Distillation

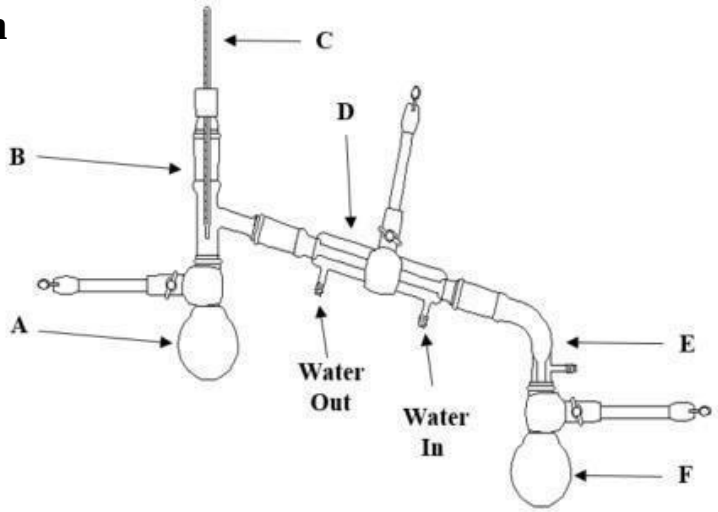
Distillation is a separation technique used when a mixture contains at least one liquid. The date of the first distillation is lost to history. Evidence points to Greek Alchemists in the first century A.D. describing the isolation of pure water from sea water (1). Distillation and the making of alcohol have long been intertwined. The making of alcoholic beverages like wine dates as far back as 4100 B.C. in what is now Armenia while beer was being made by the Egyptians as early as 5000 B.C. (2,3). The making of wine or beer does not require distillation, but some do add distilled spirits to wine to produce "fortified wine." The precise time when the distillation of alcohol began is not known. It is thought that the distillation of alcohol could have occurred in China as early as the first century A.D., but there is no concrete evidence to support this theory yet (4). The first known recorded distillation of alcohol is during the twelfth century A.D. in southern Italy at the Schola Medica Salernitana, the world's first medical school (3).

There are many different types of distillations that can be used depending upon the mixture. These different types of distillations include simple distillation, fractional distillation, steam distillation and vacuum distillation. Regardless of the type of distillation used, all distillations work using the same three basic steps. First, the mixture is heated to the boiling point vaporizing the liquid. The boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid equals the external pressure being exerted on the liquid. Second, the vapor is condensed back to a liquid. And third, the condensed liquid is collected in a separate container.

Simple Distillation

When the mixture consists of a solid dissolved in a liquid (salt dissolved in water for example), simple distillation is ideally suited to separate the liquid from the solid. Figure 1 shows an example of a simple distillation apparatus. The apparatus consists of the distillation flask or still pot, which is where the mixture is placed at the start of the distillation. The distillation flask is connected to the distillation head, which serves two main purposes. First, it allows for the placement of a thermometer into the apparatus (the thermometer should be placed just properly to allow for accurate temperature readings). Second, the distillation head allows for the connection of the condenser, which is a jacketed glass tube where a coolant such as water flows through to aid in the condensation of the vapor.

