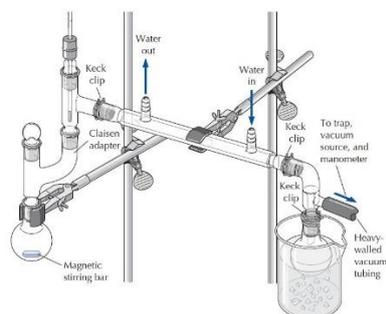
Vacuum distillation can also be performed for the solids. This is the purifying process for recovering impurities from resin, stain, other non-volatile solid materials, which are inferior in impurities in the solid matter.

5. Molecular distillation

Molecular distillation is considered as the safest mode of separation and to purify the thermally unstable molecules and related compounds with low volatility and elevated boiling point. The process distinguishes the short residence time in the zone of the molecular evaporator exposed to heat and low operating temperature due to vacuum in the space of distillation.

The separation principle of molecular distillation is based on the difference of molecular mean free path. The passage of free path for molecules should be collision free.

Langmuir and Knudsen involved in the theory of molecular distillation derived an equation which described the yield of distillate for molecular distillation.



Here the ambient pressure is lower than the 0.001 mm Hg pressure. With this method, it is possible to reduce the boiling point by 200-300 ° C.

6. Fractional Distillation Under Reduced Pressure

The difference from the simple vacuum distillation of the system is that there is a liquid mixture to be distilled and that it is separated by attaching a fraction header. In addition, the container to which the separations are to be collected is slightly different from the one used in the other.

SUBLIMATION

Sublimation is the direct change of a solid to vapour on heating without going through the liquid state. Used to separate volatile organic compounds from non volatile impurities e.g. Naphthalene, benzoic acid, anthracene, camphor.

The substances that sublime can be purified by this method, provided the impurities present does not sublime. Many organic compounds directly form vapours, when solid compounds are heated, without becoming a liquid at any stage. On cooling the vapours the solid is directly obtained.

A mixture of two compounds can be separated by sublimation.