Figure 1 Simple Distillation Apparatus

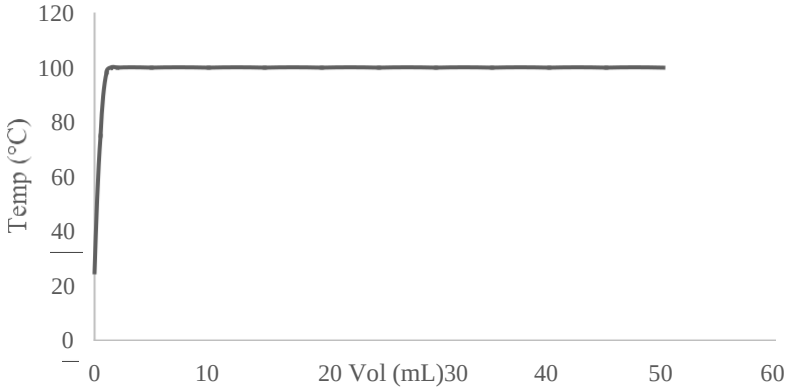


A. Distillation Flask or Still Pot
B. Distillation Head
C. Thermometer
D. Condenser
E. Vacuum Adaptor
F. Receiving Flask

The condenser is connected to the vacuum adapter which has three main functions. The first function of the vacuum adapter is to allow for the connection of a vacuum source if reduced pressure distillation is needed. The second function is to allow for the entire apparatus to remain as an open system during the distillation (heating a closed system is extremely dangerous and should usually be avoided). Finally, the third function is to connect to the receiving flask, which collects the condensed liquid.

During the simple distillation of a mixture of salt and water, the water is vaporized, condensed and collected in the receiving flask while the salt remains behind in the distillation flask. Thus, the mixture is separated into its individual components. If temperature is recorded during the distillation and plotted against the collected volume, the resulting graph will look like the one depicted in figure 2. The **plateau** represents the boiling point of the liquid being collected, which should be around 100 °C if the liquid is water at standard pressure.

Figure 2 Temperature vs Volume Graph of Simple Distillation (Salt Dissolved in Water)



When a mixture consists of two or more liquids, simple distillation can be used to separate them, but it is more complicated. Dalton's Law states that the total pressure of a mixture of two or more liquids at any given temperature is equal to the sum of the partial pressures of each liquid (see equation 1). Raoult's Law states that the partial pressure (Px) of an individual liquid is equal to the mole fraction (Nx) of the liquid multiplied by the vapor pressure of the pure liquid (PxO) at the given temperature (see equation 2). The mole fraction is equal to the number of moles of the individual liquid (*n*X) divided by the sum of all the moles (see equation 3). When a mixture consisting of two or more liquids is heated, the boiling point is reached when the sum of the partial pressures of each liquid is equal to the external pressure. Simple distillation can be used to separate a mixture of two or more liquid if the boiling point difference between the liquids is greater than 60-70 °C.

Equation 1 Dalton's Law

$$P_{tot} = P_x + P_y + \ldots$$

Equation 2 Raoult's Law

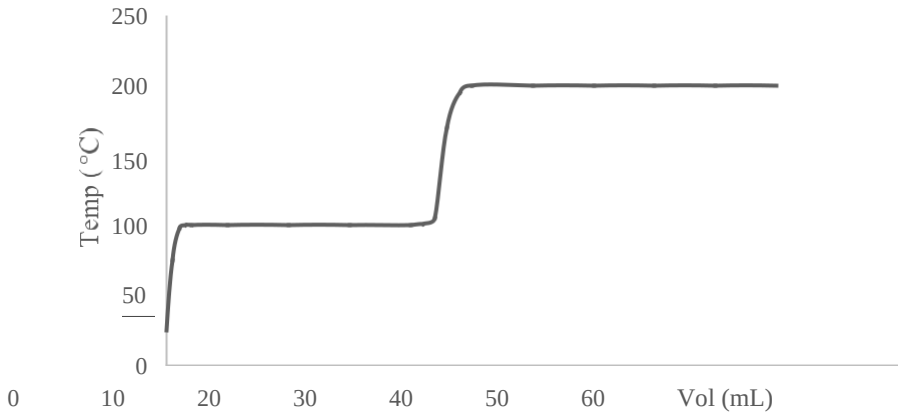
$$P_x = N_x P_x^O$$

Equation 3 Mole Fraction

$$Nx = \frac{nX}{nX+nY+..}$$

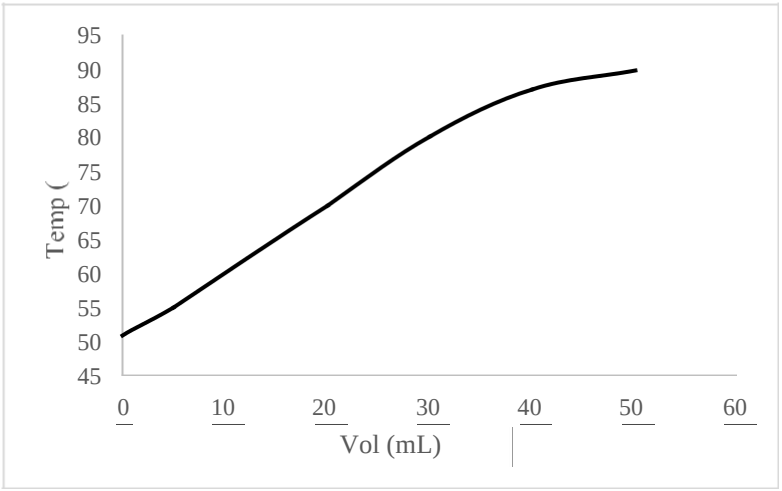
If a mixture of two liquids with a boiling point difference of 100 °C is separated by simple distillation, a graph of temperature versus volume like the one shown in figure 3 will be generated. The first plateau represents the boiling point of the lower boiling point liquid while the second plateau represents the boiling point of the higher boiling point liquid. By collecting samples in the receiving flask during a plateau, pure lower or higher boiling point liquid can be isolated.

Figure 3 Temperature vs Volume Graph of Simple Distillation (Boiling Point Difference 100 °C)



If simple distillation is used on a mixture of two liquids with a boiling point difference of 30 °C, a graph of temperature versus volume like the one shown in figure 4 will be generated. As the graph demonstrates, there are no plateaus during the distillation which means that it is not possible to isolate a pure liquid. However, if a series of simple distillations is performed on the mixture, then separation is possible. For example, during the first distillation of 100 mL, collect fractions at specific volumes, such as every 25 mL. The first 25 mL will contain the highest concentration of the lower boiling point liquid. Take this first fraction and distill it again collecting specific volumes again, such as every 5 mL. The first 5 mL fraction will contain an even higher concentration of the lower boiling point liquid. By repeating this process, it is theoretically possible to isolate pure lower boiling point liquid at some point.

Figure 4 Temperature vs Volume Graph of Simple Distillation (Boiling Point Difference 30 °C)

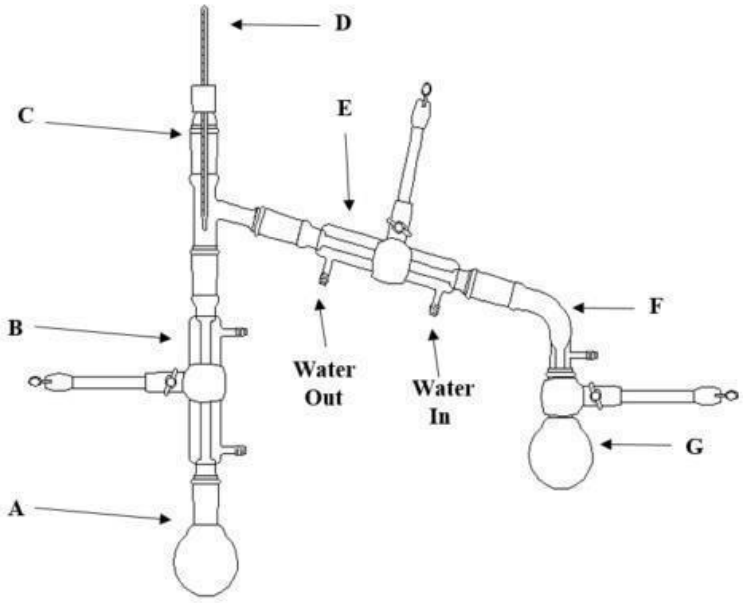


Fractional Distillation

Even though multiple simple distillations may successfully separate a mixture with a boiling point difference of 30 °C, this process is very inefficient. A more efficient method is fractional distillation. Figure 5 shows a typical fractional distillation apparatus. As the figure demonstrates, the only difference between the simple distillation apparatus in figure 1 and a fractional distillation apparatus is the insertion of a column between the distillation flask and the distillation head.

Figure 5 Fractional Distillation Apparatus

A. Distillation Flask or Still Pot
B. Column of Fractioning Column
C. Distillation Head
D. Thermometer
E. Condenser
F. Vacuum Adaptor
G. Receiving Flask



With the addition of this column (also referred as the fractioning column) to the apparatus, liquid mixtures that have boiling point differences less than 60-70 °C can be separated in one distillation. A representation of how a fractioning column functions can be seen in figure 6. As the figure shows, the column allows for more condensation/re-vaporization events to occur inside the column before the final condensation reaches the distillation head. Each condensation/re-vaporization event is called a **theoretical plate**. What is occurring within the column can be demonstrated graphically using a temperature and composition graph of the liquid and vapor phases, as shown in figure 7. For the example in figure 7 the boiling point of the initial mixture is determined by drawing a vertical line until it intersects with the liquid line. The composition of the vapor that is formed when this initial mixture boils is determined by drawing a horizontal line until it intersects with the vapor line. By continuing to draw lines vertically and then horizontally, it is possible to determine how many theoretical plates will be necessary to obtain a pure sample. Thus, the initial 5% / 95 % mixture of A and B (L_1) in figure 7 has a boiling point of 87°C and the initial vapor (V_1) is composed of 20% A and 80 % B. In order to isolate 100 % A, it requires a fractioning column that contains five theoretical plates.

Figure 6 Fractional Distillation Example

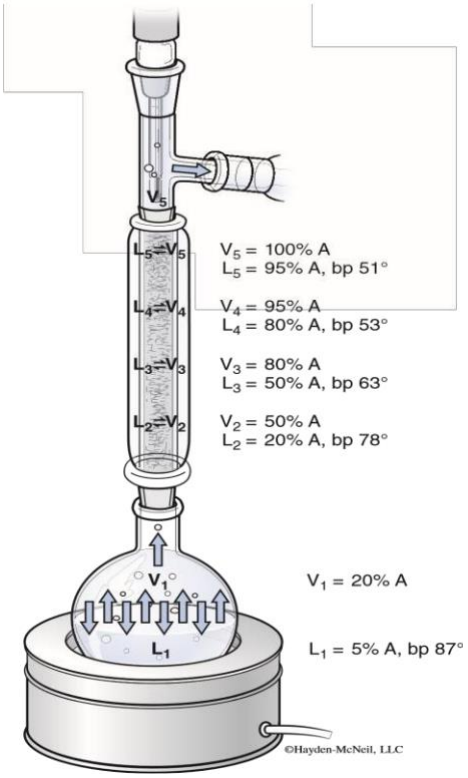
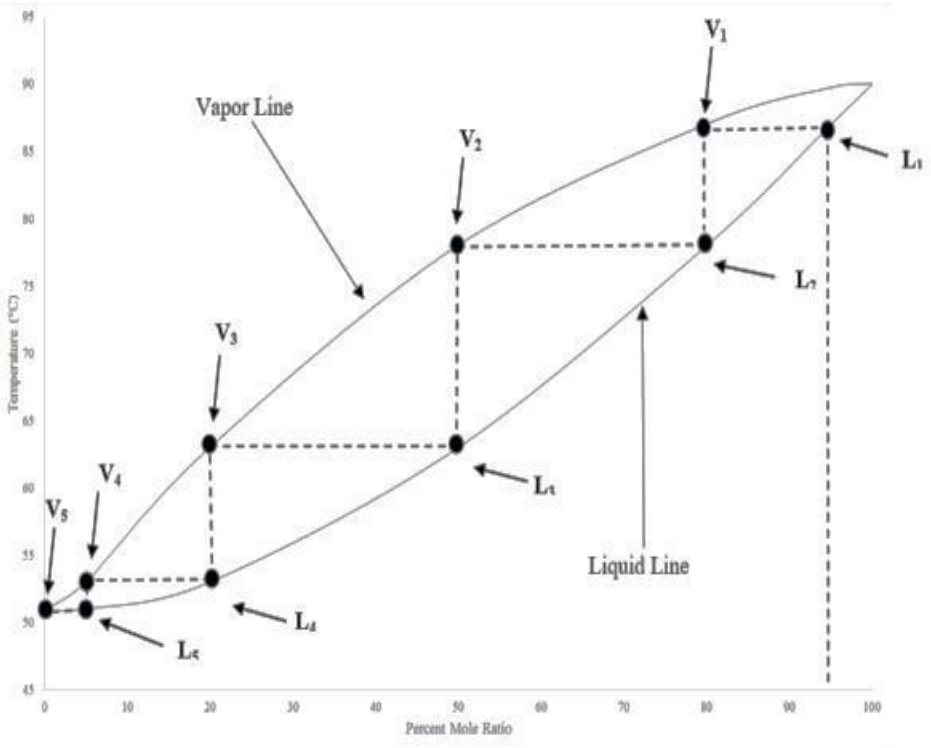


Figure 7 Vapor/Liquid Phase Diagram



The smaller the boiling point difference between the two liquids, the more theoretical plates are needed to separate them. The number of theoretical plates a fractioning column has is determined by two factors. The first factor is the surface area within the column. As the surface area increases, the number of theoretical plates increases. Increasing the surface can be achieved by a few different methods. First, simply increase the length of the column. Second, different types columns of will have different surface areas based upon the design (see figure 8). Finally, packing the column with different materials like glass beads, glass wool or steel sponge will also increase the surface area within the column.

The second factor that affects the number of theoretical plates is the temperature gradient that exists between the distillation head and the distillation flask. An ideal temperature gradient is one where the temperature in the distillation flask equals the boiling point of the mixture and the temperature in the distillation head is equal to the boiling point of the lower boiling point liquid. The change in temperature from the distillation flask to the distillation head should be a gradual decrease to ensure optimal separation. To achieve the optimal temperature gradient, a few conditions must be considered.

1. The first condition to consider is proper heating. If too much heat is added to the distillation flask, more heat will be transferred into the column which will result in fewer theoretical plates meaning that the separation of the liquids will not be complete. Conversely, if the too little heat is added to the distillation flask, not enough heat is transferred into the column which will result in little or no vapor reaching the distillation head.

Figure 8 Different Fractional Distillation Columns

A. Hempel

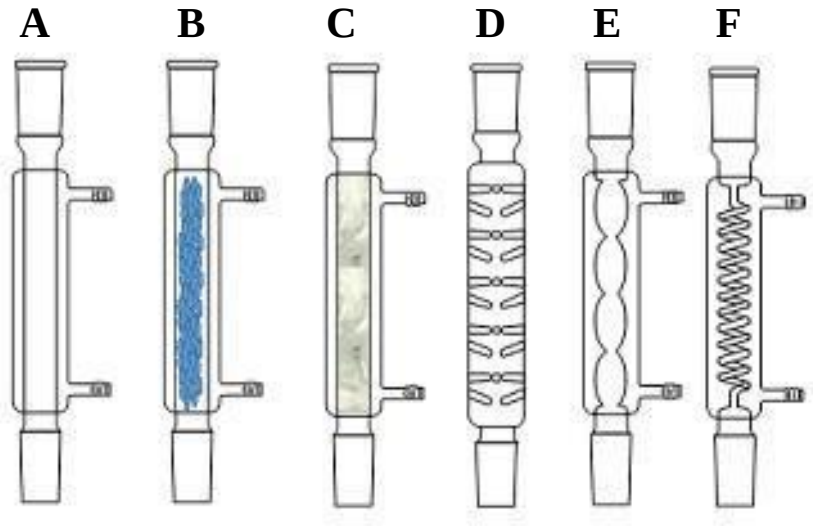
B. Hempel Packed with Glass Beads

C. Hempel Packed with Glass Wool

D. Vigreux

E. Allihn

F. Graham



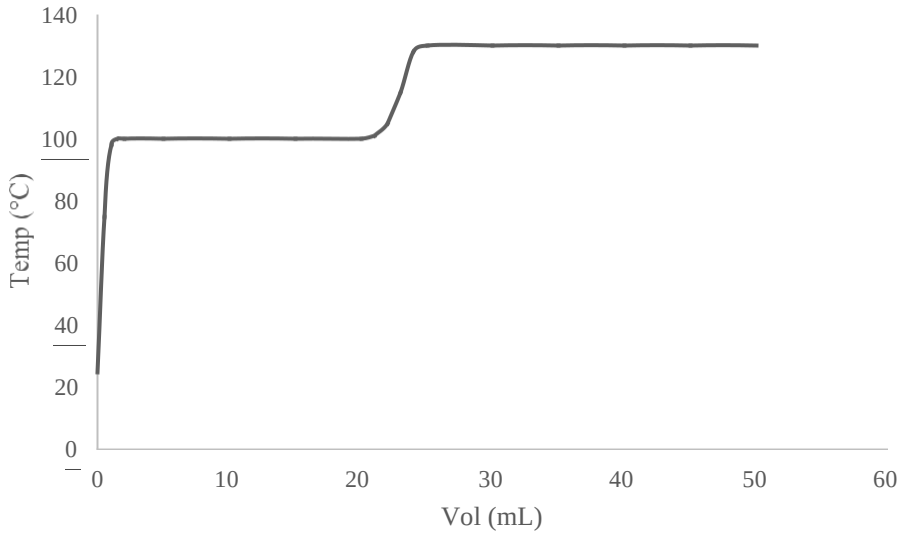
2. Since the rate of heating is so important, care must be taken to ensure that the proper amount of heat is being added. Thus, monitoring the distillation during the entire process is necessary. One method to monitor the distillation to ensure correct heating is to determine the **reflux ratio**. The reflux ratio is equal to the number of drops returning to the distillation flask divided by the number of drops being collected in the receiving flask. The higher the reflux ratio, the more efficient the separation. Another method to monitor the distillation to determine if the correct amount of heat is being added is to look at the rate of collection in the receiving flask. Ideally, the rate of collection should be no more than one drop per 1-2 seconds.

3. Another issue to consider regarding proper heating during the distillation is that the boiling point of the mixture in the distillation flask will slowly increase. Thus, the heat added will have to be increased to ensure that the distillation rate or reflux ratio is maintained. However, care must be taken to avoid increasing the heat too rapidly. If too much heat is added too quickly, then a **flooded column** might result. A flooded column is described as liquid filling column because it is boiling out of control. Addition of a stirbar or boiling chips will help prevent a flooded column by distributing the heat more evenly within the distillation flask.

4. Finally, to achieve proper heating during a distillation, it is often necessary to insulate the column to avoid loss of heat. Any air flow across the column during the distillation can result in loss of the heat within the column. Thus, loosely insulating the column with either glass wool or cotton protects the column from this loss of heat.

If the correct column is chosen (contains the appropriate number of theoretical plates) and the temperature gradient is properly managed, then a binary mixture can be successfully separated even if the boiling point difference is small. Plotting temperature against volume of such a distillation will produce a graph like the one seen in figure 9. The graph in figure 9 is very similar to the one seen in figure 3. Collecting fractions during a plateau will result in the collection of a pure liquid.

Figure 9 Temperature vs Volume Graph of Simple Distillation (Boiling Poit Difference 30 °C)



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